CHAPTER 3
Development of Supercapacitors based on conducting polymers
and its composites with graphene

3.1. Introduction

Aim of this chapter is to develop and optimize a new storage system which has high capacitance, energy density and power density and replace the dielectric capacitor in the integrated storage unit. Electronically conducting polymers are an interesting class of materials, which have received important attention because of its potential relevance in the development of super capacitor electrodes, battery cathodes [1-4], in electronic devices [5], in electrochromic displays [6-7], etc. Recently, a great interest has been dedicated to the application of electronically conducting polymers (ECPs) in electrochemical capacitors [8] because of its high specific capacitance to reach a maximum specific energy and power of the device. Among the variety of conducting polymers, polyaniline, poly(pyrrole) and poly(thiophene) need special mention owing to their potential applications, [9-14] their excellent capacity for energy storage, easy synthesis, higher conductivity and lower cost [15]. **Hybrid capacitors** combine the best features of electric double layer capacitors (EDLCs) and pseudocapacitors together into a unified supercapacitor; hence they make use of both physical and chemical charge storage mechanisms together in a single electrode. The main advantage of these hybrid electrodes over the bare conducting polymer electrodes is that these composites have been able to achieve superior cycling stability comparable to that of EDLCs while retaining the high storage capacity of faradaic electrodes. The carbon based materials provide a capacitive double layer for charge storage and also provide a high surface area backbone that increases the contact between the deposited pseudo-capacitive materials and electrolyte [16]. Conducting polymers having good electrochemical activity [17] and their composites are promising candidates as hybrid capacitor electrodes [18]. Usually, when conducting polymer is made
into composite with any form of carbon, a polymeric binder is needed. Normally insulating polymers are used as the binders which reduces the conductivity [19]. But this chapter shows the development of graphene composites of poly(pyrrole) and PEDOT without polymeric binders having very high specific capacitance, area and volume capacitance. Figure 3.1 shows the schematic representation of poly(pyrrole) and PEDOT. The conductivity of conducting polymer increases upon composite formation with the incorporation of highly conductive carbon forms [20].

The high mobility of electrons inside conducting polymer macromolecules is due to the conjugated bonds/ delocalized electrons along the polymer chains.

![Poly(pyrrole) and Poly(3,4-ethylenedioxythiophene)- PEDOT](image)

**Figure 3.1**: Schematic representation of poly(pyrrole) and PEDOT.

The energy gap between the conduction and valence bands (LUMO and HOMO) is typically of order of 1-3 eV for conducting polymers [21]. Conducting polymers can be synthesized either chemically or electrochemically, once formed; these polymers can exist in either two or three general states p-doped, n-doped, and un-doped. In the oxidized or ‘p-doped’ state the polymer backbone is positively charged and has high electronic conductivity, normally it would be in the range of 1-100 S/cm. Reduction of the p-doped polymer generates the ‘undoped’ state or neutral state; this state is usually insulating, or semi-insulating, depending on the degree of completion of the undoping process. The process of electrooxidation or electroreduction of the non-conducting state of the polymer develop mobile electronic charge carriers in the polymer, and this charging
process is referred as chemical doping. Charge neutrality has to be maintained, and therefore the insertion of an electronic charge during doping has to be accompanied by proper exchange of an ionic charge with the electrolyte solution. This requires, in turn, that a conducting polymer film of high charge/discharge activity has good electronic and good ionic conductivities. The second requirement is satisfied by a network of electrolyte-filled micropores and/or nanopores within the active film of the conducting polymer. The mobility of the ‘free’ electronic charges in conducting polymers is smaller than in semiconductor materials because of the absence of good long range order. However, the electronic conductivity normally obtained for the ‘doped’ state of a conducting polymer is 1-100 S/cm.

The mechanism of electrochemical doping of a conducting polymer film is described as; electrochemical p-doping or electrooxidation of conducting polymers takes place by the abstraction of electrons from the polymer backbone through the external circuit and incorporation of an anion from electrolyte into the polymer film to counter balance the positive electronic charge. The mechanism of electrochemical n-doping of conducting polymers proceeds by the reverse of this mechanism that is electrons are transported onto the polymer backbone by the external circuit, and cations enter the polymer from the solution phase in order to maintain overall charge neutrality. Electronically conducting polymers have high conductivities in the charged states; furthermore, their charge-discharge processes are generally fast. The mechanical stress (due to doping and de-doping) in the polymer film is related with the cycle life of conducting polymer based capacitors. However, the long-term stability during cycling is a major requirement for the use of conducting polymer based capacitors. It has been already proved [22-23] that the composites of polymers with carbon forms shows better stability; the entangled mesoporous network of carbon (CNT) in the composite can adapt to the volume change, that allows the shrinkage to be avoided and hence a more stable capacitance with cycling to be obtained. A reported article showed the comparison of cycling stability of PANI and its carbon composite. The initial specific capacitance of the cell is 554 F g⁻¹, but this value rapidly decreases on continuous cycling. In order to improve the cycleability, a composite of polyaniline with
multi-walled carbon nanotubes (CNTs) is synthesized. A high initial specific capacitance of 606 F g\(^{-1}\) is obtained with good retention on cycling \[24\].

The practical purpose of ECPs are depends on their stability in ambient conditions. We have focused on two conducting polymers poly(thiophene) and poly(pyrrole) which are reported with very good electrical conductivity in the p-doped state, good thermal and chemical stability and fast electrochemical switching. The established polymer synthesis route is electro polymerization which is an easy and inexpensive process and was used for the current study. The raw material is the monomer of the corresponding polymer and polymerization carried out with a constant voltage/current source hence the production cost is also very low. Here we deals with the synthesis of poly(pyrrole), PEDOT (Poly(ethylene dioxy-thiophene)) and their composites with graphene as the materials for the development of supercapacitors.

Graphene has high electronic conductivity, low mass density, very high specific surface area (2630 m\(^2\) g\(^{-1}\)) hence we selected this material to make composites. Graphene consists of a two dimensional sheet of covalently bonded carbon atoms and finds a multitude of applications in devices \[25\]. The very high in-plane conductivity and surface area makes it an attractive material for use in dye sensitized solar cells \[26\], supercapacitors \[27\] and other high technology niche areas. An authoritative review of graphene-its electronic structure, synthesis methods, characterization, functionalization and its composites has been written \[28\]. Electrochemical double layer capacitors show properties of very high power density, energy density and long cycle life \[29\]. Graphene as a constituent of the electrode material overcomes many of the limitations of activated carbon. The very high surface area, superior stiffness, strength, thermal and electrical conductivity, electronic transport properties, chemical inertness are the properties that make graphene superior than any other form of activated carbon. Further, in contrast to other high surface area carbons, the effective active surface area of graphene consists of large open flat layers, not surfaces consisting of complex pores. Hence, ion transport in graphene is much higher than in activated carbons. This property of graphene has been exploited for many of the capacitance studies. Graphene based electrodes benefit from improved mechanical integrity, higher electronic and ionic conductivity and larger electrode specific capacitance and
greater stability in charge-discharge cycling compared with the pure conducting polymers [30].

3.2. Development of bare poly(pyrrole) and poly(pyrrole)/Graphene composite supercapacitors

Electropolymerization technique was employed to synthesize poly(pyrrole) and its composites with graphene composites. Developed electrodes were characterized in detail and the capacitive behavior was studied.

3.2.1. Synthesis and characterization of poly(pyrrole) electrode

Bare polymer film was synthesized over Ti plate by electro-polymerization technique.

Electropolymerization:

Poly(pyrrole) film is formed on the polished Ti plate by the electropolymerisation of pyrrole monomer. Electro-polymerization technique is very reproducible; and gives control over the thickness of the film. 0.2M pyrrole monomer in acetonitrile was taken as the bath solution for electropolymerization. The pyrrole monomer was distilled prior to use as per established experimental procedures. Electro-polymerization was carried out galvanostatically at constant current of 1mA/cm$^2$ for different durations from 500 to 3000 seconds in a two electrode system. Platinum wire used as the counter electrode and Ti plate was the anode. Higher current causes more charges to flow in short time in to the solution and more monomer undergoes oxidation at a time and the polymer film formed losses its uniformity causes agglomeration. Hence lower polymerization current is preferred in electropolymerization (corresponding to the oxidation potential of monomer) to get maximum control over polymerization.

SEM:

The scanning electron microscopy (SEM) imaging was done to study the morphology of the electropolymerized pristine poly(pyrrole), which shown in figure 3.2. From figure 3.2, it is clear that the poly(pyrrole) forms a uniform film over Ti substrate which is two dimensional (smooth film) hence the surface which comes in contact with electrolyte would be the outer layer of the film.
Figure 3.2: SEM image shows the thin film morphology for poly(pyrrole) grown by electropolymerization.

FTIR:

Electropolymerization was carried out for long time (2 hrs) and the poly(pyrrole) film was peeled off from the substrate and IR spectroscopy (Figure 3.3) was taken and we confirmed the formation of poly (pyrrole) [31]. FTIR shows the presence of characteristic absorption bands at, 1465 cm\(^{-1}\) (C=C stretching of pyrrole ring), 1311 cm\(^{-1}\) (C-N stretching vibration in the ring), 1113 cm\(^{-1}\) (C-H in-plane deformation), 1045 cm\(^{-1}\) (N-H in-plane deformation), 925 cm\(^{-1}\) (C-H out-of-plane deformation), 789 cm\(^{-1}\) (C-H out-of-plane ring deformation) and 675 cm\(^{-1}\) (C-C out-of-plane ring deformation), 1644 is C=C stretching.

Figure 3.3: FTIR spectra of poly(pyrrole).
UV-Vis spectroscopy:

UV-Vis spectrometry of poly(pyrrole) film was carried out for various polymerization time; which carried out in reflection mode (Ti is opaque). Figure 3.4 shows the UV-Vis spectra of film grown from 500 seconds to 2500 seconds. Electropolymerization of pyrrole proceeds by successive addition of monomeric units to the polymer chain backbone thus elongating the polymer chain and adding to its molecular weight. At low time of polymerization, there exists a simplistic configuration of the polymer chain and thus vibrational absorption of the wavelength by the polymer chain yields a distinct peak in the UV spectra. The absorption peak is obtained at a wavelength of 493 nm for a polymerization time of 500 seconds (Figure 3.4). 493 nm is corresponding to the oxidized state of poly(pyrrole) [32].

![UV-Visible spectra of poly(pyrrole)](image)

**Figure 3.4:** UV-Visible spectra of poly(pyrrole), the absorption peak is obtained at a wavelength of 493 nm for a polymerization time of 500 seconds.

As the time of polymerization is increased, there is a broadening of the spectrum suggesting that the initial structure was open ended and 3-D porous with additional oligomeric units appending to the structure thus densifying the polymer network. A very broad spectrum is obtained for 2500 seconds growth.
Stability of electrolyte:

Aqueous 0.1M NaOH is used as the electrolyte and cyclic voltammetry carried out in different voltage window. It was found that in aqueous electrolyte when voltage of -1 V to 1 V and -1.5 V to 1.5 V is applied electrolyte is found to be stable but when the voltage window expanded above 1.5 V gas evolution was found due to water splitting. It shows water based electrolyte system can’t be used for higher voltage application hence organic based electrolyte was selected to as electrolyte system. Figure 3.5(a) shows the cyclic voltammetry carried out as per section 3.2.2 in different voltage window in aqueous 0.1M NaOH. When applied potential was less than 1.5 V the electrolyte was found to be stable (Figure 3.5(b)) and above which the water starts to split showing the instability of the electrolyte (Figure 3.5(c)).
Figure 3.5: Cyclic voltammetry carried out in different voltage window in aqueous 0.1M NaOH (b) Platinum electrode when potential window is less than 1.5 V (c) gas evolution on platinum electrode when applied potential is above 1.5 V.

It shows water based electrolyte system can’t be used for higher voltage application hence organic based electrolyte was selected. Further studies were carried out in acetonitrile.

3.2.2. Performance study of poly(pyrrole) electrode

Cyclic Voltammetry (CV):

CV technique is normally used to show the charging and discharging nature of faradaic materials. Conducting polymer being a faradaic material; CV studies were carried out to find its capacitance. Upon cycling it under goes oxidation and reduction, the specific capacitance [33] is computed from the CV curve as follows:

Capacitance \( (C) = \frac{i_{rp}}{(dV/dt)} \) \hspace{1cm} (3.1)

Specific area capacitance \( C_A = \frac{C}{\text{area}} \) \hspace{1cm} (3.2)

Specific mass capacitance \( C_m = \frac{C}{\text{mass of deposited material}} \) \hspace{1cm} (3.3)

Figure 3.6: Cyclic Voltammetry studies in 0.1M LiClO\(_4\) in a three electrode set up; Poly(pyrrole) as anode, platinum wire as cathode and saturated calomel
electrode as the reference electrode at different scan rate from 10 mV/sec to 100 mV/sec.

Where \( i_{rp} \) is the current corresponding to the reduction peak in the voltammogram and \( dV/dt \) is the voltage scan rate in volt per second. From the graph it is clear that as the scan rate increases there is a negative shifting of reduction potential. As the scan rate increases voltage application become faster and not all part of electrode material get enough time to undergo redox reaction. Thus with the increase of scan rate there is a severe kinetic limitations in charge transfer [34]. Hence more work needs to be done to reduce the system completely. This might be the reason for the shifting of potential in negative direction.

The electrolyte used for the CV studies was 0.1M LiClO\(_4\) in acetonitrile. Polymer coated Ti plate was taken as anode, platinum wire as cathode and the reference electrode was a saturated calomel electrode. Cycling of electrode carried out for different scan rate from 100mV/sec to 10mV/second, which is shown in figure 3.6 for 2500 seconds (succeeding study shows that the maximum capacitance is for 2500 seconds) growth of polymeric film. CV shows oxidation and reduction peaks of polymer. The charge storage capability of conducting polymers is due to its ability to undergo electro-oxidation or electro-reduction; oxidation or p-doping of conducting polymers takes place by the substruction of electrons form the polymer backbone through the external circuit and the incorporation of an anion from solution into the polymer backbone to counter balance the positive charge. In reduction or n-doping the electrons are transported onto the polymer chain by the external circuit, and cations from the electrolyte enter the polymer chain in order to sustain overall charge neutrality [35].

Poly(pyrrole) (Ppy) is a p-type material [36] hence it undergoes oxidation by the incorporation of anion from the electrolyte (ClO\(_4^-\)) into the polymeric chain while discharging and neutralization by release of the same. Oxidation is analogous to discharging and neutralization is corresponding to charging [37].

**Charging process:**

\[
Ppy^{x+} + xClO_4^- + xe^- \rightarrow Ppy + xClO_4
\]

**Discharging process:**

\[
Ppy + xClO_4^- \rightarrow Ppy^{x+} + xClO_4^- + xe^-\]
The time of polymerization varied from 500 sec to 3500 and the cyclic voltammetry was studied at a scan rate of 10mV/second which is shown in figure 3.7. From the CV it is clear that as the time of polymerization increases the corresponding oxidation and reduction current is increasing but after a particular time of polymerization the current starts to reduce. The maximum capacitance is obtained for 2500 seconds of polymerization which corresponds to 200 µg deposited polymer and the capacitance is $C_A = 47\ \text{mF/cm}^2$, $C_m = 190\ \text{F/g}$.

It is well known that as the time of polymerization goes up the chain length of polymer increases; the initial increment in capacitance with polymerization time (Figure 3.7, 3.8) is due to the growth of polymeric chain which induces maximum faradaic sites reaction. But after optimum time of polymerization further growth densifies the polymer film (reduces the porosity), hence effective sites for faradaic reaction get reduced; which in turn reduces the capacitance. From this we could draw an assumption that the area capacitance depends not only on the quantity of deposited mass but also on the morphology of the electrode.

**Figure 3.7:** Cyclic voltammetry (CV) variation with time of polymerization for bare poly(pyrrole) film at 10 mV/sec.
3.2.3. Cycling stability

The electrochemical stability of polymer is studied by cycling of CV, Figure 3.9 shows the variation upon 25 times of cycling at 100mV/sec and how polymer degrades upon cycling. After 25 cycling the reduction peak is almost missing which indirectly shows the instability of capacitor electrode. Enlargement (swelling) and shrinkage of polymer due to the oxidation and reduction may lead to degradation of the electrode during cycling. It occurs because of the insertion/deinsertion of counter ions (doping) into the polymer chain, which is the reason for a volume change.

Figure 3.8: Graph shows the variation in area capacitance with time of polymerization for bare poly(pyrrole) film.

Figure 3.9: Cycling studies: 25 cycles of CV carried out for same Ppy electrode.
3.2.4. Charging-discharging

The charging and discharging nature of electrode is studied in a three electrode set up with standard calomel electrode as reference electrode by applying a constant external current; the voltage variation with time is noted (Figure 3.10). Current density of 1 mA/cm² is applied and voltage is found to increase to 0.2 V in 5 seconds. The energy and power density is calculated from the charge discharge curve. These values computed as per guidelines in ref [38].

![Graph showing charging and discharging nature of Ppy electrode at a constant external current of 1 mA/cm².]

**Figure 3.10:** The charging and discharging nature of Ppy electrode at a constant external current of 1 mA/cm².

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Energy density} = \frac{(\text{Area under charging curve} \times \text{charging current})}{\text{mass of deposited material}}$</td>
<td>Equation 3.4</td>
</tr>
<tr>
<td>$\text{Power density} = \frac{1}{2} \times \frac{(\text{maximum voltage} \times \text{discharging current})}{\text{mass of deposited material}}$</td>
<td>Equation 3.5</td>
</tr>
</tbody>
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The discharging behaviour shows a sudden IR voltage drop and then a slow decay of voltage. The IR drop accounts for the internal resistance of electrode. Here mass of deposited material is 200 µg; the calculated energy density is 0.7 Wh/Kg; power density is 0.5 kW/Kg. In conclusion, we have successfully synthesized and characterized supercapacitive electrodes composed of Ppy. Such an electrode has yielded mass specific capacitance of 190 F/g, area
capacitance of 47 mF/cm², and energy density of 0.7 Wh/Kg and power density of 0.5 KW/Kg with poor stability.

3.3. Development of poly(pyrrole)/Graphene composite supercapacitors

Poly(pyrrole)/Graphene composite electrodes were synthesized using electrophoretic deposition of graphene, upon which the poly(pyrrole) layer was electropolymerised. Ordinary porous carbon has reasonable values of surface area but is limited by its low conductivity; [39] reports exist of supercapacitors made up of graphite electrodes [40]. Newer and novel forms of carbon such as carbon nanotubes [41] have been researched as alternative materials in supercapacitor electrodes. There have also been reports of use of sulfonated graphene along with conducting polymers such as poly(pyrrole)(Ppy) in supercapacitor electrodes [42]. The specific capacitance demonstrated was as high as 285 Fg⁻¹. Use of both graphene and highly conducting polymers in a composite mode is expected to have high synergistic storage capacity. In the present study, we use graphene nanolayers as a scaffold for electropolymerization and create a composite electrode for the supercapacitor.

3.3.1. Synthesis and characterization of poly (pyrrole)/Graphene composites

Electrophoresis:

The composite electrode was synthesized by first electrophoretic deposition (EPD) of a thin layer of commercially purchased graphene (source: graphene was purchased commercially from Quantum Materials Corporation Ltd, Bangalore, India) on a titanium substrate. Graphene was mixed with a metal salt, 4 mM nickel nitrate (Fischer scientific), and sonicated in isopropanol for 1 hour. For electrophoretic deposition, the titanium plate was made the cathode in a bath solution as prepared above. The anode was a platinum wire and the potential applied was 20 V for 30 minutes.
Nickel acts as a binder for the graphene and also facilitates charge transport and deposition during electrophoresis. The method of electrophoresis has been used to deposit thin layers of carbon nanotubes [43] as well as activated carbon [44] on various substrates. EPD of the graphene film is achieved via transport of positively charged graphene sheets (adsorbed with nickel ions at the edges) toward a negative electrode and via deposition of graphene with charge neutralization under an applied electric field. When a graphene sheet arrives at the ITO substrate, nickel ions adsorbed on the planar surface/edges of the graphene are reduced electrochemically to form metallic nickel because graphene has electrical conductivity, which allows electrons to conduct from the ITO substrate to the layer of graphene. Metallic nickel appears to be appropriate as a metal binder for attaching the edges of graphene because of its higher electrical conductivity compared with that of the polymer binders. The layer formed was used as a substratum for electro-polymerisation of pyrrole.

**SEM:**

Figure 3.11 shows the SEM images of porous 3-D structure (Figure 3.12) of the composite electrode. The Ppy is nucleated on the graphene islands on the titanium substrate. Ppy polymerizes on graphene utilizing the extremely high specific surface area of graphene and this mode of polymerization is beneficial by exposing maximum surface sites for faradiac redox reactions of the supercapacitor.
electrode. SEM clearly shows that the composite electrode structure is highly porous. This porosity enhances the electrode interaction with the electrolyte. Apart from polymerization nucleation centers, the graphene layer also functions as a mesh of tiny current collectors, which facilitate rapid charging and discharging cycles of the Ppy layer.

![SEM images](image.png)

**Figure 3.12:** SEM images of electro polymerized pyrrole on graphene platelets.

**Raman spectroscopy:**

In the present work, Raman spectra of graphene (Figure 3.13) and graphene/polypyrrole composite was recorded and shown in figure 3.14 which were collected using source of 488 nm laser. Raman spectroscopy is a powerful probe for characterizing sp$^2$ and sp$^3$ hybridized carbon atoms in graphite, diamond-like carbon, diamond, polyaromatic compounds, fullerenes, or carbon nanotubes. Raman fingerprints of single, bi and few layer graphenes are dissimilar and have been investigated by several groups [45-47]. The symmetry allowed E$_2$g mode at the G-point, usually termed as the G-mode. It is an in-plane optical vibration of carbon atoms with the frequency appearing at approximately 1583 cm$^{-1}$.

The other Raman modes: D-mode, is a disorder-activated Raman mode seen at 1350 cm$^{-1}$ (D-mode), second order Raman scattering 2680 (2D- or D*-mode), 2950 (D+G-mode) and 4290 cm$^{-1}$ (2D+G-mode) [28]. Characteristic peak of graphene is present in graphene/poly(pyrrrole) composite. Generally, spectra recorded with excitations of 488 nm or shorter are dominated by the C=C stretch near 1575 cm$^{-1}$ for both the oxidized and neutral states of polypyrrole.
3.3.2. Performance study of poly(pyrrrole)/Graphene composite electrode

Cyclic Voltammetry (CV)

To study the electrochemical performance of the composite electrode, cyclic voltammetry (CV) studies were carried out for different scan rate from 10 mV/sec to 100 mV/sec the polymerization time is 1500 seconds. The electrolyte used for the CV studies was 0.1M LiClO₄; and the reference electrode was a saturated calomel electrode. Figure 3.15, shows the CV curves for various scan rates at a given polymerization time (1500 s). The area capacitance of 151
mF/cm², volume capacitance 151 Fcm⁻³ and specific capacitance 1510 Fg⁻¹ are obtained for a scan rate of 10 mVs⁻¹ for the sample polymerized for 1500 seconds. Figure 3.16 shows the CV of graphene, Ppy, Gr/Ppy composite in 0.1M LiClO₄ electrolyte. Graphene shows no electrochemical activity as would be expected (graphene based electrodes exhibit electrical double layer capacitance). The CV curve of the graphene/Ppy composite electrode is also superimposed for comparison showing the expansion of the area under the curve.

**Figure 3.15:** Cyclic voltammetry (CV) curves for various scan rates at 1500 seconds polymerization.

**Figure 3.16:** CV of graphene, Ppy, Gr/Ppy composite in 0.1M LiClO₄ electrolyte.
Figure 3.17: (a) CV of Ppy electrode for different time of polymerization from 500 to 3000 sec. (b) A plot of area capacitance versus time of polymerization (or layer thickness) shows a gradual increase of capacitance up to a maximum (1500 sec) and thereafter it reduces and maximum obtained area capacitance is 150 mF/cm$^2$.

The area in the CV curve of the composite electrode shows an incredible improvement compared to pristine Ppy and graphene electrodes; over 90% of the area is contributed by the oxidation and reduction peaks. This substantial electrochemical performance could be contributed by the porous surface morphology of the composite electrode. The area capacitance of the composite graphene/Ppy films deposited at various times was measured using CV studies.

The time of polymerization is varied from 500 seconds to 3000 seconds. The nature of the CV curves (Figure 3.17 (a), various polymerization times for 10 mV s$^{-1}$ scan rate) indicates that the currents corresponding to the reduction and oxidation peaks are increasing with increasing polymerization time up to a maximum optimum value and thereafter decreasing. A plot of area capacitance versus time of polymerization (or layer thickness) shows a gradual increase of capacitance up to a maximum 1500 seconds and thereafter it reduces (Figure 3.17(b)).

The above capacitance behaviour could be explained by invoking the polymerization process. At very long times of polymerization, the oligomers compact the porous network in a way that the 3-D network is lost and replaced by
equivalent thin film morphology. This drastically lowers the faradaic reaction sites and leads to a decrease in capacitance.

In composite, Ppy is nucleated on the graphene layer hence the as formed layer of composite itself forms highly porous film (it is visible from SEM). Polymer utilizes the extremely high specific surface area of graphene and this mode of polymerization is beneficial by exposing maximum surface sites for faradaic redox reactions with electrolyte. SEM (figure 3.12) clearly shows that the bare polymer electrode is a uniform 2D structure so it has limited area for interaction with electrolyte. Thus the porosity enhances the electrode interaction with the electrolyte giving rise to very high area capacitance. The improvement in capacitance is found to be 3 fold (47 to 150 mF/cm²). Apart from polymerization nucleation centres, the graphene layer functions as a mesh of tiny current collectors, which facilitate rapid charging and discharging cycles of the Ppy layer.

### 3.3.3. Cycling stability

The cycling stability is characterized with the CV study (Figure 3.18); after 25 times CV cycling (100 mV/sec) the composite electrode shows lesser degradation compared to that of pristine poly(pyrrole). The stability of the conducting polymer is poor but it shows better stability upon composite formation.

![Figure 3.18: Cycling studies: 25 times CV cycling the composite electrode.](image-url)
3.3.4. Galvanostatic charge-discharge

Galvanostatic charge-discharge (discharge is forced by external current) studies were conducted on the graphene/Ppy composite film (Figure 3.19) with a deposited film weight of 100 µg cm\(^{-2}\).

![Figure 3.19: Galvanostatic charge-discharge (discharge is forced by external current of 1 mA/cm\(^2\)) studies on the graphene/Ppy composite film.](image_url)

The charging and discharging is carried out by applying constant current of 1 mA/cm\(^2\). Comparing the charge discharge of bare polypyrrole and polymer composite, it was found that polypyrrole develops 0.2 V (Figure 3.10) where as polypyrrole composite can develop 0.6 V (figure 3.19), which is nearly three times higher than bare polypyrrole. Also bare polymer showed area capacitance ~45 mF/cm\(^2\) where as ppy/composite showed 3 times higher capacitance (150 mF/cm\(^2\)). The energy density and power density is calculated as per section 3.2.4 [38]; computed energy density is 5.7 Wh kg\(^{-1}\), and the power density is 3 kW kg\(^{-1}\).

Energy and power density are reasonably centrally located within the standard Ragone plot for supercapacitors. We have successfully synthesized and characterized high performance super capacitive electrodes composed of a graphene/Ppy composite. Such an electrode has yielded high values of specific capacitance of 1510 F g\(^{-1}\), area capacitance of 151 mF cm\(^{-2}\) and volume capacitance of 151 F cm\(^{-3}\).
3.4. Development of bare PEDOT and PEDOT/Graphene composite supercapacitors

There are literature reports on PEDOT - (various carbon) composites used in supercapacitor applications and a survey of the reported work shows that the PEDOT-carbon composites yield a moderate value of specific capacitance of up to 160 Fg$^{-1}$ and area capacitance up to 0.5 F cm$^{-2}$ [18, 48-52] with a perfect stability during cycling. In our study, graphene - Poly(ethylene dioxy-thiophene) (PEDOT) composite electrodes were synthesized by electrophoretic deposition (graphene) followed by electropolymerization of Ethelyne dioxythiophene (EDOT) and were investigated for its electrochemical properties. This composite electrode also demonstrated much higher capacitance values when compared to literature and a thin film of PEDOT. The stability and the thermal properties of the composite were also found to be superior, which was attributed to the unique morphology of electrodeposited graphene. Here we developed bare and composite PEDOT supercapacitor electrodes and detailed characterization carried out.

3.4.1. Synthesis and characterization of PEDOT capacitor electrode

Electropolymerization:

Electropolymerization of EDOT for PEDOT thin film: The ITO (indium tin oxide) coated glass plates (1 cm$^2$, Solaronix SA, Switzerland) were cleaned and dried. 0.05M EDOT monomer solution was prepared in water (10 ml). The deposition of PEDOT was carried out at room temperature in a one compartment cell by electropolymerization at room temperature using a Potentiostat and Galvanostat AUTOLAB. A three electrode system was employed with saturated calomel electrode as a reference electrode. A platinum electrode was used as the counter electrode. Deposition was carried out at 1.8 V for different durations.

SEM:

Morphology of the prepared electrodes has been analysed using SEM (JEOL-JSM-6490). AFM (JEOL-JSPM-5200) has also been used to obtain data on the surface morphology of PEDOT thin film. SEM image of the PEDOT thin film electropolymerized is shown in Figure 3.20 and it shows a globular porous morphology.
AFM:

Figure 3.21 shows the AFM (Atomic Forced Microscopic) image of electropolymerized EDOT on Ti substrate, shows particular morphology. Film shows uniformity with thickness ~600 nm.

FTIR:

Figure 3.22 shows the FTIR spectra of electropolymerized EDOT. Analysis has been done for polymer characterization using Perkin Elmer, Spectum RX1 by KBr method.
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Raman spectroscopy:

The electropolymerised PEDOT was also analysed for its Raman signature (Figure 3.23), which agrees well with literature [53].

The peak at 1510 cm$^{-1}$ is originated from the asymmetrical stretching of C-C, and the peak at 1431.3 cm$^{-1}$ is from symmetrical stretching of C-C. A peak from C-C antisymmetrical stretching mode can be seen at 988.7 cm$^{-1}$ [53]. Upon polymerization, the monomers are linked and oxidized, so that the resulting polymer is in its positively charged (doped) state. PEDOT is a p-dopable material.

![FTIR spectra of electropolymerized EDOT](image)

**Figure 3.22**: FTIR spectra of electropolymerized EDOT

![Raman spectra of PEDOT](image)

**Figure 3.23**: Raman spectra of PEDOT.
conducting polymer hence it undergoes switching between p-doped state and neutral state by the incorporation and release of chlorate anions in the electrolyte.

\[
\text{PEDOT}^0 \rightarrow \text{PEDOT}^+ : \text{ClO}_4^- + e^- \quad (\text{Discharging})
\]

\[
\text{PEDOT}^+ : \text{ClO}_4^- + e^- \rightarrow \text{PEDOT}^0 \quad (\text{charging})
\]

Upon oxidation, \(\text{PEDOT}^0\) releases an electron and attracts \(\text{ClO}_4^-\) ion from the electrolyte and neutralizes. When an electron flows to oxidized electrode \(\text{PEDOT}^+ : \text{ClO}_4^-\) releases \(\text{ClO}_4^-\) back to electrolyte and absorbs this electron and get reduced to \(\text{PEDOT}^0\). The reduction reaction is nothing but the charging and oxidation corresponds to discharging.

3.4.2. Performance study of PEDOT electrode

Cyclic Voltammetry:

Electrochemical behaviour of PEDOT is measured by CV analysis. For Cyclic Voltammetry measurements, a three-electrode system was used with potentiostat/galvanostat (PG stat) system.

![CV curve of the PEDOT thin film for varying time of polymerization (300 to 2100 seconds).](image)

**Figure 3.24:** CV curve of the PEDOT thin film for varying time of polymerization (300 to 2100 seconds).
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Figure 3.25: CV curves at various scan rates for a fixed polymerization time (1800 seconds).

The sample is connected to positive terminal and a platinum electrode was used as counter electrode. A calomel electrode served as reference electrode. 0.1M LiClO₄ was used as electrolyte for CV measurements. The figure 3.24 shows the CV curve of the PEDOT thin film for varying times (300 to 2100 seconds). From the capacitance data, it becomes clear that 1800 seconds of polymerization gives optimum values. Above optimum time of polymerization the area capacitance is starts to reduce

CV curve shown in figure 3.25 is for the sample of maximum area capacitance (1800 seconds) for different scan rate, the capacitance can be calculated using the reduction current obtained from CV curves (for 1800 seconds). The capacitance is calculated and found that 82.5 Fg⁻¹ at 40 mVs⁻¹ and area capacitance of 40 mF/cm². The time of polymerization varied from 300 to 2100 seconds and area capacitance calculated from CV.

3.4.3. Cycling stability

To test the intrinsic stability of the electropolymerised thin film of PEDOT, repeated CV scans were taken at a scan rate of 40 mVs⁻¹ (Figure 3.26). After 30 scans, the original CV curve has considerably shrunk showing loss of stability. We have successfully synthesized and characterized high performance
supercapacitive electrodes composed of a PEDOT and such an electrode has yielded high values of mass specific capacitance of 82.5 F/g and area capacitance 40 mF/cm². Decay of capacitance may be due to the degradation of polymer.

![Graph of Cycling study: 30 repeated CV scans of PEDOT film](image)

**Figure 3.26:** Cycling study: 30 repeated CV scans of PEDOT film (at a scan rate 40 mVS⁻¹).

### 3.5. Development of composite PEDOT/Graphene electrode

The composite electrodes were made as discussed above i.e., by electrophoretic deposition of graphene followed by electropolymerization of EDOT monomer. 5 mg of graphene (source: graphene was purchased commercially from Quantum Materials Corporation Ltd, Bangalore, India) powder was finely dispersed in Isopropyl Alcohol and Nickel Nitrate is added the electrophoretically deposited; at 20 V for 30 minutes as mentioned in section 3.3.1. By keeping the graphene electrode as the working electrode EDOT monomer was polymerized in three electrode sysrm with electropolymerization voltage being 1.8 V. The duration of polymerization of EDOT was varied for different samples. Weights of the coatings were evaluated.

**SEM:**

Figure 3.27 shows the SEM image of the composite film electrode formed with 8 minutes of polymerization. It appears from the image that the polymer has
formed a sheath around the network of nanotubules/nanochannels. This morphology gives a very high surface area for the composite thus maximizing the electrochemical interactions with the electrolyte.

![SEM image of the composite film electrode formed with 8 minutes of polymerization.](image)

**Figure 3.27:** SEM image of the composite film electrode formed with 8 minutes of polymerization.

### 3.5.1. Performance study of PEDOT/Graphene electrode

**Cyclic Voltammetry:**

Figure 3.28 shows the electrochemical activity of the composite film with the CV done in 0.1 M LiClO₄ (in acetonitrile) electrolyte for different time intervals of polymerization, at a scan rate of 40 mVVs⁻¹. It is seen that maximum specific and area capacitance values are obtained at a polymerization time of 8 minutes. Figure 3.29 shows the CV curves at a fixed polymerization time for different scan rates. The area and mass specific capacitance calculated. The composite electrode yielded by electrochemical measurements, a average specific capacitance of 1410 F/g and a median area capacitance of 199 mFcm⁻² at a scan rate of 40 mVs⁻¹. Above optimum time of polymerization the area capacitance is starts to reduce. It is observed that the specific capacitance and the area capacitance vary according to the duration of deposition. This implies that the surface morphology and the porosity of the thin film are the main causative factors to the capacitance. Further increase in the thickness of the thin film resulted in a reduction in capacitance values.
Figure 3.28: CV curve of the PEDOT/Graphene composite film for varying time of polymerization (2 to 15 minutes).

Figure 3.29: shows the CV of the composite film in 0.1M LiClO₄ electrolyte for time of polymerization 8 minutes for different scan rate.

This may be due to the loss of porosity of the electrode with increased film thickness. About 15 electrode samples were prepared under the same conditions keeping the polymerization time fixed at 8 minutes and a detailed study of the
variation of specific capacitance and area capacitance was carried out. The average median specific capacitance is 1410 Fg\(^{-1}\), while the area capacitance is 199 mFcm\(^{-2}\). The high values can be attributed to the high surface area provided by the composite to the electrolyte, which maximizes the faradiac interactions.

3.5.2. Cycling stability

The Cyclic voltammetry measurement is used to study the cycling stability of the electrode, a three-electrode system was used with potentiostat /galvanostat (PG stat) system. The ware and tare of polymer film due to the insertion and release of ClO\(_4\)\(^-\) anion causes degradation of polymer network. Here PEDOT/Graphene showed around 80% cycling stability after 50 cycles at 40 mV/sec in cyclic voltammetry and fares much better than a thin film of PEDOT.

![Cycling studies: 50 repeated CV scans of PEDOT/Graphene film (40 mVS\(^{-1}\)).](image)

The role played by the graphene is to form a very high surface area network of nanotubes/nanochannels which serves as nucleation centers for the PEDOT polymer. The PEDOT thus adopts the nano morphology of the underlying graphene. Graphene, on account of its high electrical conductivity also serves to improve PEDOT conductivity at reducing potentials and hence the overall capacitive performance of the composite. These electrodes demonstrated high capacitance values (1410 F/g, 199 mF/cm\(^2\)) and showed excellent electrochemical
stability (Figure 3.30). The capacitive behaviour was explained on the basis of the unique nanostructural morphology of the graphene and the electrodeposited PEDOT. These electrodes are suited for high performance supercapacitor and electrochemistry applications.

3.6. Conclusion

We have successfully synthesized and characterized high performance super capacitive electrodes composed of a Graphene/Ppy and Graphene-PEDOT composites. Graphene/Ppy has yielded high values of specific capacitance of 1510 Fg\(^{-1}\), area capacitance of 151 mFcm\(^{-2}\) and volume capacitance of 151 Fcm\(^{-3}\) which have been explained with the help of the particular process of polymerization operating in such structures and the resultant cohesive polymer network. We also extended the same work with another conducting polymer PEDOT and observer same kind of behavior. Graphene-PEDOT composite electrodes show median specific capacitance of 1410 Fg\(^{-1}\) and median area capacitance of 199 mFcm\(^{-2}\) at a scan rate of 40 mVs\(^{-1}\). The composite electrode also showed better electrochemical stability in repeated CV compared to pristine polymer. The composite electrode morphology maximizes the faradiac interaction sites for the hybrid supercapacitor electrode and yields high electrochemical capacitance.
3.7. References


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