Graphene Based Supercapacitors

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Abstract- *Graphene based nanomaterials are encouraging for applications in different energy storage devices and supercapacitors because of their intriguing properties such as being having highly tunable surface area, astonishing electrical conductance, very high chemical stability and commendable mechanical behavior. This review provides a gist of recent progress on graphene-based materials for supercapacitor electrodes, graphene-based and pure graphene nanocomposite films for flexible capacitors, graphene hydrogel based nano composites for electrochemical double layer capacitors, with and without binder materials, graphene nanofiber based electrodes, and using eutectic ionic liquid mixtures as electrolytes for graphene based supercapacitors. There are intensive and on going researches on the rationalization of their structures at wide varying scales and dimensions, development of effective and low price synthesis techniques, style and architecture of graphene-based materials, furthermore as clarification of their electrochemical performance. It's indicated that future studies ought to specialize in the general device performance in energy storage devices and large-scale method in low prices for the promising applications in transportable and wearable electronic, transport, electrical and hybrid vehicles.*

Keywords- Graphene, Supercapacitors, nanocomposite films, electrochemical double layer capacitors, eutectic ionic liquid.

I. INTRODUCTION

Supercapacitors or ultracapacitors have attracted appreciable recent attentions thanks to their high power density, high charge/discharge rates, and long cycle life performance. They are thought of as one of the foremost promising electrochemical energy storage devices, having a posibility to enhance or eventually replace the batteries for energy storage applications, i.e., those for wearable and transportable electronics, electrical and hybrid vehicles. predominantly having the energy storage mechanisms, supercapacitors are often classified into to 2 main classes, i.e., electrical double layer capacitors (EDLCs) and pseudocapacitors. For EDLCs, the capacitance is originated from the buildup of charges at the electrode-electrolyte interfaces. Therefore, optimising the specific surface area and pore size and enhancing electrical conductivity are the effective ways in which to attain a high storage capability.
Graphene is a well-known two-dimensional carbon monolayers composed of all-sp2-hybridized carbons with a number of the foremost intriguing properties, i.e., light-weight, high electrical and thermal conductivity, extremely tunable surface area, robust mechanical strength and chemical stability. These outstanding properties modify graphene and graphene-based materials to seek out applications in high performance structural nano composites, electronics, and environmental protection and energy devices as well as each energy generation and storage. The mixture of those outstanding physical, mechanical and chemical properties make graphene-based materials highly attractive for electrochemical energy storage and sustainable energy generation, i.e., Li-ion batteries, fuel cells, supercapacitors, and photovoltaics and solar cells. Boosting the general electrochemical performance of graphene-based materials still remains an excellent challenge. Graphene-based materials are extensively investigated as a conducting network to support the oxidation reactions of transition metal oxides, hydroxides and conducting polymers. During this review, recent development on the preparation ways, resultant structures and electrochemical performance of graphene-based materials designed for applications in supercapacitors was summarized.. The corresponding phenomenon involving primarily capacitance mechanisms along with effective ways in which to attain high energy storage performance were also mentioned.[1][2]

II. ADVANCEMENT IN EDLC

A. Advanced Hummer's approach and Tip Sonication

With the usage of a changed hummer's approach and tip- sonication for graphene synthesis, right here that show graphene-based totally supercapacitors with excessive balance and substantially-advanced electric powered double layer capacitance and strength density with fast charging and discharging time at a excessive present day density, due to advanced ionic electrolyte accessibility in deeper regions. The cellular can deliver a specific capacitance of approximately $137fg^{-1}$ and hold 98 % of its preliminary value after 10,000 cycles, suggesting that the robust overall performance of

supercapacitors at high current rates is appropriate for fast charging-discharging programs. This advanced performance can be attributed to the distinctly porous nature of graphene with minimum restacking with crimple nature wrinkles and the progressed modern-day gathering technique.

Although supercapacitors are not as exact as the present battery devices in term of strength density, further studies on this point should lead to graphene primarily based supercapacitors with advanced power density this is comparable with lithium ion batteries however with a better power density and a fast charging system. The charge storage in supercapacitors is primarily based on electrochemical double layer capacitance i.e. formation of interfacial double layer on active materials. There are several reports on graphene based supercapacitors, in recent, to improve precise capacitance the use of diverse electrolytes like potassium hydroxide, natural electrolyte and ionic electrolytes. [3][4]

B. Use of Graphene Composites.

Metallic oxide graphene composites which have been used to enhance the capacitance overall performance encompass MgO, Fe_3O_4, MnO_2, and cobalt oxide. Though those steel oxide composites have proven enhancements at the unique capacitance and power density however the charging time and discharging time are nevertheless too low for a high powered application in which the electricity shipping ought to be rapid to numerous load programs. In addition improvement in capacitance has been finished with the aid of the use of various ionic beverages.

The important thing of graphene synthesis for excessive performance supercapacitors is to have an excessive surface location and excellent electric activation. It's far widely recognized that the electrochemical overall performance of graphene may be more desirable with the aid of enhancing their surface and morphological properties. [5][6]

III. FABRICATION, TESTING AND CHARACTERISATION OF SYNTHESIZED GRAPHENE COIN CELLS

The working electrode become fabricated with 75 wt% of graphene powder, 18 wt% of ketjen black and 7wt% of teflonized acetylene black (tab), which turned into pressed form on a stainless-steel (SS) mesh, beneath a pressure of three hundred kg/cm^2 and dried at 140 ° c for 5 hrs in an oven. The electrochemical measurements have been accomplished using coin-type CR2032 cells.

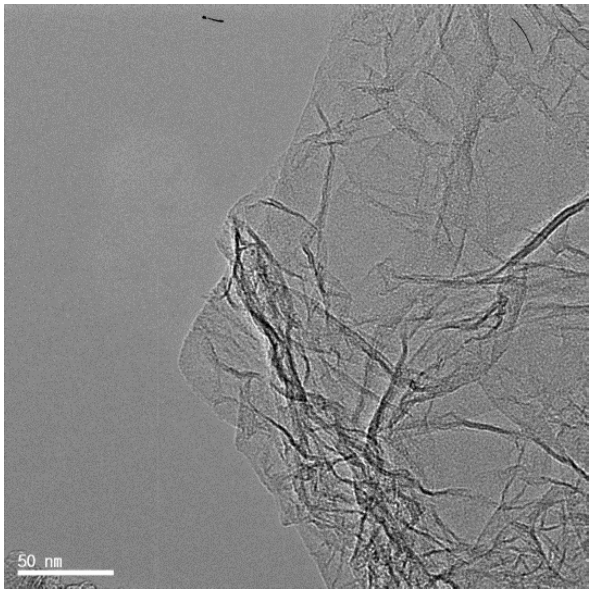

Fig 1. Wrinkles and crumpling of graphene sheet.

From the picture, it's far truly seen that the organized graphene is crippled and wrinkled in nature. Such structure allows in now not restacking and prevents stacking of the graphene sheets together. The TEM photograph shows the presence of single layer and notably porous nature of the synthesized graphene. The wrinkle and cripple nature of the graphene facilitates for extra access of the electrolyte during electrochemical activities. Aside from the superior houses of synthesized graphene, the decreased fee/discharge time might be attributed to the greater green contemporary collecting method that have employed on this work together with the usage of (SS) mesh and ketjen black conductive additive in cellular assembly.

The surface morphology of the graphene appears to be fairly porous, giving extra access to the electrolyte. This could have excessive surface get right of entry to even if they're stacked to electrode configuration. Because the average pore length of the nanocomposite is higher than the measurement of the ionic liquid ions (~0.7 nm), it enables ions to house within the pores and hence results in higher electrolyte accessibility and improves the fee storage. This mesoporous nature might permit electrolyte to access even the indoors region of electrode while it's miles pressed as an electrode.

Having an excessive electricity density, energy density and precise capacitance of 64.18 whkg^{-1}, 8.75 kwhkg^{-1} and 150.9 fg^{-1} at current density 5 Ag^{-1} that is found out by way of quite porous graphene primarily based supercapacitors. The retention of the capacitance after numerous tens of thousands of cycling is solid. The porous nature of the graphene and immensely reduced graphene increases the

accessibility for ion diffusion and very high conduction. The supercapacitor is an electricity storage device with high specific capacitance and short charging time. Supercapacitor shows solid operation after several tens of hundreds of cycles at high Amperes. The gadget showcase a specific capacitance at high current rate which is comparable to the value mentioned to date at a very low current level.[7][8]

IV. GRAPHENE BASED SUPERCAPACITOR NANOFIBER ELECTRODES

Supercapacitor cells were created exploiting nanofiber conductors fabricated via the electrospinning method to check the consequences of graphene and carbon black content on electrode structure and supercapacitor performance. The supercapacitor cells created employing a lower carbon electrospinning mixture (15% and 25% graphene with 8% PAN and also the 8% PAN solely concentration) resulted within the highest capacitance values within the range of 374-428 F/g.

Attributed to the exceptionally porous structure formed from stacking nanofibers on top of every other; which creates high porous regions that give a decent path for ions to travel through. The molecular mechanism of charge storage within the higher capacitance value samples, within the low carbon mole solution, need additional study; but, recent analysis is indicating to nitrogenated functionalities and ion desolvation within the amorphous structure, as potential causes for the higher capacitance values. [9]

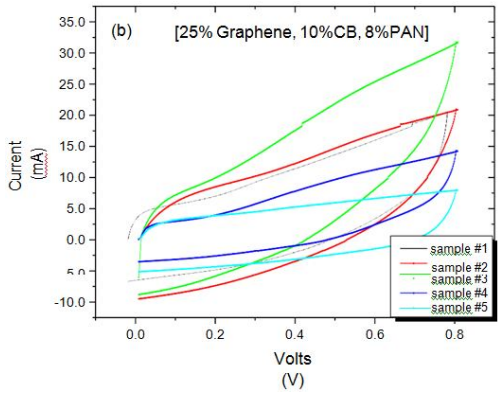

Fig 2. CV graphs for 25% graphene, 8% PAN, heat treated at 800˚C, submerged in 1M H_2SO_4. [10]

V. FLEXIBLE GRAPHENE BASED SUPERCAPACITORS

The development of flexible supercapacitors has become a crucial task because super- capacitors are equipped with the advantages of high-power and the high-energy density of batteries.2 Thus, mechanical flexibility would be an extra advantage.

Graphene has become one of the essential components in the fabrication of flexible electrodes because of its exceptionally high mechanical strength, extreme surface area, and highly conductive property which add extra advantages in preventing the electrode framework from being ruptured as a result of the mechanical bending/twisting of the flexible device. [11]

A. Graphene Nanocomposite Based on Electrode Type

As recorded, a graphene/CB hybrid film was fabricated and utilized directly as a supercapacitor electrode, for which reduced graphene oxide (rGO) was mixed with different amounts of CB and subjected to vacuum filtration to obtain the nanocomposite film. The rGO/CB film was free-standing and possessed flexible properties. The presence of CB electively acted as spacer, that prevented the restacking of rGO layers; but, higher CB content resulted in agglomeration where graphene was used by combining 10 wt % PTFE binder and 5 wt % super-p, that was then created into coin-size condenser cells. 4 The electrodes were separated via a Celgard porous membrane and 1-ethyl-3- methyldizolium tetrafluoroborate (EMIMBF4) as the organic electrolyte.

The morphology of the curvilineal graphene sheets indicated a capability to stop shut stacking. Therefore, the mesoporous structure was maintained even when being com-stacked into an electrode structure. The pore size of the graphene structure was within the range of 2−25 nm. In distinction, graphene sheets prepared via standard chemical reduction processes which were mentioned to possess an improved tendency to restack with each other, which significantly reduced the effective surface area because the inter-graphene gaps were smaller than 1 nm, therefore resulting in a significantly smaller capacitance of 50 Fg^{-1}.

B. Using Binder and Binder-Less Electrode

Recently the synthesis of binder-less electrodes was mentioned in a number of paper. The binder-less properties offer various advantages, as well as a value reduction from eliminating the binder cost and stepping-down of the electrical interference between the elements at the interface.

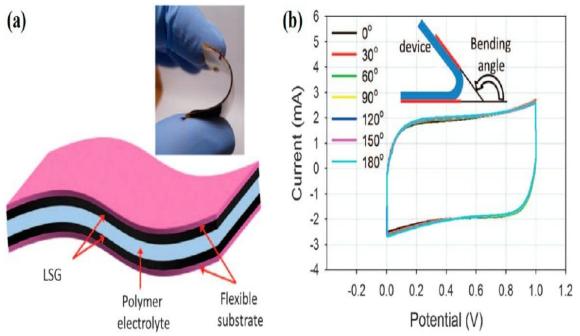

Fig 3. (a) Design and fabrication of flexible, all-solid-state LSG electrochemical capacitor. (b) Bending the device had almost no effect on its performance, as seen in these CVs collected at a scan rate of 1000 mV s^{-1}.

A typical supercapacitor device was made up by sandwiching associate ion porous separator or a polymer gel electrolyte between two identical LSG electrodes (Fig 3), which resulted in a very thin device with a total thickness of 100 μm. The fabricated supercapacitor showed remarkable flexibility, with the bending of the device having almost no effect on its electrochemical performance.

The graphene hydrogel was prepared via a modified hydrothermal reduction method and had a thickness of ∼3 mm. it had been immersed in a 1 M H_2SO_4 aqueous solution nightlong. The graphene hydrogel was specifically cut and pressed on a gold-coated polyimide substrate with a pressure of ∼1 MPa to obtain a thin film with a real mass of ∼2 mg/cm^2. Similar to previous reports, a solid-state super-capacitor was fabricated by sandwiching a layer of PVA/H_2SO_4 polymer electrolyte between identical electrodes made of the graphene hydrogel/polyimide film.[12][13]

VI. GRAPHENE BASED SUPERCAPACITORS USING EUTECTIC IONIC LIQUID MIXTURE ELECTROLYTE

The outstanding performance of such compact graphene film in the eutectic ionic liquid mixture electrolyte makes it a promising alternative to activated carbon for supercapacitor applications, particularly below hot temperature conditions.

The eutectic ionic liquid mix comprises of the same anion (bis(fluorosulfonyl) imide (FSI)) with two opposite cations (pyrrolidium (PYR) and piperidinium (PIP)) having similar molecular formula.These Films were then immersed in 10 wt% (0.27 M) ionic liquid mix of acetonitrile for about 72 hours, to exchange the acetonitrile in graphene film with the ionic liquid solution. After this some samples were collected, pressed between two glass plates and placed in a vacuum oven under 80°C. After 48 hours completion, the volatile acetonitrile was fully evaporated and nonvolatile ionic liquids were left inside the graphene film, which was anticipated to put up a boundary to the restacking of graphene layers. Due to the densification, the width of the graphene film was significantly decreased (from around 180 mm to 60 mm), whereas the diameter was measured about to 5.4 mm. Herein, the graphene film was well prepared and ready for electrochemical tests. [14]

Graphene films were used as working electrodes directly after vacuum drying without any binders. A eutectic ionic liquid mixture composed of (1:1 by weight or molar ratio) N-methyl-N- propylpiperidinium bis(fluorosulfonyl) imide (PIP13-FSI) and N- butyl-N-methylpyrrolidinium bis(fluorosulfonyl) imide (PYR14- FSI) was prepared and used as the electrolyte [15].

GF stands for graphene films without electrolyte, obtained by vacuum filtration that is containing water inside. GF-IL are the graphene films retrieved from electrolytic immersion which contains ionic liquid mix electrolyte after acetonitrile evaporation. The (0 0 2) peak around 26.0° of pristine graphite (GP) matches to an expected in between spacing of 0.336 nm. For graphite oxide (GO), maximum peak shifts to 9.0° due to the increased in between spacing to 0.976 nm after the completion of oxidation. No spikes were observed for graphene film (filled or empty) with electrolyte. For the graphene film it was expected that, (GF no electrolyte), containing around 90 wt% of H_2O, the peeled off graphene layer chips will be separated from each other by H_2O, preventing restacking, which was later confirmed. Contrary to this, in electrolyte filled graphene films GF-IL (only nonvolatile electrolyte), the electrolyte was assumed to stop restacking. [16][17]

A layered structure like this is expected to be at the origin of the solidification of the films when compared to standard 3-dimensional disordered structure, which results in a high volumetrical energy density. These results show that the combination of dense graphene films with a eutectic ionic liquid mixture can be promising as an alternative to conventional porous carbons for supercapacitor applications.

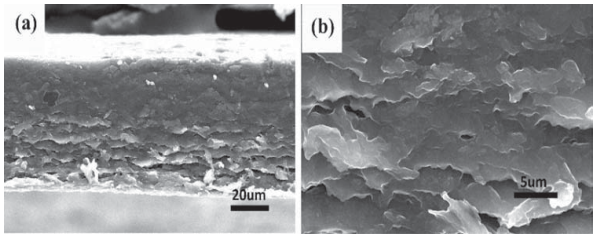

Fig 4. SEM images of cross-section morphology of graphene film after electrochemical tests. Scale bar: 20 *m*m (a), 5 *m*m (b).

On the boundary conditions the high gravimetrical and volumetrical capacitances are obtained at room temperature (165 $F.g^{-1}$ and 50 $F.cm^{-3}$, respectively), this large potential window (3.5 V) and temperature operation range (from -30°C to 80°C) make them optimum for creating high energy density supercapacitors.

A most gravimetric capacitance of 175 $F.g^{-1}$ (85 $mAh.g^{-1}$) was reached at 80°C. Despite the capacitance at -40°C was limited at 60 $F.g^{-1}$ (30 $mAh.g^{-1}$), 130 $F.g^{-1}$ (63 $mAh.g^{-1}$) and 100 $F.g^{-1}$ (49 $mAh.g^{-1}$) were still achieved at -20°C & -30°C respectively. The potential window was enhanced up to 3.5 V at room temperature and 3.2 V at 80°C, therefore resulting in substantial improvement within the cell energy density. in addition, a volumetric capacitance of 50 $F.cm^{-3}$ was also achieved with a thick graphene film of 60 mm. [18]

VII. CONCLUSION

Graphene-based materials in numerous forms have proved to be wonderful candidates of electrode materials in electrochemical energy storage systems, such as supercapacitors. In recent years, considerable efforts are employed on the structural style, material fabrication, performance analysis, furthermore as understanding of the key electrochemical phenomena is observed. to comprehend the expected complete utilization, the standard and reproducible amount of the electrode materials each will have to be compelled to be additionally improved, especially with the event of the foremost desired structures tunable in nano-, micro-, meso- and macro-scales. The low price and effective method to generate graphene-based materials is that the chemical exfoliation of graphite into GO and also the subsequent affordable reduction of go to rGO. However, before the massive scale application of this facile production technique in electrochemical energy storage devices, the stabilization of single or few-layer graphene sheets in numerous solvents and also the preservation of their intrinsic properties should be addressed so as to break the bottleneck of re-stacking of graphene sheets.

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