Development and Characterization of Super capacitor Using Graphene for Small Capacity Energy Storage Applications

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Abstract - *Super capacitors have attracted a lot of attention due to their efficient energy storage. Compared to batteries, super capacitors have higher capacitance, energy, and power densities per unit mass than conventional capacitors. Carbon-based materials are most promising in super capacitor applications due to their outstanding physical and electrochemical behaviour. This work demonstrated a facile method to synthesize a Nano composite electrode consisting of graphene from rGO and carbon black as active material. It was found that the Nano composite electrode with 80 % graphene, 10 % carbon black and 10% PVDF as binder studied with NMP as solvent and PVP/LiClO4 as a gel-type electrolyte which acts as separator also due to which weight and size reduced compared to aqueous electrolyte super capacitor. It is expected that the current density will be higher than pure graphene-based super capacitors since the carbon black is added, which increases the conductivity of the electrode and also the thermal stability of the super capacitor device. A pouch cell super capacitor was fabricated using above mentioned materials with their proportions on the flexible steel current collector, and performance parameters will be evaluate*d.

***Key Words*: Super capacitor, grapheme, Energy Storage, ultra capacitors, Charge Discharge**

1. INTRODUCTION

Due to their adequate energy storage, Supercapacitors have received a lot of interest supercapacitors offer higher capacitance, energy, and power densities per unit mass than traditional capacitors. The most promising materials for supercapacitor applications are Carbon-based materials since they have exceptional physical and electrochemical behaviour. Supercapacitors are used for applications where the requirement of power density is high for a short duration of time, i.e. The areas where there is a need to absorb or bear the high impulse of voltage like a hybrid transportation system, to store the energy generated during regenerative braking system, grid stabilization and nowadays in the critical domains like space and military.

However, nano-based materials showed high performance concerning charging ability, capacity, and cyclability. It has the ability to provide more power density and can charge and discharge in a fraction of a second.

1.1 Supercapacitor Energy Storage Method:

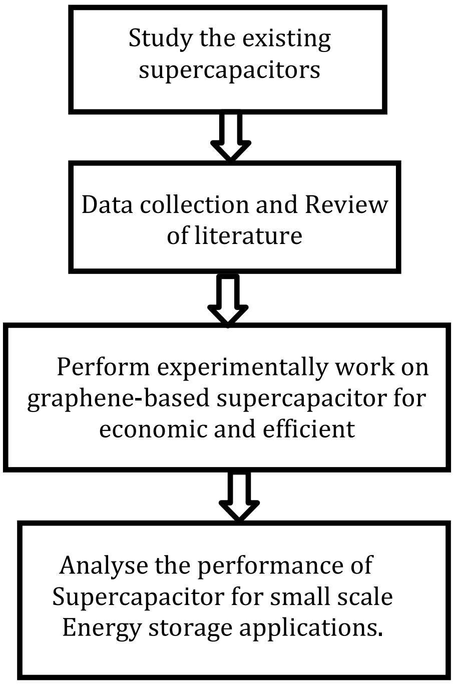
Supercapacitors, often referred to as ultracapacitors or electric double-layer capacitors, are energy storage technologies exhibiting extremely high capacitance and low internal resistance. The separation of charges at the electrode/electrolyte contact serves as the energy storage mechanism in this instance. In contrast to batteries, this device, in particular, has comparatively high energy storage and delivery capacity. A supercapacitor model consists of a separator, two electrodes, and an electrolyte, although the device's performance largely depends on the electrode material. Supercapacitors have flexible packaging, high power, extended life cycle, wide operating ranges (-40^{0}C to 77 ^{0}C), are lightweight, and require little maintenance

1.2 Applications of a supercapacitor:

Modern electrical and electronic equipment has very strict safety requirements for high current, energy, and power requirements. One way to satisfy these excessive demands for high power density is to use capacitors, which emit a lot of energy quickly. Additionally, under ideal circumstances, capacitors can replace batteries in electric vehicle systems by fusing their high power density with the high energy density of batteries. The amount of energy stored as ions between the electrolyte and the electrode is the basis of the supercapacitor's working theory. As renewable energy sources represent a crucial component of such systems, distributed power generating networks and autonomous renewable energy systems are gaining appeal.

By integrating energy storage devices, such systems' dependability and efficiency can be considerably improved. The usage of supercapacitor-based energy storage systems, which can deliver critical energy bursts for a brief duration, helps to reduce power quality issues. Systems for converting wind energy or P.V. energy storage are necessary to control fluctuations. To handle these variations and keep the output voltage constant, supercapacitors can be utilised as energy storage devices.

2. METHODOLOGY: Work flow chart



2.1 Materials and design of supercapacitor

Graphene – Graphene is used as active material coated on the electrode substrate or current collector since it has high active surface area and mesoporous nature, and ability to adsorb ions on its surface area when potential is applied. Before using it for application, it is crushed on a mortar and pestle. The specific capacitance is given in terms of f/g or f/cm^2, so it is clear the particular capacitance is inversely proportional to the area of the electrode. From experiments, it is clear that 2.065 f/g specific capacitance is obtained from the electrode of the area of 6.2 cm^2, i.e. of the size 2.5 cm x 2.5 cm. For the application of the device at 12 V, considering the scope of the project and the availability of equipment, it is feasible to make a supercapacitor of 5 f/g specific capacitance, a voltage of 1.45 V and a current of 5 mA. Now, to get around 5 f/g specific capacitance, the electrode should possess an area of 16 cm^2, so the dimensions of the electrode will be 4 cm x 4 cm. For this application, the required voltage is 12 V which supercapacitors can be achieved by connecting 13 such manufactured devices. As we have, q = cxv, For 13 supercapacitors, the equivalent capacitance connected in parallel is 13 x 0.85 = 11.05 f and the total charge which gives the voltage output when the the supercapacitor is discharged can be obtained by multiplying the voltage of the supercapacitor device and equivalent capacitance, which is, 11.05 x 1.1 = 12.15 C. It is clear from the above values that the parallel connected supercapacitors will have an equivalent capacitance of 11.05 f, and the total charge stored by these is 12.15 C. The full voltage it can deliver after discharge is the amount of payment stored in it. So the system can provide an output voltage of 12 V. As per the design, the device is expected to show the measurements of current, voltage and specific capacitance around 5 mA, 1.45 V and 4.61 f / g, respectively

Results of prepared device:

The device shows slightly lower parameters than the expected values, which are as follows:

Specific capacitance = 3.42 f/g,

Voltage = 1.1 V and current = 5 mA,

capacitance = 0.85 f.

The device's performance depends on various conditions, including the material used for preparing the device, such as active materials, binder, electrolyte, solvent, and the coating of active material on flexible steel substrate, etc.

2.2 Manufacturing of Supercapacitor:

Active materials used for the device

Figure 1: Active material

Graphene acts as an active material for the ultracapacitor device along with PVDF (polyvinylidene difluoride) as a binder or adhesive agent for the active material on the flexible steel substrate used for the supercapacitor electrode

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Preparation of flexible steel for coating

Figure 2: Ultrasonication of flexible steel

The flexible steel is firstly cleaned using zero-number polish paper before undergoing any further process. Afterwards, it is cleaned using distilled water in the ultrasonicator, as shown in the picture. Again it is sonicated in the ultrasonicator using acetone, ethanol and distilled water.

Coating of active material on flexible steel substrate

Figure 3: Coating of active material

The coating of active material is done on the flexible steel substrate using a hot vacuum rolling coater machine. The cleaned substrate is placed as shown in the picture, and the vacuum is turned on so the substrate can be stuck flat on the surface.

Coating of active material

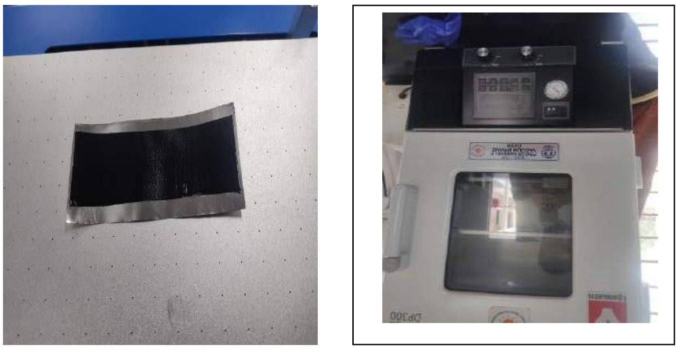

Figure 4: Coating and drying of electrode

The slurry is prepared using active material and N.M.P. (N-Methyl-2-pyrrolidone) as required and poured before the coating blade. Afterwards, the edge coats the slurry uniformly on the flexible steel substrate, as shown in the picture. It is dried in the coater at 60 degree Celsius, and then it is dried at 120 degree Celsius in the pressurized programmable oven.

Wrapping of device

Figure 5: Application of electrolyte

After drying, the gel-type electrolyte is applied to the prepared electrode surface, the mixture of PVP and $LiClO_4$ (polyvinylpyrrolidone and lithium perchlorate). This gel electrolyte which acts as a separator for supercapacitor devices.

3. CHARACTERIZATION AND TESTING

Among the various techniques of characterization, the three methods are essential are as follows:

1. X-ray powder diffraction (XRD)

2. Raman Spectroscopy
3. Fourier Transform Infrared Spectroscopy (FTIR)

1. **X-Ray Power Diffraction:**

The figure also includes the XRD pattern of graphite, which demonstrates the existence of two distinctive peaks in the XRD pattern of the graphene product. (around 12 and 26), From the XRD pattern, we can conclude revealed the structure of carbon atoms or molecules was preserved in graphene, but the diffraction peak widened, and the intensity decreased. This is due to the fact that when graphite was converted into graphene, the layer's size shrunk. Also, it is suitable for the application of supercapacitors

2. **Raman Spectroscopy:**

This is used to detect the polarity of the material, i.e. rotational and other states in the molecular system. Here, the band of graphene was observed at 1587 $cm^{-1,}$ which may arise from certain defects such as vacancies and grain boundaries. From the spectra data , it is seen that there is a peak at 2700 $cm^{-1,}$ This represents the quantity of graphene layers. Due to a few layers of imperfect graphene in the produced material, it is seen that the band has widened in this case. It contains only lower defects and better graphitization, so it possesses good electrochemical properties.

3. **Fourier Transform Infrared (FTIR):**

It is a method used to obtain the infrared spectrum of the material's absorption and emission and detect the different functional groups present in the material. From the spectra data , we can see the peak at 1200 cm^{-1}; no other functional groups are present except C-C and C=C. This material can be used for the applications like supercapacitors.

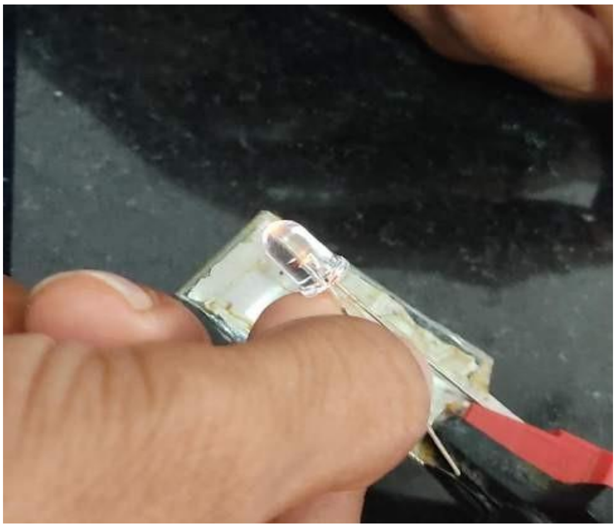

Figure 6: Testing of Supercapacitor

3.1 Testing of Supercapacitor:

The performance of the supercapacitor is evaluated by doing several tests. The nature of the device is known by cyclic voltammetry, i.e. whether the device shows EDLC characteristics or Pseudo capacitance characteristics. The total life cycle of the supercapacitor and the percentage drop in the performance of the supercapacitor after processes are evaluated by galvanostatic charge-discharge.

4. RESULTS

The primary test to evaluate supercapacitor is Galvanostatic charge-discharge, Cyclic Voltammetry, and Electrochemical Impedance Spectroscopy.

4.1 Cyclic Voltammetry (CV):

It is an electrochemical method that gauges the current that forms in an electrochemical cell, where the voltage is higher than what the Nernst equation predicts. A working electrode's potential is cycled to execute the operation, and the resulting current is then measured.

The shape of the CV tells us the behaviour of the electrode, whether it is showing pseudocapacitance or EDLC nature. This CV is performed under a cycling potential of 0.01 Vs^{-1}. The above shape of the CV curve it is clearly showing that the electrode exhibits pseudocapacitive behaviour.

4.2 Electrochemical Impedance Spectroscopy (E.I.S.):

It is an electrochemical multifrequency A.C. measuring method. It gauges the metal/solution interface's electrical resistance (Impedance) over a broad frequency range. The system under investigation is described using a variety of models. The most popular and simple model for electrochemical capacitor E.I.S spectrum is a streamlined Randle's model, as seen in the Figure.

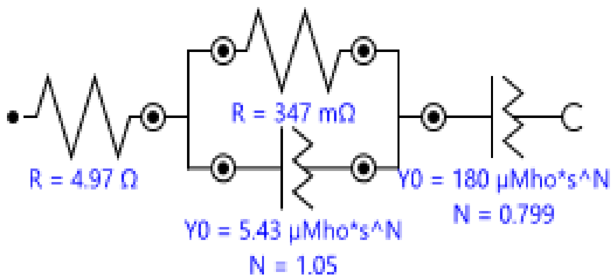

Figure 7: E.I.S. equivalent circuit (simplified Randle's model)

The above Figure shows that the internal resistance is about 347 mΩ and the solution resistance is about 4.97 Ω. This data helps in choosing material for supercapacitor devices. From the spectra, it is clear that the experimental curve slightly deviates from the ideal angle of the fitted E.I.S. data since the ideal supercapacitor does not exist in reality, and a number of outcomes cause flaws in the system.

4.3 Scan Rate:

The electrode potential ramps linearly versus time in cyclic phases during cyclic voltammetry (CV). The experiment's scan rate is the pace at which the voltage changes over time in each of these phases. From the curve, it is seen that, as applied potential is increased, the corresponding current is also increased, exhibiting its good capacitive behaviour. The potential is increased from 10mV to 100mV.

4.4 Galvanostatic Charge Discharge:

By measuring the potential difference across the capacitor as a function of time, this experiment aims to better understand how capacitors charge and discharge. The short time constant means that the Capacitor will charge and discharge at a faster rate and vice versa.

The charge-discharge is carried out at 4,5,8, and 9 mA, and the results are as follows

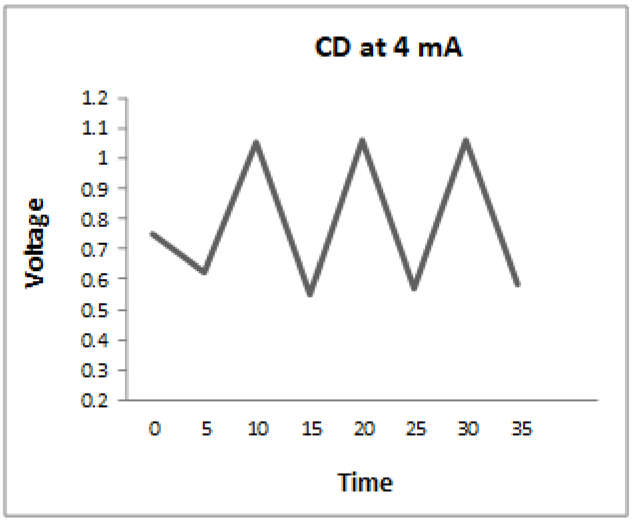

Chart -1: Charge Discharge at 4 mA

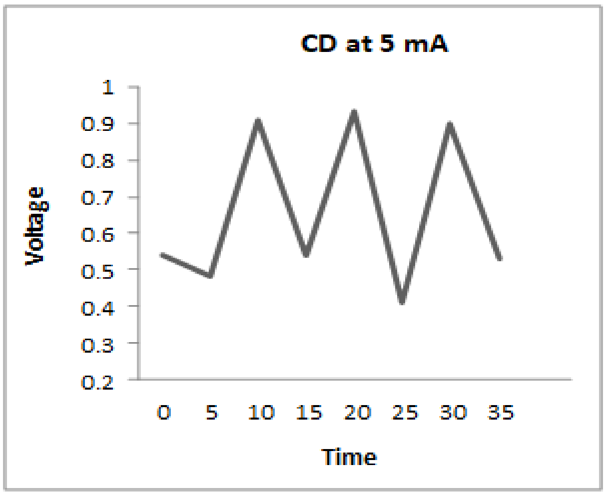

Chart -2: Charge Discharge at 5 mA

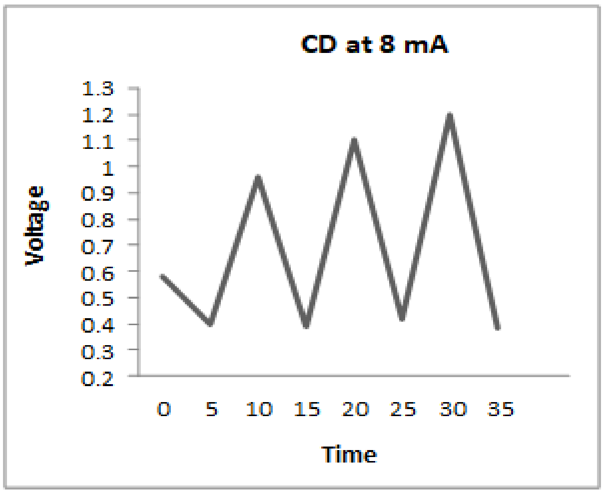

Chart -3: Charge Discharge at 8 mA

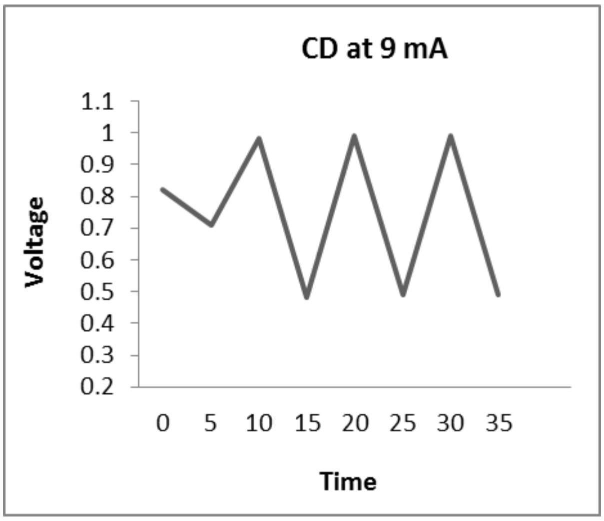

Chart -4: Charge Discharge at 9 mA

From the above graphs, it is clear that the discharge time is higher at 5 mA, so the stability is performed at this current, i.e. at 5 mA, to calculate the specific capacitance, energy density and power density.

The stability check is done for around 1000 cycles, and the results are as Follows:

Deposited weight of electrode – 0.188 g
The empty weight of the electrode - 0.168 g
Active weight of electrode – 0.02 g
Potential window (ΔV) – 0.7 V
Current (I) – 5 mA
Specific capacitance $C_{sp} = I \times \Delta t / m \times V$
Energy density $E = ½ CV^2$
Power density $P = E / t$ 100th cycle- Δt = 3.84 s

Csp = 1.37 f/g, E = 0.335 Wh/Kg, P = 314.6 W/Kg
200th cycle- Δt = 5.92 s
Csp = 2.11 f/g, E = 0.518 Wh/Kg, P = 315 W/Kg
300th cycle- Δt = 5 s
Csp = 1.78 f/g, E = 0.437 Wh/Kg, P = 314.9 W/Kg
400th cycle- Δt = 6.11 s
Csp = 2.18 f/g, E = 0.534 Wh/Kg, P = 315 W/Kg
500th cycle- Δt = 6.2 s
Csp = 2.21 f/g, E = 0.542 Wh/Kg, P= 314.9 W/Kg
600th cycle- Δt = 7.33 s
Csp = 2.61 f/g, E = 0.641 Wh/Kg, P = 314.96 W/Kg
700th cycle- Δt = 7.37 s
Csp = 2.63 f/g, E = 0.644 Wh/Kg, P = 314.96 W/Kg
800th cycle- Δt = 7.53 s
Csp = 2.68 f/g, E = 0.658 Wh/Kg, P = 314.9 W/Kg
900th cycle- Δt = 8.63 s
Csp = 3.08 f/g, E = 0.755 Wh/Kg, P = 314.9 W/Kg
1000th cycle- Δt = 8.71 s
Csp = 3.11 f/g, E = 0.762 Wh/Kg, P = 314.9 W/Kg

From the outcomes above, the stability for 1000 cycles is calculated at around 65 %.

5. DISCUSSION AND CONCLUSION

The N.M.P. solvent is suitable for the active materials and the binder mixture. Slurry gets coated correctly and uniformly on the flexible steel substrate due to the addition of N.M.P. to other organic solvents. Adding black carbon increases the conductivity and other performance parameters. Without adding black carbon, the active material is not coated on the flexible steel substrate properly. Due to the use of a gel-type electrolyte, which acts as a separator between two electrodes, size and weight are reduced compared to aqueous electrolytes. The overall thermal stability of the device is enhanced due to the addition of black carbon. The electrode exhibits a specific capacitance of 3.42 f / g. The discharge time we get from the galvanostatic charge-discharge experiment is about 8.75 s. The voltage it can provide after discharge is about 1.1 V, and the device's current is 5 mA. From all the parameters, it is clear that by using different active materials, substrates and electrolyte combinations, the performance of the electrode can be increased by functionalizing the active material

Conclusion:

It can be concluded that:

1. Graphene is one of the most viable active materials for the flexible supercapacitor device due to its nature and electrochemical properties.

2. Adding black carbon helps bind active material on the current collector, increases the conductivity, and improves other capacitance performances and thermal stability of the electrode.

3. Due to their flexible nature and high performance, these supercapacitors are used on a vast scale in the domains like automobile, power, defence, consumer electronics etc.

4. The device shows results slightly lower than expected results since the performance of the device depends on various factors such as experimental conditions, material etc. from the results outcomes of the prepared electrode or supercapacitor device, it can be concluded that the device can be used in applications like microgrid fluctuation control where the bursts are needed for A short duration of time and applications where the backup is needed for some time and in consumer electronics by compacting the size of it.

5. The flexible nature of the device leads to a wide range of opportunities for its applications. This initial goal achievement motivated me to further enhance the performance by altering each component of the supercapacitor which includes electrode material and the electrolyte solution.

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