Chapter-3

From Dead Leaves to High Energy Density Supercapacitor

In this work, functional microporous conducting carbon with high surface area of about 1230 m$^2$g$^{-1}$ is synthesized by a single step pyrolysis of plant dead leaves (dry waste, ground powder) without any activation and studied for supercapacitor application. Although the detailed study performed and presented here is on dead Neem leaves (Azadirachta indica), the synthesis method is generic and applicable to most forms of dead leaves. Indeed we have examined the case of dead Ashoka leaves as well. The comparison between the Neem and Ashoka leaves brings out the importance of the constitution and composition of the bio-source in the structural and electronic properties of carbon. We have also studied the cases of pyrolysis of green leaves and un-ground dead leaves against the ground dead leaves powder. The concurrent high conductivity and microporosity realized in the case of ground dead leaves powder materials are key to the high energy supercapacitor performance.

Dead leaves to Supercapacitor
3.1 Introduction

Waste management is one of the most prevalent problems of big cities. Fortunately, through several environmental awareness programs communities have begun to separate dry and wet waste matter. Most such waste is a rich source of carbon but may contain other elements in different proportions depending on the source. In most of the municipal waste management centers, the waste from natural sources is directly burnt off. This produces ash and hazardous gaseous pollutants. There have been some initiatives to employ the ash in certain applications in the form of passive fillers. But other than this there has not been much effort on reusing or converting the natural waste to a significant application. With extensive ongoing research work around carbon-based opto/electronic/energy applications, if the natural waste and some of the man-made waste is harnessed towards electronically active functional forms of carbon, one could get a value-added product for diverse and growing carbon-based applications.

Carbon is the most naturally occurring abundant material exhibiting variety of molecular and structural forms such as graphite, diamond, nanotubes, graphene, fullerene, nano-diamonds, amorphous carbon, porous carbon etc. with various applications.\(^{[1-6]}\) Amongst these porous carbon and graphene have high surface area, chemical inertness, and synthetically tunable electrical, thermal and optical properties. These versatile properties of specific carbon based materials make them efficient to be used in supercapacitors, batteries,\(^{[7,8]}\) and as superabsorbents for gases and toxins.\(^{[9]}\)

Supercapacitors have been attracting significant research interest lately due to their wide range of applications in electrical vehicles, digital devices, pulsing techniques etc. due to their high durability, high power density and fast charging-discharging mechanism.\(^{[10-12]}\) Mostly activated carbon materials having high surface area (2000-3000 \(\text{m}^2\text{g}^{-1}\)) are used as electrode materials in supercapacitor applications with specific capacitance around 250-350 \(\text{Fg}^{-1}\).\(^{[13-21]}\) Clearly efforts aimed at enhancing these properties by suitably engineering of the synthesis of functional carbon while concurrently reducing costs is a desirable research endeavour.
Scientists have tried several interesting synthetic routes to obtain high quality carbon. These include carbonization of organic/polymeric precursors, chemical vapour deposition, excimer laser ablation of graphitic targets, sputtering / plasma based synthesis, arc discharge synthesis, chemical methods etc. More recently researchers have started utilizing organic waste materials for the synthesis of carbon for specific absorbant or charge storage applications. Waste materials such as food, agricultural wastes, and even insects have already been utilized as a bio-source of carbon in graphene synthesis. Activated carbon has also been synthesized by pyrolyzing waste material with some chemical or physical additives as agents for activation. The purpose of such activation is to enhance the surface area and introduce porosity to make the materials functionally more effective. Physical activation mainly includes activation with steam, CO₂ etc. and chemical activation involves uses of chemicals such as NaOH, KOH, CaO, Ca(OH)₂, K₂CO₃, etc. which are known as porogens.

In this work we demonstrate synthesis of high surface area microporous conducting carbon material by one strep pyrolysis of plant dead leaves (abundant waste material) without any chemical or physical activation and have examined its properties for supercapacitor application. Although the detailed study performed and reported here is on dead Neem leaves (Azadirachta indica), the process is clearly generic and applicable to most forms of dead leaves. Indeed we have examined the case of dead Ashoka leaves as well. The comparison between the Neem and Ashoka leaves brings out the importance of the constitution and composition of the bio-source in the nature of carbon formed and its properties. We have also examined and compared the cases of pyrolysis of green leaves as well as un-ground dead leaves with that of ground dead leaves powder in full details. To the best of our knowledge there is only one report by Beguin et.al. in the literature wherein they have demonstrated synthesis of high surface area carbon from waste sea-weeds without any activation. Using the functional carbon derived from dead plant leaves (CDDPL) as a charge storage material in a supercapacitor, we have achieved very promising results: a high specific capacitance (400 Fg⁻¹) and very high energy density 55 Wh kg⁻¹ at a current density of 0.5 Ag⁻¹. The areal capacitance value of the carbon derived from dead...
(Neem) plant leaves (CDDPL) is also significantly high (32 µF cm\(^{-2}\)). Moreover, in an organic electrolyte the material shows a specific capacitance of 88 Fg\(^{-1}\) at a current density of 2 Ag\(^{-1}\). These performance features can be attributed to the high specific surface area associated with the narrow micropore distribution as well as high electrical conductivity of the CDDPL material. This performance is clearly superior to that of most commercially available and synthetically obtained activated carbon forms that have been used in ultracapacitor charge storage networks.

Despite their high power density capability supercapacitors always struggle with the limitation of low energy denisty. To solve this problem hybrid capacitor designs - two different electrodes- have strated to become more popular. Such hybrid capacitors have also been classified into three categories, namely the composite type, assymetric type and battery type. Detail description of these types has been provided in chapter 1. In our work apart from EDLC type supercapacitor we have also used the dead leaves derived carbon as electrode material in battery type hybrid capacitor configuration. In Li ion hybrid electrochemical capacitor configuration with Li\(_4\)Ti\(_5\)O\(_{12}\) capacity of ~32 mAhg\(^{-1}\)and a specific capacitance of 72 Fg\(^{-1}\) is obtained with the leaf derived carbon. This is comparable with the results obtained from the commercial activated carbon electrode materials. The details pertaining to these studies are presented and discussed in this chapter.

### 3.2 Experimental

#### 3.2.1 Materials

Neem (Azadirachta indica) dead leaves were collected from National chemical laboratory campus (please see the photo in Figure 3.1). N-Methyl-2-pyrrolidone (NMP) was used from Rankem chemicals and PVP (Polyvinylpyrrolidone) was obtained from Aldrich Chemicals. Ashoka (Saraca asoca) leaves were also obtained locally.

#### 3.2.2 Synthesis of functional carbon

The dead Neem leaves were collected in large quantity, thoroughly washed, cleaned and dried at 60°C in an oven. These dried leaves were crushed to get fine
powder which was stored in a completely dry atmosphere. For the synthesis of functional carbon 10g Neem leaf powder was heated in an alumina crucible at 600°C, 800°C or 1000°C for 5 hrs in different experiments in argon atmosphere at a heating rate of 10°C per min in a split tube furnace. Figure 3.1 shows the process pathway used for the synthesis of carbon from dead leaf powder and subsequent supercapacitor measurements.

![Image: Neem Tree, Neem dead leaves, Carbon after high temperature pyrolysis, Crushed powder]

**Figure 3.1:** Schematic diagram for the synthesis of functional carbon from dead leaves and the supercapacitor based thereupon.

For the sake of comparison pyrolysis of dead leaves from another plant source namely Ashoka (*Saraca asoca*) was also performed at 1000°C for 5 hrs and the corresponding material was studied. In all cases the light green coloured Neem leaf powder was changed to black coloured carbon after heating. This carbon was then thoroughly washed and ground in a mortar pestle to get fine powders. This carbon was characterized by several techniques. The process discussed in this work is easily scalable to large amount for the synthesis of functional mesoporous conducting carbon. We also examined and compared the cases of pyrolysis of green leaves as well as un-ground dead leaves with that of ground dead leaves powder.
3.2.3 Electrochemical Measurements in 1M H₂SO₄

All the electrodes were prepared on glassy carbon. Two glassy carbon substrates having similar area were used for each measurement. The carbon material was loaded on the substrate following standard procedure protocol used for supercapacitor measurements. Thus, 80 wt % Neem leaf derived carbon (CDDPL) was mixed with 15 wt % conducting carbon (acetylene black) and 5wt% PVP binder. To the above mixture 2-3 drops of NMP (N-Methyl-2-pyrrolidone) were added and ground thoroughly to make viscous slurry. Then this slurry was coated on the glassy carbon substrate with 1 mg loading in 1 cm² area. After making the electrodes they were dried in vacuum for 24 hrs at 60°C for the measurements. Electrochemical cyclic voltametry studies were performed in 1M H₂SO₄ solution between potential range 0-1V at various sweep rates.

3.2.4 Electrochemical Measurements with 1M LiPF₆ in EC: DEC

All the electrochemical measurements were conducted in two electrode coin-cell (CR2016) assembly. For the coin cell assembly, electrodes were made of 4 mg of leaf derived carbon, 2 mg of super-p (conducting carbon) and 1 mg of binder TAB-2. Supercapacitors were assembled with two symmetric carbon electrodes and separated by Whatman paper and filled with 1M LiPF₆ in EC:DEC (by 1:1 wt.%, DAN VEC) electrolyte solution. Cyclic voltammetric (CV) studies were carried out using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat.

3.2.5 Electrochemical Impedance Spectroscopy Measurements

Electrochemical Impedance Spectroscopy measurements (EIS, Autolab PGSTAT 30 (Eco-Chemie)) were performed for symmetrical supercapacitor cell consisting of the dead Neem leaf derived carbon electrodes in both 1M H₂SO₄ (aqueous) and 1M LiPF₆ in EC: DEC (organic) electrolytes. The frequency range used for the study was from 10 kHz to 10 mHz in the presence of AC amplitude of 10 mV with no external DC applied voltage.
3.2.6 **Electrochemical measurements for battery type hybrid supercapacitor**

All the electrochemical measurements were carried out by the standard two electrodes CR 2016 coin cell assembly. The composite test electrodes were formulated with 80% active material, 10% of conducting carbon (Super-P), 10% of binder (teflonized acetylene black, TAB-2) with ethanol as a solvent and pressed over 200 mm\(^2\) stainless steel mesh (Goodfellow, UK). For the single electrode performance (half-cells), insertion type 100 material Li\(_4\)Ti\(_5\)O\(_12\), Neem leaf derived carbon and commercial AC were used as working electrode materials and metallic lithium served as both the counter and reference electrode. Micro-porous fibrous paper (Whatman, Cat. No. 1825-047, UK) was used as a separator and filled with 1M LiPF\(_6\) in ethylene carbonate (EC) / dimethyl carbonate (DMC) (1:1 wt %, Selectipur LP 30, Merck KGaA, Germany) as electrolyte solution for both the half-cell and Li-Hybrid electrochemical capacitor assembly.

3.2.7 **Characterization**

The functional carbon products synthesized from dead leaves by the different protocols stated above were examined by X-ray powder diffraction using Philips X’Pert PRO diffractometer with nickel-filtered Cu K\(\alpha\) radiation, Raman spectroscopy using LabRAM HR800 from JY Horiba and high-resolution transmission electron microscopy (IFEI, Tecnai F30, FEG with 300 kV). The surface area values of all the samples were determined by Brunauer Emmett Teller (BET) adsorption method (Quadrasorb automatic volumetric instrument). Cyclic Voltametry measurements were performed by Auto Lab (model PGSTAT 30, eco-chemie).

3.3 **Results & Discussions**

Analysis of the composition of fresh Neem leaves (Table 3.1), reveals a 59.4% moisture content. In dry leaves the moisture content is far less and hence the primary constituents of dead Neem leaves are carbohydrates, fibers and protein. Carbohydrate has been established as an important source of functional carbon.\(^{[56-58]}\) The fiber, which is mainly composed of cellulose, lignin and hemicelluloses, also contributes to carbon source. Besides these organic components, Neem leaves also
contain Ca and Mg in minute amounts. Interestingly Ca and Mg salts have already been independently used as porogens to create pores in the synthesis of activated carbon. Thus the natural presence of these minerals in dead Neem leaves should help create pores in the synthesized carbon without activation, as discussed later. **Figure 3.2a** shows XRD pattern of the carbon synthesized from Neem dead leaves at 1000°C. The two broad peaks around 20~23.3° and 43.8° represent graphitic carbon, albeit with some disorder. The specific nature can be further elucidated by Raman spectroscopy. **Figure 3.2b** shows the Raman spectra for the same carbon material. The peaks present around 1320 cm⁻¹ and 1590 cm⁻¹ correspond to the characteristic D and G bands of carbon, respectively. The D (defect) band (1320 cm⁻¹) is due to the breathing mode of κ-point phonons of A₁g symmetry and the G (graphitic) band (1580 cm⁻¹) is assigned to the E₂g phonon of sp² carbon atoms. The high I_D: I_G ratio (1.15) indicates presence of disorder in the carbon matrix.

<table>
<thead>
<tr>
<th>Moisture</th>
<th>59.4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proteins</td>
<td>7.1%</td>
</tr>
<tr>
<td>Fat</td>
<td>1.0%</td>
</tr>
<tr>
<td>Fibre</td>
<td>6.2%</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>22.9%</td>
</tr>
<tr>
<td>Minerals</td>
<td>3.4%</td>
</tr>
<tr>
<td>Vitamin C</td>
<td>218 mg/100g</td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>73.30 mg/100g</td>
</tr>
</tbody>
</table>

**Table 3.1: Chemical composition of fresh Neem leaves**

The HRTEM image in **Figure 3.2c** shows a highly porous network morphology which is revealed to be in the form of faceted nanometric pores in **Figure 3.2d**. The pore size of just 2 nm or less is reflected in **Figure 3.2e**. The onion-like n-layer graphitic character (measured d-spacing equal to 0.34 nm) is brought out in **Figure 3.2f**. This renders good conductivity.
Figure 3.2: (a) XRD Spectra, (b) Raman Spectra, (c-f) HR-TEM images, of the carbon derived from dead plant leaves (CDDPL)

Figure 3.3a depicts the pore size distribution (PSD) for Neem leaf derived carbon (CDDPL material) as obtained by N$_2$ adsorption which shows a bimodal distribution of micropores and mesopores. Since nitrogen is known to undergo condensation process in micropores, $^{[62]}$ to obtain a more reliable pore size distribution (PSD) we also performed the gas adsorption-desorption experiments with CO$_2$ at 273K. The PSD thus obtained is plotted in Figure 3.3b. This figure clearly shows a bimodal distribution of 0.5 to 1 nm (5-10 Å) micropores along with a small proportion around 2 nm (20 Å) mesopores. The inset of Figure 3.3a shows BET nitrogen adsorption-desorption isotherm at 77K of the CDDPL material, while the inset of Figure 3.3b shows the isotherm for CO$_2$ adsorption case. The isotherm of Figure 3.3a corresponds to a hysteresis loop that is characteristic of a type IV isotherm. This hysteresis loop indicates capillary condensation which arises due to different mechanisms of adsorption and desorption in micropores. The loop described above can be further categorized as H4 type (associated with narrow pore size distribution). Low pressure hysteresis is observed in the isotherm plot which is also due to presence of micropores in the system. The specific surface area measured in accordance with the standard BET method is 1230 m$^2$g$^{-1}$. 
Figure 3.3: (a) Pore size distribution in N\textsubscript{2} for Neem leaf derived carbon, inset is the adsorption desorption isotherm for N\textsubscript{2}; (b) Pore size distribution in CO\textsubscript{2} for Neem leaf derived carbon, inset is the adsorption-desorption isotherm for CO\textsubscript{2}

Figure 3.4: (a & b) Pore size distribution and N\textsubscript{2} adsorption isotherms of carbon pyrolyzed at different temperature (600°C, 800°C and 1000°C)

The surface area value thus realized without any activation or pre/post treatment is quite high as compared to other cases of synthetic carbon obtained by using activating agents such as KOH, K\textsubscript{2}CO\textsubscript{3} etc. which specifically introduce pores for the enhancement of surface area. The high surface area compounded with a bimodal size distribution comprising of micropores and mesopores is useful from the standpoint of supercapacitor application. Micropores have high surface area to volume ratio and when present in significant amount play important role in the adsorption-desorption processes via diffusion. Mesopores contribute to the large surface but also provide high adsorbate accessibility by providing wider transport
channels to micropores.\footnote{63}

![Figure 3.5: Resistivity of carbon materials synthesized at 600°C, 800°C and 1000°C; inset is the schematic diagram of conductivity measurements under pressure.]

For comparison we also examined the surface area and pore distribution for the carbon pyrolized at other temperatures such as 600°C and 800°C. The pore distribution diagram and adsorption desorption isotherms for all the three cases (600°C, 800°C and 1000°C) are provided in Figure 3.4a and b. In the case of the sample pyrolyzed at 800°C the surface area is significantly lower, down to 229 m²g⁻¹, whereas in case of the sample pyrolyzed at 600°C the surface area is even lower, only 49 m²g⁻¹. In the 600°C sample mostly micropores are observed, whereas in the 800°C sample some mesopores appear but with a broad size distribution.

We also estimated the conductivity of carbon obtained by pyrolysis at 600°C, 800°C or 1000°C for 5h in flowing argon, because it is also an important parameter for supercapacitor application. Since it is very difficult to make a mechanically strong pellet out of porous carbon powder for conductivity measurements, all the conductivity measurements were carried out under an applied fixed and measured pressure (50 kg cm⁻²). The schematic diagram of the measurement process is depicted in the inset of Figure 3.5, where the powder is placed in a die and a known pressure is applied. The contact is
Figure 3.5: From the resistivity values it is observed that with increase in the maximum pyrolysis temperature the resistivity decreases rapidly. The resistivity values of the samples synthesized at 600°C, 800°C and 1000°C are found to be ~1.25 ×10^8 Ω cm, ~19 Ω cm, and ~ 1.7 Ω cm, respectively. Clearly, the carbon synthesized at 1000°C is found to be highly conducting in nature.

Electrochemical measurements were performed to evaluate the performance of the material in the context of supercapacitor application in both aqueous and organic electrolyte media. The corresponding results are summarized in Figure 3.6. We observed that the electrochemical (supercapacitor) properties of the samples
pyrolyzed at 600°C and 800°C are much inferior to those of the sample pyrolysed at 1000°C (Figure 3.7 and Table 3.2).

Figure 3.7: (a & b) Cyclic Voltammetry and charge discharge curves for Neem leaf derived carbon at 800°C; (c and d) Cyclic Voltammetry and charge discharge curves for Neem leaf derived carbon at 600°C

Therefore, in the following discussion we focus on carbon obtained by pyrolyzing dead leaves at 1000°C. As shown in Figure 3.6a, a nearly perfect rectangular shaped loop is obtained for a sweep rate of 5, 10, 20, and 50mVs⁻¹ without any redox peaks (oxidation or reduction). In the supercapacitor context such a rectangular shape represents a perfect electrical double layer formation (reversible adsorption and desorption of the ions) across the surface of the carbon, a testimony to the high specific surface area microporous character of the material. From the data shown in Figure 3.6a, it can be seen that the capacitive behaviour is maintained even at a very high scan rate. This performance at high scan rate establishes the high power capability of the microporous CDDPL material.
Table 3.2: Comparison of Specific capacitance, Energy density and power density of all the three carbon materials synthesized at 600°C, 800°C and 1000°C

For quantitative considerations, the specific capacitance is calculated from the galvanostatic charge discharge values by using the following equation 3.1:

$$Cs = \frac{2I}{m} \frac{dt}{dv}$$  \hspace{1cm} 3.1

Where \( Cs \) is the specific capacitance (Fg\(^{-1}\)), \( I \) is current, \( m \) is the active mass and \( (dv/dt) \) is the slope obtained from the discharge curve. The typical charge-discharge plots at 2Ag\(^{-1}\) current densities are shown in Figure 3.6 b. The specific capacitance values are calculated at different current densities ranging from 0.5 Ag\(^{-1}\) to 10 Ag\(^{-1}\), and are given in Figure 3.8. The highest specific capacitance value 400 Fg\(^{-1}\) is obtained at a current density of 0.5 Ag\(^{-1}\). As the current density increases the specific capacitance value decreases which is related to the limited diffusion of the active ions on the electrode surface because of fast charging. At high current density all the micropores are not accesible to the electrolyte , hence the relative capacitance is less as compared to the capacitance at low current density.
Figure 3.8: Plot of specific capacitance with different current densities which shows even at very high current density (10 A g\(^{-1}\)) the specific capacitance is still high as 290 F g\(^{-1}\).

The areal capacitance of the CDDPL obtained at 1000\(^\circ\)C has also been determined. Areal capacitance is very important in supercapacitor applications for small electronic devices.\[^{64-65}\] Generally a low mass loading of active materials is used in supercapacitors for obtaining very high gravimetric capacitance. However as a consequence their areal capacitance values are suppressed (5-12 \(\mu\)F cm\(^{-2}\)).\[^{66-70}\] Interestingly though, the CDDPL material obtained in our study shows a significantly high value of areal capacitance (32 \(\mu\)F cm\(^{-2}\)) as compared to other waste carbon based materials used for energy storage. For comparison purposes and to see the generic nature of the carbon forming process involving dead leaves, we also tested another dead-leaf source, namely Ashoka Leaves. Similar protocols were followed for the carbon synthesis.

The cyclic voltametry measurements for Ashoka leaf-derived carbon are shown in Figure 3.6 c. They also show a perfect rectangular shape suggesting that a double layer is being formed. From the galvanostatic charge discharge measurements (Figure 3.9) the specific capacitance comes out to be 250 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\). This is also quite good, although inferior to that of Neem leaf derived carbon.
Figure 3.9: Charge Discharge curve of Ashoka leaf derived carbon at 1Ag⁻¹ and 0.5Ag⁻¹ with 1M H₂SO₄

To compare the performance of both types of leaves we studied the morphology/constitution and composition of green leaf, dead leaf and dried leaf powder (obtained by grinding). Figure 3.10 shows that in the case of Neem leaf the morphology changes slightly from that of green leaf (Figure 3.10 a) to dry leaf (Figure 3.10 b), but it changes drastically from dry-leaf to dry-leaf powder (Figure 3.10 c), the latter obtained by grinding of the dry leaves. Even in the capacitance performance, the green leaf derived carbon (195Fg⁻¹) and dry leaf derived carbon without grinding (373Fg⁻¹) showed less specific capacitance than the ground dry leaf powder (401Fg⁻¹) which can be attributed to the lack of proper porosity.

The Cyclic Voltamtery curves of green leaf derived carbon and dry leaf derived carbon without grinding at a scan rate of 20mvs⁻¹ are shown in Figure 3.11a and b, respectively. From Figure 3.10c it is clearly seen that there are large porous structures present which is due to the loss of some matter during the process of grinding. As the powder itself is porous, one can expect that after pyrolysis also it may generate a porous carbon matrix. As seen from SEM micrograph, these porous structures are absent in the case of Ashoka green leaf (Figure 3.10d), dry leaf (Figure 3.10e) and dry leaf powder (Figure 3.10f).
These constitutional differences affect the surface area and porosity of carbon derived from these leaves. The elemental mapping of Neem and Ashoka dry leaf is presented in Figure 3.12a and b which show that in the case of Neem dry leaf the Ca (pink) content is comparatively much higher and well distributed than in the case
of Ashoka dry leaf. These results were also confirmed with the EDAX analysis shown in Table 3.3.

From the EDAX results, the Ca to C ratio for Neem leaves is clearly seen to be much higher in comparison to Ashoka leaves. The Ca content increases from green leaf to dry leaf and finally to dry leaf powder due to loss of some organic mater because of mechanical heat genearted from the grinding process. Apart from Ca there is also a small percentage of Mg present. The stated Ca content is very useful in our case as Ca is known to be a good porogen.

![Elemental mapping of Neem Leaf and Ashoka Dry leaf](image)

**Figure 3.12:** Elemental mapping of (a) Neem Leaf (b) Ashoka Dry leaf. Red- C, Green- O, Pink- Ca, Blue- Mg, Yellow- Al

There are many reports wherein researchers have mixed Ca salts in the samples for the creation of pores and to incres in the surface area. In case of leaf these minerals are well dsitributed in the leaf matrix as shown in the elemental maping which helps in natural creation of pores, enhancing the surface area. As the Ca content is high in the case of Neem leaf, there are more well defined pores and larger surface area (1230m$^2$g$^{-1}$) in the corresponding carbon as compared to the Ashoka leaf derived carbon, which has a surface area of 705m$^2$g$^{-1}$ **Figure 3.13.**
Table 3.3: EDAX analysis of Neem and Ashoka leaf derived carbon

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Neem Green Leaf</th>
<th>Neem Dry Leaf</th>
<th>Neem Dry Powder</th>
<th>Ashoka Green Leaf</th>
<th>Ashoka Dry Leaf</th>
<th>Ashoka Dry Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>78.06</td>
<td>72.47</td>
<td>71.51</td>
<td>75.48</td>
<td>74.18</td>
<td>72.87</td>
</tr>
<tr>
<td>O</td>
<td>15.26</td>
<td>17.92</td>
<td>13.53</td>
<td>19.80</td>
<td>21.99</td>
<td>22.09</td>
</tr>
<tr>
<td>Ca</td>
<td>5.89</td>
<td>6.94</td>
<td>11.32</td>
<td>1.85</td>
<td>1.98</td>
<td>2.21</td>
</tr>
<tr>
<td>Mg</td>
<td>0.10</td>
<td>0.21</td>
<td>1.30</td>
<td>0.18</td>
<td>0.16</td>
<td>0.21</td>
</tr>
<tr>
<td>Ca/C Ratio</td>
<td>0.075</td>
<td>0.095</td>
<td>0.16</td>
<td>0.024</td>
<td>0.026</td>
<td>0.030</td>
</tr>
</tbody>
</table>

Table 3.4 compares different carbon materials synthesized from natural waste and their performance in supercapacitors. This table clearly shows that the carbon derived in our case without any activation or special treatment shows an excellent performance than other waste material derived carbon (Bamboo, waste coffee beans, sugarcane baggase etc.). The very high performance can be attributed to the availability and wettability of the micropores whose dimensions are comparable to the dimensions of the solvated ions (cations or anions). To obtain a high performance supercapacitor it is important to understand the effect of surface area and pore size. Generally capacitance value increases with an increase in the BET surface area; but in some cases limitation in capacitance value is encountered even when the surface area is very high (more then 2000 m$^2$/g). [13-21]
Table 3.4: Comparison of the properties of carbon materials synthesized from waste and their use in supercapacitor

The pore size therefore plays a more important role in determining the charge storage capacity. Thus by engineering the pores properly high capacitance value can be achieved even at low surface area. Micropores less than 2 nm are critical for charge storage, and it is also seen that the pore size g to 0.5 nm is suitable for aqueous (1M...
H$_2$SO$_4$) based electrochemical supercapacitor. In H$_2$SO$_4$ electrolyte, the sizes of the Hydrated SO$_4^{2-}$, (H$_2$O)$_{12}$ (Hydration number calculated around 12.16) and H$_3$O$^+$ are around 5.33Å and 4.2Å, respectively. Thus, the pore size in the CDDPL exactly corresponds to that of hydrated ions. The solvent ions thus perfectly fit into the available porous carbon network without wastage of free space. Such water-tight accommodation of these ions in the porous carbon matrix results in a strong confinement of these ions in the small carbon pores. A strong confinement would consequently lead to a distorted solvated ionic shell causing a greater interaction between the carbon network (electrode) and the trapped charged ions of the electrolyte which leads to increase in the value of the supercapacitance.

From the pore size distribution (Figure 3.3) it can be observed that, there are also some pores of around 2nm diameter. These bigger pores must clearly help in the transport of the ions from the surface to the bulk of the electrode so that the micropores can be accessed properly.

The energy density and power density are calculated by the following equations:

$$S_E = \frac{C_s(\Delta V)^2}{2}$$
$$S_p = \frac{S_E}{t}$$

Where $S_E$ is the specific energy density, $S_p$ is the specific power density, $C_s$ is the specific capacitance of the active material (Fg$^{-1}$), $t$ is the discharging time and $\Delta V$ is the potential window in 1M H$_2$SO$_4$ for charging and discharging.

The specific energy, power density, specific capacitance and aerial capacitance values for different current densities of our CDDPL material are presented in Table 3.5. It can be clearly noted that at 0.5 Ag$^{-1}$ our carbon synthesized at 1000°C shows very significant energy density value of 55 Wh Kg$^{-1}$. As the current density increases energy density gets suppressed. This is because at very high current density only some parts of the pores (surface mainly) are accessed by the electrolyte leading to very fast discharge, whereas at low current density all the pores including those near the surfaces and also in the bulk are accessed by the electrolyte and hence
discharges are slow. In our case, even at a very high current density 10 Ag⁻¹ there is only a limited drop in the value of energy density (30.63 KW kg⁻¹).

The comparative specific energy and power density table is shown in Table 3.6 where it can be clearly identified that the energy and power density of the carbon derived from Neem dead leaves is higher than that for other carbon materials synthesized from waste. Also it shows comparable energy and power density with graphene and graphene/CNT based composites.

<table>
<thead>
<tr>
<th>Current Density (Ag⁻¹)</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Capacitance (Fg⁻¹)</td>
<td>401</td>
<td>302</td>
<td>285</td>
<td>268</td>
<td>259</td>
<td>258</td>
</tr>
<tr>
<td>Areal Capacitance (µFcm⁻²)</td>
<td>32.0</td>
<td>24.5</td>
<td>23.17</td>
<td>21.7</td>
<td>21.05</td>
<td>21.0</td>
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<td>Power Density (WKg⁻¹)</td>
<td>569</td>
<td>1191</td>
<td>2526</td>
<td>3620</td>
<td>6480</td>
<td>11685</td>
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<tr>
<td>Energy Density (WhKg⁻¹)</td>
<td>55</td>
<td>42</td>
<td>40</td>
<td>37</td>
<td>36</td>
<td>35.8</td>
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Table 3.5: Calculated specific capacitance, areal capacitance, power densities and energy densities of CDDPL material at different current densities

The Ragone plot of Figure 3.14 can be used for further analysis of the performance of our material. Usually increase in the power density compromises the energy density value. But in our case the CDDPL shows no significant decrease in the energy density. At current drain time of 10s the energy and power density values are found to be 35 Wh Kg⁻¹ and 11685 W kg⁻¹, respectively, which are significantly higher than other aqueous based charge storage reports. These high values clearly demonstrate the stable performance of the carbon derived from dead plant leaves which is the result of the beneficial effects of the large number of tiny micropores present in the carbon matrix.
In case of aqueous medium the potential window is limited to about 1(V), hence the achievable energy density is also limited. Hence supercapacitor measurements in organic electrolyte are more important since the potential window can be extended to 3(V). We therefore tested the performance of the dead leaf derived carbon with an organic electrolyte 1M LiPF<sub>6</sub> in EC:DEC in a potential window of 0-3(V). Figure 3.6 d-f shows the CV and charge discharge data for both the Neem and the Ashoka leaf derived carbon. Figure 3.6 d shows the CV curves of Neem leaf derived carbon at various scan rates (2, 5, 10, 20, 50mvs<sup>-1</sup>) in an organic electrolyte. It can be clearly seen that the curves show rectangular nature in all the scan rates. The specific capacitance of 88Fg<sup>-1</sup> is calculated from the charge discharge curve measured at a current density of 2Ag<sup>-1</sup> which is shown in Figure 3.6 e.

Table 3.6: Comparison of energy density and power density of various carbon materials with dead leaf derived carbon

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<th>Materials</th>
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<th>Max energy Density</th>
<th>Max Power Density</th>
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<td>Activated carbon from waste coffee beans</td>
<td>1M H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>20 WhKg&lt;sup&gt;-1&lt;/sup&gt;</td>
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<td>46</td>
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<tr>
<td>Carbon from sea weeds</td>
<td>1M H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>19.5 WhKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>-</td>
<td>55</td>
</tr>
<tr>
<td>Activated carbon from sugarcane bagasse</td>
<td>1M H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>10 WhKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
<td>Binder free RGO-CNT film</td>
<td>1M H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>59.9 WhKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>250 WKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>75</td>
</tr>
<tr>
<td>Ultrathin graphene film</td>
<td>2M KCl</td>
<td>15.4 WhKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>55 WKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>76</td>
</tr>
<tr>
<td>Graphene-CNT</td>
<td>0.5M H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>21.74WhKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>78.29 kWKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>77</td>
</tr>
<tr>
<td>Carbon derived from dead leaves</td>
<td>1M H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>55.5 WhKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>10 kWKg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Our Work</td>
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Figure 3.14: Ragone plot (plot of energy density vs power density)

Similar measurements were also done with Ashoka leaf derived carbon for the same current density (Figure 3.15), which gave a specific capacitance value of 21 F g\(^{-1}\) which is less as compared to Neem leaf carbon. This decrease in specific capacitance is due to the decrease in the surface area and porosity in case of Ashoka leaf derived carbon. The energy density for Neem leaf derived carbon in organic electrolyte is calculated to be 56 Wh Kg\(^{-1}\) at 2 A g\(^{-1}\) from equation 2 which is higher (40% enhancement) than that the case of aqueous electrolyte, which is 40 Wh Kg\(^{-1}\) at 2 A g\(^{-1}\) current density.

Figure 3.15: Charge discharge data of Ashoka leaf derived carbon at 2 A g\(^{-1}\) current density in organic electrolyte.
Figure 3.16 a shows the Nyquist plot for carbon in 1M H$_2$SO$_4$ in the frequency range from 10 kHz to 10 mHz. This figure clearly shows an almost vertical straight line parallel to the imaginary axis ($Z''$) at low frequency region showing nearly ideal capacitor behaviour. The data in the middle frequency region reflect the consequences of certain key factors such as porosity, thickness of the electrode etc. for the diffusion of the ions through the porous network of the electrode.\textsuperscript{[82-83]} These introduce an initial semicircle character into the straight line behaviour at high frequency range, which shifts the capacitor behaviour towards a lower frequency value on the real axis. Hence, on the whole the impedance spectrum for a supercapacitor can be divided into two parts consisting of low frequency and high frequency regions. The transition point of these two regions is known as the ‘Knee frequency’ below which the capacitance nature dominates.\textsuperscript{[84]} 

The inset of Figure 3.16 a shows the magnified high frequency region showing the semicircle. The fitted equivalent circuit consists of an equivalent series resistance (ESR) in series with a parallel combination of capacitor (C$_{dl}$, double layer capacitance) and resistor (R$_f$) in series with Warburg impedance element (W) corresponding to the electrolyte ion diffusion into porous network of carbon electrode material. The ESR shows the total contact resistance between the current collector-electrode material and ohmic resistance of the electrode-electrolyte interface.

In our case (with 1M H$_2$SO$_4$) ESR comes out to be 2.67 Ω showing a good conducting behaviour.\textsuperscript{[85]} Further effort is needed to reduce it by optimizing the device and contact properties. The Warburg impedance element has a small contribution indicating good access for the electrolyte ions into porous carbon material even at higher frequencies. The knee frequency in this case is 57 Hz below which the capacitive behaviour dominates. This is in good agreement with the knee frequency domain reported for the carbon based supercapacitors.\textsuperscript{[86-87]}

Figure 3.16 b gives the Bode phase plot which indicates that in the low frequency region the phase shift is $\sim 90^\circ$ (sharper slope) indicating primarily an almost full double layer charge storage phenomenon and near absence of faradic (redox) type charge storage phenomenon.\textsuperscript{[88]} A shallower slope accounts for more faradic (redox) type charge storage phenomenon.
Figure 3.16: (a) Nyquist plot for carbon electrode in 1M H$_2$SO$_4$, inset shows the magnified higher frequency region; (b) Plot of Bode phase angle with frequency; (c) Frequency dependant real and imaginary capacitance plot; (d) Plot of total impedance vs frequency

The plots of frequency dependant real ($C'$) and imaginary ($C''$) components of capacitance are shown in Figure 3.16 c. In the low frequency region the capacitance ($C'$) remains constant at ~ 0.4 F which is the saturated capacitance at low frequency. The capacitance value decreases sharply above 0.1 Hz and becomes constant above 10 Hz. At low frequency, electrolyte ions penetrate deep inside the pores of carbon material accessing more electrode surface thereby contributing to the high capacitance value. At higher frequencies electrolyte ions can only have access to the surface of carbon materials whereas the deeper pores are not accessed giving rise to a sharp decrease in the capacitance. The sharp peak in the graph of frequency dependant imaginary component of capacitance ($C''$) shows a maximum capacitance ($C''$) at a frequency $f_0$ which corresponds to relaxation time as $\tau_0 = 1/f_0$ which is ~1.2 s. This relaxation time signifies the minimum time needed to discharge all the energy from the device with an efficiency of >50%.\[^{[89]}\] This low relaxation time (~1.2 s) also
indicates the maximum accessibility of the outer surface of Neem leaf derived carbon material to the electrolyte ions.

**Figure 3.16 d** shows the plot of total impedance (Z) vs frequency (Hz) for dead Neem leaf derived carbon. When the frequency is low during the potential applied, the electrolyte ions try to penetrate deeper into the electrode from the orifice to the bottom of the pores. Hence at low frequency the bottom of the pores will also contribute to the resistive and capacitive elements leading to higher impedance as shown in **Figure 3.16 d**. At high frequency the electrolyte ions are only able to penetrate near the orifice of the pores hence resistive and capacitive elements near the orifice alone can respond. The penetration depth increases with decrease in the frequency. A straight line in is obtained at low frequency region which is due to the accumulation of ions at the bottom of the pores whereas in the middle frequency region a straight line is obtained due to the semi-infinite ion migration (dipoles) through various micropores. A horizontal line in the high frequency region signifies the dominance of electronic transport over this regime.\[^{90-91}\]

The Nyquist plot for supercapacitor with carbon electrode in 1M LiPF\(_6\) in EC:DEC is shown in **Figure 3.17 a**. The inset shows the magnified high frequency region. The low frequency region is similar to the case of aqueous electrolyte which shows purely capacitor behaviour. The major difference is however observed in the high frequency region, as shown in **Figure 3.17 b**, wherein a shift of the semicircle is seen towards higher value on the real axis, which is accounted for by the electrolyte viscosity which resists the penetration of electrolyte into the micropores at higher frequencies. The bigger semicircle also indicates the lower ionic conductivity of the electrolyte which in turn affects the electrolyte-electrode interface resistance.\[^{82}\]
From electrochemical impedance spectroscopy measurements we can conclude that the carbon electrodes show nearly ideal capacitive behaviour with low ionic resistance inside the porous structure indicating the fast diffusion of electrolyte ions into the porous network. The phase angle ~ 90° shows the dominant contribution of double charge storage mechanism and nearly complete absence of any redox reaction making the carbon derived from dead Neem leaves a suitable material for supercapacitor application.

Along with EDLC type supercapacitor we have also studied the performance of Neem leaf derived carbon as electrode in hybrid supercapacitor. Although, EDLC delivers excellent power density, it has limitations of energy density beyond ~10 Wh kg⁻¹. Hence, EDLC alone is incapable of powering hybrid electric vehicles and electric vehicles. On the other hand, Li-ion batteries (LIB) provides high energy density, but the desired power density is not sufficient to drive such vehicles. In this context it is very difficult for individual system to offer the desired energy and power density. The solution to this problem can be to integrate both EDLC and LIB in a single system to achieve both high energy and power density. This configuration is known as Li ion hybrid electrochemical capacitor. Generally this configuration consists of Li-insertion type electrode (battery component) coupled with high surface area.
area carbonaceous materials preferably activated carbon as counter electrode (supercapacitor component) in Li-ion conducting non-aqueous electrolytes.

Among various Li insertion type materials such as pre-lithiated graphite, Li$_4$Ti$_5$O$_{12}$ [92, 93], LiCrTiO$_4$ [97-98], LiFePO$_4$ [99] etc, spinel phase Li$_4$Ti$_5$O$_{12}$ is found to be appropriate materials due to its salient features such as no volume variation during Li-insertion/extraction (Zero strain host), appreciable theoretical capacity (~175 mAh g$^{-1}$) with high reversibility, thermodynamically flat operating potential (~1.55 V vs. Li), easy synthesize and eco-friendliness. [100] Among the carbonaceous materials, graphene, and porous carbons are found significant due to their high specific capacitance with good cycleability in EDLC configuration, high surface area (~2000 m$^2$ g$^{-1}$), excellent electrical conductivity and good chemical and thermal stabilities. [101] In this work we have used the Neem dead leaves derived carbon as electrode material in Li ion hybrid configuration along with Li$_4$Ti$_5$O$_{12}$.

The capacitive behaviour of the Neem leaf derived carbon tested above the open circuit voltage (OCV) (vs. Li) is attributed to the reversible adsorption and desorption behaviour of anions present in the electrolyte (PF$_6^-$) and subsequent electric double layer formation across the electrode/electrolyte interface. [98, 102-105] Also, such single electrode performance is very crucial to balance the mass between the electrodes during the fabrication of Li-Hybrid electrochemical capacitor. Generally, in conventional symmetric supercapacitor the applied potential is equally distributed among the two electrodes. Whereas, in the asymmetric configuration, particularly Li-Hybrid electrochemical capacitor the two electrodes undergo different energy storage mechanisms hence the applied potential gets divided into specific capacitance of the individual electrodes.

This un-equal distribution leads to the partial utilization of the electro-active material, resulting in to suppression of energy density. [98, 105] Therefore the mass balance between the electrodes is necessary for the complete utilization of the active material and to achieve high energy density Li-Hybrid electrochemical capacitor. Therefore, half-cell was constructed with dead leaves derived carbon and tested from OCV to the decomposition potential of conventional carbonate based electrolyte (3-4.6 V vs. Li).
Figure 3.18: a) Typical galvanostatic charge-discharge curves of various carbonaceous materials in single electrode configuration between 3-4.6 V vs. Li at current density of 100 mA g⁻¹, in which metallic lithium acts as counter and reference electrode. (b) Plot of specific discharge capacitance vs. cycle number. The data points are collected after every 10 cycles.

Figure 3.18 a shows galvanostatic charge-discharge curves at a current density of 100 mA g⁻¹. The leaf derived carbon electrode shows linear variation of potential with respect to time. Such linear variation corresponds to the perfect reversible adsorption/desorption of PF₆⁻ anions. [98-103] The leaf derived carbon showed a reversible capacity of ~32mAhg⁻¹ which is comparable to the commercially used activated carbon.

The reversible capacity can be converted into the specific capacitances (CSP) by using the following equation proposed by Amatucci et al. [103]

\[
Cs(F/g) = \frac{i(A) \times t(s)}{3600 \times m(g)} = \text{mAh/g (Observed Capacity)} \tag{3.4}
\]

\[
= \text{Observed Capacity (mAh/g)} \times 3600 / \text{dV(mV)}
\]
Where, $I$ is applied current, $t$ is discharge time, $m$ weight of the active material and $dV$ is testing window of the aforementioned half-cell configuration (1600 mV).

However, the said relation is valid if the variation of voltage with respect to time is linear. By using this equation the specific capacitance was calculated to be 72 F g$^{-1}$ for Neem leaf derived carbon in Li ion hybrid capacitor configuration. Plot of the specific discharge capacitance vs. cycle number is given in Figure 3.18 b, where it can be clearly seen that the electrode exhibit a very stable cycling performance except for a minor fading in the initial cycles. Capacitance fading in initial cycles is common for the case of non-aqueous electrolytes [93]. Even after 1000 cycles the fading in the specific capacitances is noticed to be very negligible.

Based on the electrochemical performance of the spinel phase Li$_4$Ti$_5$O$_{12}$ under the same current rate, the active material loading of anode (Li$_4$Ti$_5$O$_{12}$) to leaf derived carbon cathode was optimized into 1:5.26 for the fabrication of Li-Hybrid electrochemical capacitor. The cell was constructed using Neem leaf derived carbon as cathode and insertion type spinel phase Li$_4$Ti$_5$O$_{12}$ anode and cycled over 1-3 V testing range at various current densities under the optimized mass loadings described above. The results are shown in Figure 3.19 a.

**Figure 3.19:** a) Galvanostatic charge-discharge profiles conducted between 1-3 V for Leaf derived carbon /Li$_4$Ti$_5$O$_{12}$ Li-Hybrid electrochemical capacitor; b) Ragone plot of Li-Hybrid electrochemical capacitor comprising of leaf derived carbon cathode.

The constructed hybrid cell showed minor ohmic drop ~3 V followed by monotonous discharge curve and a sudden drop of potential (~1.4 V onwards). This
monotonous discharge curve corresponds to the breaking of the electric double layer across the electrode/electrolyte interface and simultaneous extraction of Li from the spinel lattice. Specific energy ($E_{sp}$) and power densities ($P_{sp}$) of the Li-HEC are calculated using the following relation,

$$P_{sp} = \Delta E \times I / M$$ \hspace{1cm} 3.5

and

$$E_{sp} = P_{sp} \times t$$ \hspace{1cm} 3.6

Where $\Delta E=(E_{max}+E_{min})/2$ and $E_{max}$ and $E_{min}$ are respectively the potential at beginning of discharge and at the end of discharge curves of galvanostatic cycle and $M$ is the active mass loading of both electrodes (mg, anode + cathode). [98,104,105-106] The specific energy density of ~26 Wh kg$^{-1}$ was obtained for the Neem leaf derived carbon. Figure 3.19 b shows the Ragone plot constructed from the energy density and power density values calculated at different current densities. This Ragone plot shows high energy density and power density for the Neem leaf derived carbon electrode.

### 3.4 Conclusion

In summary high surface area microporous functional (conducting) carbon is synthesized from the dry waste of dead plant leaves (Neem and Ashoka) without any external activation and studied for supercapacitor application. The carbon synthesized at 1000 °C from Neem leaves exhibits a very high charge storage capacity with specific capacitance of 400 Fg$^{-1}$ and energy density of 55 WhKg$^{-1}$ in 1M H$_2$SO$_4$. The capacitance is also tested with organic electrolyte (1 M LiPF$_6$ in EC:DEC) which shows a specific capacitance of 88Fg$^{-1}$ at a current density of 2Ag$^{-1}$ and with a energy density value of 56 WhKg$^{-1}$. The energy density is realized to be 40% higher in the case of organic electrolyte than the case of aqueous electrolyte at the same current density of 2Ag$^{-1}$. This high supercapacitor performance can be attributed to a specific nature of microporosity combined with high surface area (1230 m$^2$g$^{-1}$) which is due to the uniform distribution of the minerals present in the leaf. These minerals are known to be good porogen which create pores during the process of pyrolysis. The generic nature of the proposed process of dead leaves is confirmed by a similar study on another plant, namely Asoka. The corresponding carbon material shows a specific capacitance of 250Fg$^{-1}$ in aqueous and 21Fg$^{-1}$ in organic media. Both the leaf-types...
show very good performance with Neem leaf exceeding the other. We show that the differences can be traced to the constitution and composition of the Bio-source. We have also studied the cases of pyrolysis of green leaves as well as un-ground dead leaves with that of ground dead leaves powder. In Li ion hybrid electrochemical capacitor configuration with \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) capacity of \( \sim 32 \ \text{mAhg}^{-1} \) and a specific capacitance of \( 72 \ \text{Fg}^{-1} \) is obtained. This is comparable with the commercial activated carbon electrode materials. This proves that carbon derived from Neem dead leaves is highly useful electrode material for supercapacitor applications.

### 3.5 References

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