Electrochemical behaviour of graphene–poly (3,4-ethylene-dioxythiophene) (PEDOT) composite electrodes for supercapacitor applications

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MS received 7 August 2012; revised 20 December 2012

Abstract. In this paper, we report on the electrochemical characteristics of graphene–PEDOT composite electrodes. The electrodes were made of indium tin oxide (ITO) substrates by simple processes of electrophoretic deposition of graphene followed by electropolymerization of EDOT monomer. The composite electrode was obtained by electrochemical measurements, a median specific capacitance of 1410 F/g and a median area capacitance of 199 mF cm⁻² at a scan rate of 40 mVs⁻¹. The composite showed good stability characteristics after repeated scans in cyclic voltammetry and fared much better than a thin film of PEDOT. The thermal stability of the composite is also much superior when compared to the polymer with a weight loss temperature of 350 °C for the composite and 250 °C for the polymer, respectively. The above electrochemical and thermal behaviours of the composite are correlated to the unique morphology of electrodeposited graphene that provides a conductive and high surface area template for electropolymerization.

Keywords. Composite materials; polymers; electrochemical techniques; electrochemical properties.

1. Introduction

Hybrid capacitors make use of both physical and chemical charge storage mechanisms together in a single electrode. The main advantage of these hybrid capacitor systems over pure conducting polymer faradaic capacitor systems is that composite materials comprising hybrid capacitors have been able to achieve superior cycling stability compared to that of electrical double layer capacitors (EDLCs), while retaining high storage capacity of faradaic capacitors. 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 pseudocapacitive materials and electrolyte (Halper and Ellenbogen 2006). Conducting polymers having good electrochemical activity (Smela *et al* 1995) such as poly(3,4-ethylenedioxythiophene) (PEDOT) and their composites are promising candidates as hybrid capacitor electrodes (Lota *et al* 2004). 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 conductivities, electronic transport properties and chemical and thermal inertnesses are the properties that make graphene superior than any other forms 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 (Do and Drzal, unpublished results).

This property of graphene has been exploited for many of the capacitance studies. For instance, Vivekchand and co-workers (2008) reported thermally exfoliated graphene-based supercapacitor with the specific capacitance of 117 F/g. Wu and co-workers (2009) and Stoller *et al* (2008) reported that the specific capacitance of 205 F/g (not including 10% inactive binder) at 100 mA/g and 135 F/g (including 3% inactive binder) at 10 mA/g with graphene oxides reduced with hydrazine hydrate for 72 and 24 h, respectively. Chen and co-workers (2010) obtained 164 F/g at 10 mV/s scan rate with graphene nanosheets electrophoretically deposited on nickel foam. Introducing graphene into polymer matrix has been quite promising. Such electrodes benefit from improved mechanical integrity, higher electronic and ionic conductivities and larger electrode specific capacitance and greater stability in charge–discharge cycling compared with the pure conducting polymers (Wang *et al* 2007).

Usually, when conducting polymer is made into composite form with any form of carbon, a binder is needed. But in the case of PEDOT, there is no need for polymeric binders. It is observed that in the composite form, conductivity in the undoped state is improved. Like most of the conducting polymers, PEDOT is poorly conducting in the

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Figure 1. Cyclic voltammograms of electropolymerized PEDOT thin film at different polymerization times ranging from 5 to 35 min (interval of 5 min) at a scan rate of 40 mV s^{-1} . A polymerization time of 30 min is optimum giving area capacitance of 40 mF cm^{-2} .

Figure 2. Cyclic voltammogram curve of electropolymerized (for 30 min) PEDOT thin film at various scan rates used (10, 20, 30, 40, 80 and 100 mV s^{-1}) in the CV studies. Polymerization time was fixed at 30 min based on optimization of area capacitance data as in figure 1.

reduced state. By combining with highly conductive carbon, the conductivity at reducing potentials can be increased (Snooke *et al* 2011). There are literature reports on PEDOT–(various carbon) composites used in supercapacitor applications. PEDOT/carbon nanotubes (CNTs) composite supplied lower capacitance values of 100 F g^{-1} (Frackowiak *et al* 2006) with a perfect stability during cycling. Additional advantage of the PEDOT/CNTs composite was a possibility

Figure 3. Raman spectrum showing signature of electropolymerized thin film of PEDOT. Observed peaks agree well with that observed in literature for PEDOT (Wang *et al* 2006)

Figure 4. Multiple cyclic voltammetry scans of electropolymerized thin film of PEDOT (30 min) at a scan rate of 40 mV s^{-1} . Original CV curve after 30 cycles has considerably shrunk which may be due to loss of stability, reduction of surface area or change of morphology.

of operating in acidic, alkaline and organic electrolytic solutions. A graphene/polypyrrole composite electrode was prepared by our group earlier (Mini *et al* 2011), which shows a stable large electrochemical capacitance (1510 F g^{-1} and 151 F cm^{-3} for gravimetric and volumetric capacitances, respectively).

Composite electrodes of PEDOT and CNTs were prepared (Lota *et al* 2004) by (a) direct polymerization on ultrasonically dispersed CNTs (130 F g^{-1}) and (b) electrochemical deposition of polymer onto the CNTs (150 F g^{-1}). Also, suspension of CNT and PEDOT was co-deposited (Peng *et al* 2006) and gave capacitances of at least 0.5 F cm^{-2} . PEDOT

Figure 5. (a) SEM image of EPD graphene on ITO. A unique curved interconnected tubular morphology of graphene is seen. (b) SEM image of PEDOT–graphene composite film electrode. Polymer has formed a sheath around network of nanotubes/nanochannels. This morphology gives a very high surface area for composite.

Figure 6. FTIR spectra of PEDOT and graphene–PEDOT composite. FTIR spectrum of graphene/PEDOT composite shows appreciable difference from that of PEDOT alone, indicating bond formation between the two materials. Characteristic vibrational peaks of PEDOT are shown below 1600 cm^{-1} . Peaks of graphene occur between 1600 and 1800 cm^{-1} due to presence of C–C and C=O.

and active carbon gave 56 F g^{-1} after 1000th cycle in the range of $0\text{--}3\text{ V}$ (Ryu *et al* 2004). Activated carbon–PEDOT composite electrodes have been prepared by electrochemical deposition of β -naphthalenesulfonate-doped PEDOT onto activated carbon electrodes. The electrodes showed a maximum capacitance of 158 F g^{-1} at a scan rate of 10 mV s^{-1} (Selvakumar and Bhat 2008). Microporous carbon spheres were infiltrated with EDOT and oxidative polymerization was carried out. The colloidal carbon–PEDOT composites show a capacitance value of 106 F g^{-1} (Kelly *et al* 2009). A survey of the reported work shows that the PEDOT–carbon composites yield a moderate value of capacitance of up to 160 F g^{-1} and up to 0.5 F cm^{-2} . Yet another

study on graphene–PEDOT composite for supercapacitors was reported (Alvi *et al* 2011). In this, the composite was prepared by chemical oxidative polymerization technique, a less controllable process and reported average capacitance was 350 F/g . There are also reports on multilayer graphene–PEDOT films by electrodeposition, yielding 154 F/g for six graphene layers (Lee *et al* 2012). PEDOT–rGO composites prepared by *insitu* polymerization process showed a capacitance of 108 F/g (Zhang and Zhao 2012). Layered PEDOT nanocomposites were prepared and enhancement of double layer capacitance and electrical conductivity was comprehensively studied (Murugan *et al* 2005).

In our study, graphene–PEDOT composite electrodes were synthesized by simple processes of electrophoretic deposition (graphene) and a superior and controlled process of electropolymerization (EDOT) and were investigated for its electrochemical and thermal properties. Graphene was chosen as a constituent material of the electrode on account of its high active surface area consisting of large open flat layers as well as its electronic transport properties. The composite electrode 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.

2. Materials and methods

2.1 Electropolymerization of EDOT for PEDOT thin film

Indium tin oxide-coated glass plates (1 cm^2 , Solaronix SA, Switzerland, sheet resistance of ITO, $5\text{--}10\text{ ohm/cm}^2$) were cleaned and dried. 0.05 M 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

Figure 7. Cyclic voltammograms of graphene-PEDOT composite electrode for various polymerization times at a scan rate of 40 mV s^{-1} . CV was done in 0.1 M LiClO_4 electrolyte. Maximum specific and area capacitance values are obtained at a polymerization time of 8 min.

Figure 8. Cyclic voltammograms of graphene-PEDOT composite electrode for fixed polymerization time of 8 min at various scan rates ($60, 80$ and 100 mV s^{-1}). Area under CV curves does not vary much with change in scan rate.

electrode. A platinum electrode was used as the counter electrode. Deposition was carried out at 1.8 V for different durations. After polymerization, plates were washed with water to remove unpolymerized monomer.

2.2 Preparation of graphene/PEDOT electrode

5 mg of graphene powder (graphene was purchased commercially from Quantum Materials Corporation Ltd., Bangalore, India) was finely dispersed in 20 ml isopropyl alcohol using ultrasonication technique. A small pellet of nickel nitrate (4 mM) was added. The graphene was then electrophoretically deposited onto the previously weighed ITO-coated glass plate by keeping it as working electrode. A platinum electrode was used as the counter electrode. The deposition was carried out at 20 V d.c. supply for 10 min. By keeping the graphene electrode as the working electrode, EDOT monomer was polymerized over the graphene under the conditions mentioned in § 2.1 with electropolymerization voltage being 1.8 V. The duration of polymerization of EDOT was varied for different samples. Weights of the coatings were evaluated.

2.3 Chemical synthesis of graphene/PEDOT for thermal and FTIR analysis

5 mg of graphene was finely dispersed in 5 ml of isopropyl alcohol into which EDOT monomer (0.05 M) was added dropwise on stirring. 0.1 M of ammonium persulfate (APS) was prepared in 5 ml water and slowly added into the solution by keeping the beaker on magnetic stirrer. The solution was kept undisturbed for 7 days at room temperature. The black product was separated, washed several times in water and isopropanol and dried at 650 °C. The obtained composite was quantified. Slurry was prepared by mixing it with a small quantity of glycerol. It was then coated over previously weighed ITO-coated glass plate using a brush and dried. The weight of the plate after coating was determined and weight of the film was then evaluated.

2.4 Characterization

For cyclic voltammetry measurements, a three-electrode system was used with AUTOLAB system. The sample was connected to positive terminal and a platinum electrode was used as counter electrode. Direction of voltage scan was from positive to negative and back. A calomel electrode served as reference electrode. 0.1 M LiClO_4 was used as electrolyte for CV measurements. Capacitance was calculated using the reduction current obtained from CV curves. Morphology of the prepared electrodes was analysed using SEM (JEOL-JSM-6490). Thermal stability of the material was studied using TG analysis (SII TG/DTA 6200EXSTAR).

Figure 9. Charge-discharge plot of graphene–PEDOT composite (5 μA applied current and weight of composite, 70 μg). Discharge was triggered even by application of low current of 5 μA suggesting that a higher proportion of current (charge) is lost due to self-discharge.

Figure 10. Statistical scatter plot of specific capacitance of graphene–PEDOT composite polymerized for a fixed time (8 min) and CV scan rate of 40 mV s^{-1} . Median value of specific capacitance within scatter band in figure is 1410 F g^{-1} .

3. Results and discussion

EDOT monomer was electropolymerized for varying times on to ITO substrates at 1.8 V as outlined in § 2.1. The electrodes thus prepared were characterized by cyclic voltammetry (CV). Figure 1 shows CV curve of PEDOT thin film obtained by polymerization for varying times (5, 10, 15, 20, 25, 30 and 35 min). From the capacitance data, it becomes clear that 30 min of polymerization gives optimum values

Figure 11. Statistical scatter plot of area capacitance of graphene-PEDOT composite polymerized for a fixed time (8 min) and CV scan rate of 40 mV s^{-1} . Median value of area capacitance within scatter band in figure is 199 mF cm^{-2} .

Figure 12. TGA diagram of graphene-PEDOT composite and PEDOT showing degradation zones for pristine polymer and composite. The first weight loss occurs for composite around 200°C , while same occurs for PEDOT around 50°C . Second weight loss event occurs at about 350°C for composite. Corresponding weight loss for polymer is about 250°C . Composite exhibits improved thermal stability.

(40 mF cm^{-2} at 40 mV s^{-1}). It is observed that the specific and area capacitances vary according to the duration of deposition. This implies that the surface morphology and thickness of thin film are the main factors contributing to the capacitance. Further increase in thickness of thin film resulted in a reduction in capacitance values. This may be

due to loss of porosity of the electrode with increased film thickness. Figure 2 shows CV curves at various scan rates for a fixed polymerization time (30 min). The electropolymerized PEDOT was also analysed for its Raman signature (figure 3), which agrees well with literature (Wang and Wong 2006). To test intrinsic stability of the electropolymerized thin film of PEDOT, repeated CV scans were taken at a scan rate of 40 mV s^{-1} (figure 4). After 30 scans, the original CV curve has considerably shrunk which may be due to loss of stability, reduction of surface area or change of morphology. Graphene was electrophoretically deposited (EPD) on ITO as per §2.2. Figure 5(a) shows SEM image of EPD graphene. A unique curved and interconnected tubular morphology of graphene is seen. This morphology presents a high surface area and the formation of this unique morphology could be explained by invoking the role played by nickel during EPD process (Wu and Lin 2010).

EPD of graphene film is achieved via transport of positively-charged graphene sheets (adsorbed with nickel ions at the edges) towards 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 possibly reduced electrochemically to form metallic nickel because graphene has electrical conductivity, which allows electrons to conduct from 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. This edge-wise binding causes the graphene sheet to curl up and form a network of nanotubules/nanochannels. As a result, the graphene sheets having electrically charged surfaces (because of adsorption of nickel ions) continue to deposit on the film possibly forming a Ni-decorated nanotubular graphene film.

This graphene-covered substratum was then used for electropolymerization of EDOT, which covers the graphene with a layer of PEDOT. The flat five-membered ring structure of EDOT monomer enables interactions with other molecules either through (i) linking through the flanking C atoms at the 2, 5 positions or (ii) π -bond formation with the delocalized electron pairs on the sulfur atom.

Thus, graphene C atoms can interact with EDOT monomer by linking the planar graphene sheet edge atoms with carbon atoms at 2, 5 positions of the EDOT ring with Ni (nickel) ions at the graphene sheet edges acting as co-ordination centres, or through local π -bonding with sulfur atom of the EDOT monomer. Non-functionalized graphene was used for our work. Polymerization was done for several times (2, 3, 4, 5, 8, 12, 15 min). Figure 5(b) shows SEM image of the composite film electrode formed with 8 min 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. Figure 6 shows FTIR spectra of

Figure 13. Electrochemical long term stability of graphene–PEDOT composite under repeated CV scans at a rate of 40 mV s^{-1} . CV curves show very good fidelity and no degradation thus, demonstrating electrochemical stability. This behaviour is far superior when compared to electrochemical stability of PEDOT thin film (figure 4).

Figure 14. (a) SEM image showing morphology of composite electrode after 1 CV scan at a rate of 40 mV s^{-1} . (b) SEM image showing morphology of composite electrode after 60 CV scans at a rate of 40 mV s^{-1} . Composite morphology shows no marked signs of degradation thus reinforcing electrochemical data.

PEDOT and the graphene–PEDOT composite. FTIR spectrum of graphene/PEDOT composite shows appreciable difference from that of PEDOT alone, indicating bond formation between the two materials. Characteristic vibrational peaks of PEDOT are shown below 1600 cm^{-1} . The bands at 983 , 840 and 693 cm^{-1} are due to the $\text{C}=\text{S}$ stretching vibrations of PEDOT (Selvakumar *et al* 2008). Bands at around 1206 and 1067 cm^{-1} are originated from stretching of $\text{C}-\text{O}-\text{C}$ bond in the ethylene di-oxy group (Patra and Munichandraiah 2007). The peak at 1360 cm^{-1} shows $\text{C}-\text{C}$ stretching. Generally, the peaks of graphene appear between 1600 and 1800 cm^{-1} due to the presence of $\text{C}-\text{C}$ and $\text{C}=\text{O}$ (Xu *et al* 2009). Figure 7 shows electrochemical activity of the composite film with CV done in 0.1 M LiClO_4 electrolyte for different time intervals of polymerization, at a scan rate of

40 mV s^{-1} . It is seen that maximum specific and area capacitance values are obtained at a polymerization time of 8 min . Figure 8 shows CV curves at a fixed polymerization time of 8 min for different scan rates. The reduction and oxidation reactions of the graphene/PEDOT composite happen in the range of $\pm (2-3) \text{ V}$, hence, the potential window of CV scan is expanded to 8 V .

As is evident from the CV data, 8 min is the optimum electropolymerization time for realizing the composite. The ‘contact junctions’ of graphene with PEDOT (EDOT) chains either established through the flanking C atoms of the EDOT or through local π -bonding with the S atom of EDOT can cause flow of charges from PEDOT (a semiconducting polymer) to the graphene (can be considered as metallic or a semiconductor with zero bandgap) and this can be a source of

enhanced self-discharge. A charge–discharge profile for the graphene–PEDOT composite is shown in figure 9, wherein discharge was triggered even by application of low current of $5\ \mu\text{A}$ suggesting that a higher proportion of the current (charge) is lost due to self-discharge.

To check consistency of the capacitance values, about 15 electrode samples were prepared under the same conditions, keeping the polymerization time fixed at 8 min and a detailed study of the variation of specific and area capacitances was carried out.

The statistical scatter of data for the scan rate of $40\ \text{mV s}^{-1}$ is studied in figures 10 and 11, which show the scatter plots for specific and area capacitances from which median scatter bands were identified and median values of specific and area capacitances computed. The purpose of imposing the scatter band is to eliminate extreme data points which may have occurred due to inherent statistical variations during sample processing steps (for example, the extreme data points are as high as $3000\ \text{F/g}$ and as low as $500\ \text{F/g}$ in figure 10; as high as $600\ \text{F/cm}^2$ and as low as 50 in figure 11) and obtain meaningful capacitance values. The median value of specific capacitance within the scatter band in figure 10 is $1410\ \text{F g}^{-1}$, while the median value of area capacitance within the scatter band in figure 11 is $199\ \text{mF cm}^{-2}$. The area capacitance values are superior to the values reported for graphene–polypyrrole composite electrodes by Mini *et al* (2011). The high values can be attributed to the high surface area provided by the composite to the electrolyte, which maximizes the faradaic interactions. The role played by graphene is to form a very high surface area network of nanotubules/nanochannels, which serves as nucleation centres for PEDOT polymer. PEDOT thus adopts 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.

It was decided to study thermal properties of the graphene–PEDOT composite when compared to PEDOT. The composites were prepared as per §2.3. Thermogravimetric analysis (TGA) was carried out and figure 12 shows TGA plot of the composite and PEDOT. The first weight loss occurs for the composite around $200\ ^\circ\text{C}$, while the same occurs for PEDOT around $50\ ^\circ\text{C}$. The second weight loss event occurs at about $350\ ^\circ\text{C}$ for the composite. The higher temperature could be attributed to the presence of graphene. The corresponding weight loss for the polymer is about $250\ ^\circ\text{C}$. Thus, the composite exhibits improved thermal stability when compared to PEDOT.

The electrochemical stability of the graphene–PEDOT composite was tested under repeated scans of $40\ \text{mV s}^{-1}$. It is seen from figure 13 that after 40 scan cycles, the CV curves show very good fidelity and no degradation thus demonstrating the electrochemical stability. This behaviour is far superior when compared to the electrochemical stability of the PEDOT thin film (figure 4). Figure 14(a and b) show SEM images of the composite electrode taken after a single

CV scan and after 60 CV scans, respectively. The composite morphology shows no marked signs of degradation thus reinforcing the electrochemical data.

Thus, we were able to synthesize graphene–PEDOT composite electrodes using simple electrodeposition techniques. These electrodes demonstrated high capacitance values ($1410\ \text{F g}^{-1}$, $199\ \text{mF cm}^{-2}$) and showed excellent electrochemical and thermal stabilities. The capacitive behaviour was explained on the basis of the unique nanostructural morphology of graphene and electrodeposited PEDOT. These electrodes are suited for high performance supercapacitor and electrochemistry applications.

4. Conclusions

Graphene–PEDOT composite electrodes suitable for supercapacitor applications were fabricated using techniques of electrophoretic deposition and electropolymerization. The composite electrodes show median specific capacitance of $1410\ \text{F g}^{-1}$ and median area capacitance of $199\ \text{mF cm}^{-2}$ at a scan rate of $40\ \text{mV s}^{-1}$. The composite electrode also showed excellent electrochemical stability in repeated CV scans and its thermogravimetric data was superior when compared to PEDOT. The electrophoretic deposition of graphene produces a unique morphology of nanotubules/nanochannels, which is faithfully adopted by the electropolymer PEDOT. Such morphology maximizes the faradaic interaction sites for the hybrid supercapacitor electrode and yields high electrochemical capacitance.

Acknowledgments

The authors acknowledge the Department of Science and Technology (Grant Nos: 100/IFD/8495/2007-2008 and 100/IFD/8495/2009-2010), Government of India and the Ministry of New and Renewable Energy (Grant No: 31/05/2009-10/PVSE), Government of India, for supporting this work. The authors are also very grateful to Amrita Institute of Medical Sciences for infrastructure support to this programme.

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