Electrochemical performance of supercapacitors based on carbon nanofoam composite and microporous poly(3, 4-ethylenedioxythiophene) thin film asymmetric electrodes

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Abstract

Electrochemical performance of supercapacitors configured using carbon nanofoam enfolded by conformal thin poly(3,4-ethylenedioxythiophene) (PEDOT) film in nanofibrous structure and electrodeposited microporous PEDOT film/graphite as two asymmetric electrodes is described. Cyclic voltammetry data at 20 mVs^{-1} scan rate show specific capacitance of carbon nanofoam-PEDOT composite electrode operating in the -0.8 to $+0.2 \text{ V}$, and microporous PEDOT in the 0 to $+0.8 \text{ V}$ voltage range are 72 and 159 Fg^{-1} , respectively. Paired in an asymmetric supercapacitor, in the balanced charge state, highly symmetrical cyclic voltammetry plots at high scan rates of 100 mVs^{-1} in -0.8 to $+1.2 \text{ V}$ voltage range testify highly capacitive behavior with high degree of charge reversibility attributed to unimpeded pore-filling and alignment of ionic charges over vast interiors of carbon nanofoam and a highly pervasive access to electrolyte ions within interconnected void network of microporous PEDOT. Linear charge-discharge characteristic of the supercapacitor at 1.0 to 3.5 Ag^{-1} current density show high rate capability and yield energy density of 13.6 Wh.kg^{-1} at the power density of 19.0 kW kg^{-1} . The long term charge-discharge tests at 1 Ag^{-1} show minimal $\sim 14 \%$ loss of specific capacitance of asymmetric supercapacitor for 10,000 cycles.

Keywords: Microporous materials, Polymers, Electrochemical techniques, Electrochemical properties, Coatings, Thin films

1. Introduction

Electrochemical storage of the electrical energy by supercapacitor devices has potential applications in the modern communication, distributed sensors arrays, industrial automation and electrical vehicles [1-3]. The ability to deliver power at a high rate exceeding 10 kW kg^{-1} with charge–discharge time of a few seconds are attractive features of energy storage **with** the supercapacitors distinguishing them from the electrochemical battery storage. Equally important, however, is to attain high energy density capability which stands poor compared to the rechargeable batteries. Supercapacitors which store electrical energy by electrical double layer capacitance (EDLC) are based on activated carbon (AC), carbon nanotubes (CNT) and morphological variants of graphene [4-5]. In EDLC supercapacitors, the capacitive energy density enhancement is achieved by large surface area and distributed open pore structure making it highly accessible to the electrolyte ions. The materials systems in which the electrical energy is stored via faradaic reversible surface redox reactions are the transition metal oxides [6] and electrically conducting polymers [7]. The basic approach for high specific capacitance in these material systems is **to form** the nanocomposites and **to create** various nanostructured forms like nanowires, nanorods, or nanoparticles. This produces mesoporosity which reduces diffusive pathways for ions and **increases** ion access for rapid surface redox reactions [7-9] which is critical for achieving high energy storage density

The increase in the energy density can also be achieved in supercapacitors cell that operate at higher voltages based on the relation, $(E = 1/2)CV^2$. This is possible in supercapacitors with

two dissimilar electrodes rooted in different storage mechanisms which operate in different electrochemical potential range. This increases the functional voltage range of the assembled supercapacitor [10-12]. In the past, asymmetric combination of the metal oxides and metal hydroxides with the structured carbons electrodes, such as Ni(OH)₂/graphene, RuO₂/graphene [13], Ni(OH)₂/CNT [14], MnO₂/ AC [15], MnO₂-graphene [11,16] and MnFe₂O₄/graphene-MnO₂ [17] have been extensively researched. A recent trend is to develop electroactive materials in the nanostructured forms such as NiO-CoO₂ nanosheets/CNT [18], Ni(Co)O nanowires/activated carbon [19], RuO₂/TiO₂ nanotube/AC [20], graphene-MnO₂ nanorod/graphene-Ag [21] and MnO₂ nanowire/graphene [12] as electrodes for supercapacitors. The electrically conducting polymers show reasonably high specific capacitance in the symmetrical supercapacitors but have not as widely been studied in the asymmetric combination. A few studies have focused on combination of activated carbon (AC) electrode [22] with various conducting polymers, polyaniline (PANI) [23, 24], poly(3,4-ethylenedioxythiophene) (PEDOT) [25], poly(3-(4-fluorophenyl) thiophene) (PFPT) [26], and poly(3-methyl thiophene) (PMeT) [27] as well as its composites with metal-oxides like polypyrrole (Ppy)-MnO₂ [28]. Balancing of the stored charge on both asymmetric electrodes is required in a supercapacitor device in order to achieve high energy density. The pseudocapacitive electrode has high charge density compared to EDLC electrode based on the structured carbons. To compensate for the deficiency in its specific capacity, the EDLC electrode mass is generally increased. However, as EDLC is an interfacial storage mechanism, it is difficult to achieve reasonable balancing of charges. Another approach to create dissimilarity in electrodes is by modifying one electrode of a symmetrical supercapacitor by making composite having both EDLC and pseudocapacitive components in proper proportions. In the past, supercapacitors pairing one electrode of graphene and carbon

nanotubes (CNT) with another electrode being the composite graphene and CNT with conducting polymer, for example composites of PEDOT- CNT [29], PANI-graphene [30], PMeT-CNT [31] and PEDOT-carbon fiber [32] have been reported.

We have investigated supercapacitor using the asymmetric electrodes based on the carbon nanofoam with nanofibrous PEDOT forming a composite structure and microporous PEDOT layer over graphite. The PEDOT has high p-conductivity [33] and a wide potential window [34]. In the microporous **form**, it can achieve higher areal capacitance even with a thin layer of low specific mass. The carbon nanofoam due to its 3-dimensional (3-D) nano architecture and the random network of interconnected nanopores distributed over its entire 3-D material form offers high surface area. Hence, it has vast interface with the electrolyte which contributes to high specific capacitance due to the electrochemical double layer. Its pore structure facilitates faster ion exchange reactions due to extensive electrolyte ion access even with the limitation of short diffusion lengths [35, 36]. Herein, we formed a composite by wrapping the carbon nanofoam with a conformal coating of ultrathin (~100 nm) film of PEDOT in the nanofiber-morphology. Thus, the carbon nanofoam pores have much improved electrical connectivity significantly increasing the areal capacitance density of the carbon nanofoam-fibrous PEDOT composite electrode. The conformal ultrathin PEDOT film formed by not occluding the underlying mesoporous structure, also improves the dynamic performance of the assembled supercapacitor. This paper reports on the electrochemical properties, impedance analysis, charge-discharge characteristics and energy-power density of the supercapacitor assembled with the two asymmetric carbon nanofoam-nanofibrous PEDOT composite and microporous PEDOT/graphite electrodes.

2. Materials and methods

An ultrathin (~100 nm) PEDOT film in the nanofibrous morphology was deposited conformal to the carbon nanofoam by ultra-short pulsed current electropolymerization method in an aqueous medium [37, 38]. In preparation, the 0.01 M 3,4-ethylenedioxythiophene (EDOT) monomer (Sigma Aldrich) was dispersed in deionized water in the presence of 0.07 M sodium dodecyl sulfate (SDS) surfactant under continuous stirring at 40°C. Later, the carbon nanofoam foil was soaked in this medium for ~40 min. The pulsed current electropolymerization was carried out in a two electrode cell with carbon nanofoam as a working and Pt foil as a counter electrode. The electrolyte 0.1 M lithium perchlorate (LiClO_4), which is also a source of the dopant anions for PEDOT conjugation, was added just prior to the initiation of electropolymerization. Though the EDOT monomer is sparingly soluble in water, it was possible to achieve aqueous dispersion of EDOT with the support from the SDS surfactant. The ionized SDS molecules with the extended dodecyl alkyls molecular chains being hydrophobic in character attach at the carbon nanofoam surface [39] while the hydrophilic OSO_3 groups project outwardly into the water. The EDOT monomers thus preferentially disperse within the hydrophobic region at the carbon nanofoam created by the attached dodecyl alkyls molecular entities [40] where these polymerize under the action of the current pulses. The PEDOT deposition by electropolymerization was carried out by applying sequential unipolar anodic current pulses of ultra-short 10 ms periods and 4 mA cm^{-2} current density. The film thickness was controlled by the number of pulsed current cycles applied for deposition. The PEDOT film growth essentially takes place when electropolymerization of the EDOT monomer attached at the carbon nanofoam surface is initiated by charge transfer during the ultra-short current ON period. The PEDOT forms in the pulsating manner under the action of the anodic current pulses which

results in the formation of a thin conformal layer in the nanofibrous morphology [41]. The other electrode consisted of a $\sim 10\ \mu\text{m}$ thick uniform microporous PEDOT film over a $250\ \mu\text{m}$ thick graphite sheet substrate. It was formed by depositing a PEDOT film by the similar pulsed current electropolymerization method using the modified pulsed current parameters which involves short current off period of 100 ms. The intervention of a short current off time between the successive current pulses is an important factor in the creation of the microporous growth morphology of the PEDOT film. The current OFF period is basically utilized to dissolve away the unsustainable oligomers or adsorbents. It also homogenizes the EDOT monomer and increases its availability by diffusion in the vicinity and across the growing PEDOT film surface over graphite substrate which results in the formation of highly porous PEDOT film. The graphite substrate unlike the carbon nanofoam shows no EDLC capacitance and acts solely as a current carrying support electrode.

The electrochemical properties of the individual electrodes and that of the assembled supercapacitor cells were analyzed by cyclic voltammetry (CV), galvanic charge-discharge (CD) and ac electrochemical impedance spectroscopy (EIS) methods. These measurements were performed in a three-electrode cell with Pt as a counter electrode in the 1 M LiClO_4 aqueous electrolyte medium. The potential was measured with reference to a saturated calomel electrode (SCE). The cyclic voltammetry measurements were performed using a Solartron electrochemical interface (Model 1287) by recording the flow of electric current on application of different potentials in the anodic to cathodic cycling direction scanned at different rates between 5 to 100 mVs^{-1} . The specific capacitance from the cyclic voltammetry data C_{sv} was determined by the relation,

$$C_{sv} = \frac{|i_a| + |i_c|}{2v_s \cdot m_{ac}} \quad (1)$$

where, i_a and i_c represent the magnitudes of the anodic and cathodic currents, respectively and v_s is the voltage scan rate. The parameter m_{ac} is the electrochemically active mass of the electrode. In the case of supercapacitor cell, the combined electroactive mass of both electrodes was taken into account. The galvanostatic charge-discharge characteristics were measured in the same cell at fix current densities between 1- 4 Ag^{-1} in various potential ranges, from 0.05 V to 0.5 V, 0.8 V and 1 V for individual electrodes and also for supercapacitor cell. The specific discharge capacitance of the electrodes from the CD data, C_{sd} is determined by the relation,

$$C_{sd} = \frac{I_d \cdot \Delta t_d}{m_{ac} \cdot \Delta V_d} \quad (2)$$

where, I_d is the constant discharge current density, Δt_d is the discharge time and ΔV_d is the voltage change on discharge measured after excluding the IR voltage drop. The ac impedance spectra were recorded in a two-electrode cell configuration in the frequency range 0.01 Hz-100 kHz with ac signal amplitude of 10 mV using the Solartron gain-phase impedance analyzer (Model:1260). The impedance data provide frequency dependence of the real Z_{Re} and imaginary Z_{Im} impedances. The Nyquist plots between Z_{Re} and Z_{Im} based on the impedance data were simulated with the electrical equivalent circuit model representing the electrochemical and electrophysical properties of the carbon nanofoam-nanofibrous PEDOT composite and the PEDOT/ graphite electrodes with the Z-plot software (Scribner Associate) which provides the characteristic resistances and various contributing factors to the capacitance. The overall supercapacitor cell capacitance from the impedance study, C_i is obtained by the relation, $C_i = (2\pi f Z_{Im})^{-1}$ where f is the signal frequency. The specific capacitance of the single electrode can be calculated as, $C_{si} = 2C_i/m_c$.

3. Results and Discussion

3.1 Electrode microstructure

Microstructure of the carbon nanofoam electrode is shown in the scanning electron micrographs (SEM) in Figure 1. Viewed in the low magnification, it features randomly crisscrossing 10-20 μm long carbon fibers. The anchored films between the carbon fibers are the platelets of carbon nanofoam. The carbon fibers act as a scaffold for these platelets transforming the entire structure as the free standing 3-dimensional carbon nanofoam foil. The carbon fibers are electrically conducting and interconnected fibers act as current carriers across the carbon nanofoam platelets. The microstructure of the carbon nanofoam platelets is revealed in a high magnification SEM image in Fig 1(b). The carbon nanofoam platelets have porous morphology

featuring aperiodic distribution of nanopores with the average size in the 40-70 nm range. Such nanoporous microstructure imparts a highly pervasive access to the electrolyte ions to diffuse through deep pores rendering a large area interface of carbon nanofoam with the electrolyte. The microstructure of the carbon nanofoam platelets after conformal deposition of a 100 nm thin PEDOT film is shown in Figure 1c. The PEDOT film forms with a nanofibrous morphology comprising of ~30 nm average diameter entangled nanofibers surrounding the underlying nanopores of the carbon nanofoam platelets. With the preservation of the underlying nanopore structure, the carbon nanofoam-fibrous PEDOT composite remains highly conducive to the efficient ion access. The surface selective ultra-short current pulse polymerization of the EDOT monomer [38] under the influence of the SDS surfactant is an important factor in realizing the nanofibrous PEDOT film morphology [39, 41]. As described above, the dodecyl alkyl groups of the SDS surfactant attached at the carbon nanofoam platelet surface create hydrophobic environment for the EDOT monomers. Under the pulsed current conditions, these polymerize as PEDOT nanofibers in close contact with the platelet surface sparing the interiors of the nanopores in the carbon nanofoam thus ensuring full access to the electrolyte ions.

The microstructure of the ~10 μm thick PEDOT/ graphite electrode is shown by the SEM micrographs in Figure 2a. It consists of thin wrinkly flakes forming clusters which are joined by loosely packed fibrous bundles of the PEDOT polymer. The clusters have ridge-like stacking of flakes formed as a result of the short periods of interrupted polymerization when anodic current pulse is off [37, 38]. As shown by the magnified image in Figure 2b, the fibrous bundles have average 50-70 nm size voids and the stacked flakes also produce microvoids rendering the entire PEDOT electrode morphology highly porous. Such microporous structure offers the least

impediment to the electrolyte ions encompassing extensive interior regions of the PEDOT film bulk.

3.2 Electrochemical analysis of carbon nanofoam composite & microporous PEDOT electrodes

The cyclic voltammetry (CV) plots in the potential range -0.8 to +0.2 V(SCE) of the carbon nanofoam-fibrous PEDOT composite electrodes at scan rates of 5, 10 and 20 mV s⁻¹ (curves-a, b and c) are shown in Fig 3A. Curve (d) in Fig 3 A depicts the CV plot of the carbon nanofoam electrode measured at 20 mV s⁻¹. The capacitive property of the carbon nanofoam electrode originates from the electrified double layer formed at the interface of its entrenched pores with the electrolyte ions. The carbon nanofoam electrode has BET surface area of ~ 400 m² g⁻¹ which enhances the double layer capacitance by expanding the interface with the electrolyte. The electrical conductivity of carbon nanofoam is limited to ~10² S cm⁻¹. Therefore, the observed lower currents of carbon nanofoam is attributed to poor electrical connectivity among the nanopores distributed across the platelets. In the composite electrode, the PEDOT nanofibers provide electrically conducting pathways connecting the distributed nanopores in the carbon nanofoam. PEDOT nanofibers also facilitate the transport of charge compensating ions thereby taking full advantage of the electric double layer. The CV plots of the composite electrode are indicative of the capacitive nature which basically originates from the alignment of the ionic charges within the interiors of the nanopores in carbon nanofoam platelets forming electrical double layer. Higher currents are realized in the composite electrode as shown by curves (a-c). Herein, the PEDOT nanofibers provide electrical pathways connecting accumulated ionic charges at the nanopores and establish long-range continuity of pore network over characteristic

lengths which improves overall current and hence the specific capacitance. Even though the PEDOT is in the partially reduced state at somewhat negative bias, it has better conducting properties compared to amorphous platelets [42]. The PEDOT nanofibers also increase the surface area of the composite and provide additional sites for ion adsorption which additionally contributes to the overall specific capacitance. The CV plots (curves-b and c) at higher scan rates of 10 and 20 mV.s^{-1} , respectively show expected increase in current and shape consistent with the inference of capacitance due to double layer and ion adsorption. The specific capacitance C_{sv} based on the CV plots measured at 20 mV s^{-1} of the carbon nanofoam is low typically 10-12 F g^{-1} which increases to 72 F g^{-1} by conformal thin PEDOT forming a composite. Figure 3B shows the CV curves with the increasing positive potentials and as observed, the current in the negative potential range remains unchanged irrespective of the positive potential scanned. It is known that adsorbed charges increase with the increase in the potential thereby making current independent of voltage, which is a characteristic of the double layer capacitance originating from surface aligned charges [43]. In the negative voltage direction scan, the observed increase in the current is suggestive of possible pseudocapacitive contribution from the thin nanofibrous PEDOT layer encrusted with the carbon nanofoam. The combined effect of the two is to increase the overall capacitance of the composite electrode.

The Nyquist plot of the carbon nanofoam-fibrous PEDOT electrode obtained from the impedance measurements in the frequency range 100 kHz to 0.01 Hz is shown in Figure 3C. It features a near vertical response of the imaginary impedance Z_{Im} without the usual Warburg impedance region which indicates fast charge transfer kinetics with the least diffusive transport limitations for the electrolyte ions. This is more vividly seen by the inset in Figure 3C which also

shows a half semicircle impedance response in the high frequency region characteristic of an electrical equivalence of a parallel capacitance and resistance circuit. The real impedance axis cutoff at high frequency provides quantitative resistive determination of the electrolyte and the mid-frequency cutoff is reflective of combined bulk resistance of the electrode-electrolyte system. The data show both electrolyte and electrode resistance contributions are small at 11 and 16 $\Omega \text{ cm}^2$, respectively. The static specific capacitance derived from the lowest frequency impedance Z_{Im} is 91.5 F g^{-1} . The charge-discharge characteristics of the composite electrode shown in Fig. 3D are typical of the capacitive charge storage. The discharge curves are nearly linear for various charging currents investigated with over 83% of stored charge transfer at high current density of 3.5 A g^{-1} . At the current density of 1.17 A g^{-1} the charging rate is slow and the discharge rate is high resulting in the low Coulomb efficiency ~74%. This could be attributed to slower faradaic charge transfer response from the encrusted PEDOT nanofiber component of the composite electrode compared to a fast response from the surface adsorbed electrical double layer charges in the mesoporous carbon nanofoam. As such the mesoporous carbon nanofoam electrode provides high specific capacitance and charge transfer rates.

The CV plots of the 10 μm thick microporous PEDOT/graphite electrode measured in the voltage range 0 to +0.8 V(SCE) at different scan rates 5-100 mV s^{-1} are shown in Figure 4A. These curves are highly symmetrical about the zero current axis and display a near ideal rectangular shape which is reflective of highly pseudocapacitive character of the PEDOT film electrode. Remarkably, even at a high scan rates of 100 mVs^{-1} , the CV curves remain undistorted and show almost an instantaneous change in the current upon voltage reversal at the end of the CV scan. This is indicative of synergic processes of electron extraction and the diffusion of

anions (doping) within the microporous PEDOT film for maintaining a charge balance. The current increases with the increase in the scan rate resulting in a systematic decline of the pseudocapacitance retention as shown in Figure 4B. The highest specific capacitance realized for this electrode is 248 F g^{-1} which decreases by 53.2 % to 116 F g^{-1} as the scan rate is increased by 20 times. Figure 4B similarly shows the dependence of specific capacitance of carbon nafoam composite electrode wherein the reduction by 65.5% from a low 5 mVs^{-1} scan rate value of 137 Fg^{-1} to 47 Fg^{-1} at 100 mVs^{-1} is observed. The charge-discharge characteristics of the microporous PEDOT/graphite electrode measured at current densities $1.1\text{-}3.3 \text{ Ag}^{-1}$ are shown in Figure 4C. The CD curves are highly linear and reminisces the isosceles triangular shape. Consistent with the inferences of the CV studies, these also show highly capacitive character of the electrode. The discharge slopes are nearly constant even with the high charge-discharge current density 3.3 Ag^{-1} . The specific capacitance values calculated from the CD curves yield a value of 96.4 F g^{-1} at 1.1 A g^{-1} and 92.4 F g^{-1} at 2.3 A g^{-1} . The electrochemical impedance data of the microporous PEDOT electrode are shown by the Nyquist plot in Figure 4D. The near vertical response of the imaginary impedance Z'' in the low frequency region shows capacitive property over the frequency domain down to 0.04 Hz . As shown in the inset of Figure 4D, the high frequency response is devoid of the usual arc like feature which suggests charge transfer resistance is insignificant and consequently a highly diffusive transport of electrolyte ions through the microporous PEDOT film host is expected. The resistance due to electrolyte and internal electrode resistance is low $\sim 7.4 \text{ } \Omega \text{ cm}^2$ as indicated by the cutoff at the real impedance axis.

A high ion diffusion rate is critical for both carbon nanofoam-fibrous PEDOT composite and pseudocapacitive PEDOT/graphite electrodes for improved performance of the assembled supercapacitor. The ion diffusivity and its correlation with the electron mobility is evaluated for both electrodes from the scan rate dependence of the peak anodic (doping) and cathodic (reduction) currents $I_{PA,PC}$ using the Randles-Sevcik Eq. 5,

$$I_{PA,PC} = 0.6104 \cdot n^{1.5} \cdot F \cdot c \cdot A \cdot \sqrt{FD/RT} \cdot \sqrt{\nu} \quad (3)$$

Where, F is Faraday number, R is ideal gas constant, ν is the scan rate in Vs^{-1} , A is the electrode area and T is the temperature in $^{\circ}K$. The active **species** concentration in electrolyte is denoted by c and the number of electrons involved in the reduction process by n . The parameter D represents apparent charge transfer coefficient by diffusion or diffusivity. The plot of the current $I_{PA,PC}$ vs $\sqrt{\nu}$ for both anodic and cathodic cycles in microporous PEDOT/graphite electrode is shown in Figure 5A. The linear dependence on $(\text{scan rate})^{1/2}$ is due to diffusion limited process in the capacitive charge storage. The slope of the linear region of the curves provides the value of diffusion coefficients for ClO_4^- anions as $6.1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $3.1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for anodic process of in-diffusion and cathodic process of out-diffusion, respectively within the bulk of microporous PEDOT film electrode. These values of ion diffusivity are by about an order of magnitude higher compared to the earlier reported values for PEDOT films synthesized by vapor transport and chemical polymerization methods [44]. This is attributed to the surfactant aided aqueous pulsed polymerization process which enables formation of highly microporous PEDOT film. Figure 5B shows similar $I_{PA,PC}$ vs $\sqrt{\nu}$ plots for the carbon nanofoam-fibrous PEDOT composite electrode. The linear dependence validating the **Randles Sevcik** relationship provides an estimate of ion

diffusion yielding D values as $6.88 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and $3.75 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for anodic and cathodic processes, respectively. The ion diffusivity values for both electrodes are well matched for use in a supercapacitor device.

3.3 Electrochemical analysis of carbon nanofoam composite-PEDOT/graphite supercapacitor

Results of the study presented in Figs 3 and 4 show that carbon nanofoam-fibrous PEDOT composite and the microporous PEDOT/graphite electrodes show substantive electrochemical capacitive behavior in the negative and positive biased conditions, respectively. Both electrodes show high charge transfer rate ability and significant capacitance density ideal for pairing in asymmetrical supercapacitor configuration. In assembly of such supercapacitor device, the charge stored by the individual electrode should be equally balanced. The charge is given by $Q_{n,p} = m_{n,p} \cdot A_{n,p} \cdot \Delta E_{n,p} \cdot C_{n,p}$, where the suffixes n and p denote the negative and positive bias active electrodes and Q, m, A, C and ΔE are the charge, areal active mass, electrode area, specific capacitance and the operating voltage range of the electrodes, respectively. Using these electrode parameters including the areal mass, conditions for equal charge state on both electrodes was attained in the design of the supercapacitor device. The supercapacitor assembly with the two asymmetric electrodes is shown in Figure 6 and various components are marked. The supercapacitor cell was tested in 1 M LiClO_4 aqueous medium ensuring participation of ClO_4^- anions both in PEDOT doping during electropolymerization for efficient dopant conjugation and in the charge storage process.

Figure 7 shows the cyclic voltammetry (CV) plots of carbon nanofoam-fibrous PEDOT composite electrode showing EDLC capacitive properties in the potential range -0.8 to + 0.2 V(SCE) and that of the microporous PEDOT/graphite electrode showing the faradaic

pseudocapacitance in the potential range -0.1 to +0.8 V(SCE). These CV curves measured at 10 mV s^{-1} scan rate testify both electrodes are charge balanced and are ideally disposed for pairing in the asymmetric supercapacitor design. A detailed cyclic voltammetry study of the asymmetric supercapacitor cell assembled using the two electrodes was carried out at various potential ranges and at different voltage scan rates. Figures 8a and b show a series of CV plots in the potential range -0.8 to +0.8 V, -0.5 to +0.8 V, -0.2 V to +0.8 and 0 to +1.0 V measured at two different scan rates of 50 mV s^{-1} and 20 mV s^{-1} , respectively. These plots have quasi-rectangular shape over wide potential window and are highly symmetrical about the zero voltage axis. Most notably, the observed sharp transition of current at a rapid rate on voltage reversal at the end of the anode cycle indicates rapid charge kinetics owing to unimpeded and faster ion transport by diffusion. The specific capacitance calculated from the CV plots increasingly scales with the increase in the operating potential as shown in Figure 9. Typically, for a potential window of 1V specific capacitance of 59.2 F.g^{-1} is obtained which increases to 83.3 F.g^{-1} at 1.6 V as measured at 20 mV.s^{-1} scan rate. To elucidate on the charge transfer rate kinetics, further cyclic voltammetry studies were done by varying voltage scan rates in the range 10-100 mV s^{-1} . The representative results are presented in a series of CV plots in the voltage range -0.8 to +0.8 V, 0 to 1 V and 0 to +1.2 V in Figures 10a, b and c, respectively. The CV curves are nearly rectangular in shape and highly symmetrical in the anodic and cathodic voltage scans and more importantly, these features are retained even at higher scan rates without any noticeable distortion. These data confirm that asymmetric electrode supercapacitor has significant capacitive charge storage ability with a high degree of reversibility. The CV plots show a consistent increase in the current with the increase in the voltage scan rates which translates into somewhat decrease in the specific capacitance. The change in the specific capacitance as a

function of scan rate calculated using Eq. 2 is shown in Figure 10d. Typically, the decrement in specific capacitance is attributed to the diffusion limitation of the ions not synchronous with the electronic processes. For the microporous PEDOT/graphite electrode, this implies diffusion limitation of the anions in permeation through the micropores in the electrode bulk and for the carbon nanofoam-fibrous PEDOT composite electrode, reduced access of ions to the vastly distributed nanopores interface with electrolyte ions appears to be the reason. In the present study of the asymmetric supercapacitor, the specific capacitance reduction is rather gradual in the higher voltage scan rates (Figure 10d). Thus, in the characteristic time constant as ordained by the given scan rate, the charged ions (Na^+ and ClO_4^-) instead of being constrained by short diffusive transport and thereby accessing only the surface are still able to diffuse though the bulk of the electrodes owing to high porosity. A sizable concentration of charged ions is able to infiltrate and a large fraction of the PEDOT/graphite electrode is faradically active. Similarly, the high surface area and the 3-D architecture of the carbon nanofoam-fibrous PEDOT composite electrode has extensive access to the electrolyte ions. Thus, unimpeded pore filling by the electrolyte requires only a short diffusive transport of ions for the electric double layer formation and surface adsorption. Together, these aspects of both electrodes in the asymmetric supercapacitor configuration support significantly improved charge storage ability.

The galvanostatic charge-discharge (CD) characteristics of the asymmetric supercapacitor cells measured at various 1.0 to 3.5 Ag^{-1} current densities for the cell potential of 0.8 V are shown in Figure 11A. The discharge curves for all current densities are ideally linear, highly symmetrical and triangular in shape reflective of high Coulomb efficiency and high capacitive charge storage attributes of the supercapacitor cell using the two asymmetric electrodes. Furthermore, the slope of discharge current remains invariant through the increasing current

density and even at the high discharge rate of $\sim 3.5 \text{ Ag}^{-1}$ which is indicative of high power **delivering** ability of the supercapacitor. Figure 11B compares the charge-discharge curves measured at +0.5, +0.8 and +1 V cell potentials for a constant charging current density of 1.5 A g^{-1} . The discharge time of the supercapacitor cell scales linearly with the cell voltage. These characteristic taken together suggest high rate capability of the stored charges for the asymmetric supercapacitor without the loss of the capacitive properties which is consistent with the inferences drawn from the cyclic voltammetry studies. The CD characteristics show only a minimal IR drop in the region at the start of the discharge cycle which is a measure of the equivalent series resistance ESR of the asymmetric supercapacitor device. Typically, the ESR values are $\sim 4.2\text{-}6.5 \text{ } \Omega \text{ cm}^2$ and show little dependence on the charging/discharging current density. The main contribution to the ESR values originates from the intrinsic resistance of the electrode. For the microporous PEDOT/graphite electrode, low ESR values imply a high degree of anion conjugation and for the carbon nanofoam-fibrous PEDOT composite electrode, a stable and high electric conductivity.

3.4 Electrochemical AC impedance spectroscopy of asymmetric supercapacitor cell

The electrode /electrolyte interface properties and the nature of the diffusive ion transport at the interface in the asymmetric supercapacitor cell were examined using the electrochemical impedance spectroscopy (EIS). The impedance spectrum was recorded using a sinusoidal ac signal of 10 mV amplitude with a mean dc bias of 0 and 0.4 V in the frequency range 100 kHz to 0.01 Hz and the data **were** analyzed as Nyquist plots between the real Z_{Re} and imaginary Z_{Im} impedances measured at these frequencies. Figure 12 shows Nyquist plots of the asymmetric

supercapacitor at dc bias of 0 V by curve (a) and at 0.4 V by curve (b). At 0 V dc bias in the high frequency region, it shows inductive behavior (curve a) and moving towards the mid frequency range around 2.5 kHz, the real axis cutoff takes place at $4.16 \Omega \text{ cm}^2$. The real axis intercept quantifies effective internal resistance contributed by the uncompensated electrolyte resistance. The Nyquist plots are fitted by an equivalent circuit shown in the inset of Fig. 12. The main capacitive elements of the circuit are represented by the constant phase elements due to double layer capacitance, CPE_{dl} and pseudocapacitance, CPE_{psuedo} . The resistive circuit components include the charge transfer resistance, R_{CT} and bulk electrolyte-electrode series resistance, R_S . The complex-plane plots do not show the usual well-formed semicircle in the mid frequency region although a small arc fitted by simulation over a small frequency region (inset of Figure 12) shows a second cut-off at the real Z_{Re} axis at $5.89 \Omega \text{ cm}^2$ which represents combined electrode-electrolyte resistance. The difference $1.73 \Omega \text{ cm}^2$ suggests the combined resistance of the electrochemical electrode, current carrying electrode and contact resistance is fairly low for the supercapacitor device. The Warburg impedance in low frequency region characterized by a 45° slope carries information on the ion transport. The Warburg region in this case (shown in the inset) is extremely short indicating that the penetration of electrolyte ions within the microporous regions of PEDOT/graphite and carbon nanofoam composite electrodes is highly pervasive and the diffusive transport of electrolyte ions at the electrode interface is not restrictive. The vertically rising imaginary impedance over the low frequency region exhibits highly capacitive character of the asymmetric electrode supercapacitor. Linear extrapolation of the vertical impedance to the real axis shows intercept at $6.13 \Omega \text{ cm}^2$ which suggests the charge transfer resistance of about $2 \Omega \text{ cm}^2$. The knee frequency characterizing the transition from the Warburg to capacitive regime takes place at $\sim 8 \text{ Hz}$ down to 0.01 Hz indicating large capacitive frequency

domain of the asymmetric supercapacitor. This is suggestive of possible use of the asymmetric supercapacitor for high power application that requires fast charge and discharge response. The specific capacitance calculated from the lowest frequency (0.01 Hz) imaginary impedance $C_i = (2\pi f Z_{Im})^{-1}$ is $\sim 80.9 \text{ F g}^{-1}$. The impedance plot with the 0.4 V dc bias is shown by curve (b) in Fig 12. It is evident on comparison with the zero bias impedance plot (curve-a) both mid frequency arc and the Warburg impedance region are eliminated. A nearly vertical line in the complex plane representing a typical ideal capacitor property is observed. Absence of the semicircle like feature indicates the charge transfer resistance in this case is fairly small $< 0.5 \Omega \text{ cm}^2$ indicating kinetically fast electrochemical processes. The elimination of the second real axis cut-off indicates highly conducting phase of the PEDOT resulting from increased conjugation (doping) under the dc bias and the usual fast charge (electron) transfer at carbon nanofoam composite electrode. Consistent with this explanation, one also observes that the specific capacitance value has also increased to 86.1 F g^{-1} . These specific capacitance values are fairly consistent with the values calculated from the cyclic voltammetry data.

3.5 Ragone plots of energy–power density of asymmetric supercapacitor cell

Besides the electrochemical performance assessment, the device functional aspects of the asymmetric supercapacitors are better described by the energy density E_D and power density P_D parameters. The energy density, E_D and power density P_D of the supercapacitor cell were calculated from the CD data using the following relations,

$$E_D = \frac{1}{2} \cdot \frac{1}{2} \cdot C_{sd}(V_d)^2 \quad (4)$$

$$P_D = \frac{(V_d)^2}{4m_{ac} \cdot ESR} \quad (5)$$

ESR refers to the equivalent series resistance of the supercapacitor cell given as,

$$ESR = \frac{V_{drop}}{2 \cdot I_d} \quad (6)$$

where, V_{drop} is sudden voltage drop at the start of the discharge curve due to internal resistance and the other terms V_d , I_d , C_{sd} and m_{ac} are defined earlier as the supercapacitor cell voltage, discharge current density, specific discharge capacitance of supercapacitor cell given by Eq.2, and electroactive electrode mass, respectively. The Ragone plots in Figure 13 show the energy-power density dependence of the carbon nanofoam-fibrous PEDOT composite–microporous PEDOT/graphite asymmetric supercapacitor device measured at cell voltages 0.5, 0.8 and 1.2 V. At higher operating voltage, the decrease in the energy density with the corresponding increase in the power density is rather gradual. The maximum energy density of 13.6 Wh kg^{-1} was realized at the power density of 19.0 kW kg^{-1} for asymmetric supercapacitor measured at the functional voltage of 1.2 V. The power density value of 29.4 kW kg^{-1} was the highest recorded using the discharge characteristic measured at 1.2 V corresponding to the energy density of 10.8 Wh kg^{-1} . This implies that the supercapacitor can still retain ~80% of the maximum storage energy density when discharged at the highest power density. Table-I shows the energy and

power density of aqueous electrolyte supercapacitor systems paired with carbons, conducting polymers and metal oxides electrodes in various symmetrical and asymmetrical configurations. The energy density values obtained in this work are higher in comparison to the symmetrical supercapacitors using the paired pseudocapacitive nanotube PEDOT electrodes (5.6 Wh kg^{-1}) [45] and paired double layer carbons such as activated carbon fibers (8.1 Wh kg^{-1}) [46], single walled carbon nanotube SWNT (10 Wh kg^{-1}) [47] and carbon nanotube CNT (6.1 Wh kg^{-1}) [48] electrodes. When compared with the aqueous electrolyte asymmetric supercapacitors based on the conducting polymer paired with metal oxide or carbon electrodes, the energy-power density values obtained in this work are quite promising. As shown in the Table-I, for MnO_2 paired with PEDOT [10], polypyrrole [10] and graphene [49] as asymmetric supercapacitor, the energy density of 13.5 , 7.4 and 14.9 Wh kg^{-1} , respectively have been reported. The PEDOT and polypyrrole conducting polymers paired with carbon maxsorb [10] and polypyrrole with CoO [50] electrodes in asymmetric supercapacitor configuration showed energy density of 3.82 , 7.64 and 5.5 Wh kg^{-1} , respectively. With the exception of more complex composites based on graphene and carbon nanotubes with conducting polymers [51], the energy density values realized in the present study aptly exemplify the efficacy of the carbon nanofoam electrode for the asymmetric supercapacitor configuration and is ascribed to the optimum access to the electrolyte ions via 3-dimensional mesoporous structure of the carbon nanofoam which presents a much larger interface for ions. Furthermore, the microporous structure of the PEDOT/graphite electrode with open voids also exhibits ubiquitous interface with electrolyte. Both factors enable optimum electrochemical utilization of the bulk of both electrodes and also greatly facilitate the insertion-extraction of Li^+ cations and ClO_4^- anions for fast charge –discharge processes thereby improving the power density.

3.6 Long term charge-discharge cyclic performance of asymmetric supercapacitor cell

From the applications perspective, a stable long-term cyclic charge-discharge characteristic of the supercapacitors is an important performance criterion. The supercapacitor cell having asymmetric carbon nanofoam-fibrous PEDOT and microporous PEDOT/graphite electrodes was subjected to cyclic life test for 10,000 continuous sequential charge-discharge (CD) cycling at constant current density of 1.0 Ag^{-1} in the potential range 0.05 to 0.8V. The specific capacitance at every 200th cycles was evaluated and the cyclic performance for 10,000 CD cycles are presented in Figure 14. The inset figure shows the charge-discharge curves for the 1st, 400th, 3000th, 6000th, 8000th and 10,000th cycles. The CD curves retain their triangular shape with over 85% Coulomb efficiency even after 10,000 cycles. Statistically, for the first ~3,000 charge-discharge cycles, practically no loss of specific capacitance is observed. Beyond 3,000 cycles, a gradual but steady decline in the specific capacitance with some random undulations are observed. Overall decline in the specific capacitance from its initial value through 10,000 cycles is nominally at 14% which testifies to a highly stable energy storage ability of the supercapacitor cell. The excellent cycling ability of the asymmetric supercapacitor arises from the highly pervasive access to electrolyte within the interiors of mesopores in the carbon nanofoam and interconnected void network of the microporous PEDOT/graphite with the least ion diffusion limitation. The marginal decrease in specific capacitance is possibly due to loss of mechanical flexibility of PEDOT which would result in reduced ion access.

4. Conclusions

The supercapacitor cell configured with carbon nanofoam enfolded with a conformal electrodeposited thin PEDOT film in the nanofibrous structure forming a composite electrode and $\sim 10\text{ }\mu\text{m}$ thick microporous PEDOT/graphite asymmetric electrodes have shown optimum energy density of 13.6 Wh g^{-1} and a high power density of 29.4 kW g^{-1} . These values are considerably higher compared to symmetrical supercapacitors based on the PEDOT conducting polymers or the structured carbons. In the asymmetrical supercapacitor structure, this improvement is due to differing operating voltages and the energy storage mechanisms; EDLC for the carbon nanofoam-fibrous PEDOT composite and faradic for the PEDOT/graphite electrodes. At the optimum power density, the observed energy density of 10.8 Wh g^{-1} shows that nearly 80% of the optimum energy density is retained. The undistorted and highly capacitive discharge characteristics of supercapacitor cell were observed even at a high 3.5 Ag^{-1} current density. Such high degree of charge reversibility is attributed to unimpeded pore filling and alignment of ionic charges over vast nanopore interiors of the carbon nanofoam and a highly pervasive access to electrolyte ions within the interconnected void network of the microporous PEDOT/graphite electrodes. The asymmetric supercapacitors showed only a minimal $\sim 14\%$ loss of specific capacitance when subjected to 10,000 charge-discharge cycles at constant current density of 1 A g^{-1} asserting excellent long term charge-discharge ability.

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Table-I: Energy and power density of conducting polymer, carbon and oxide based symmetric and asymmetric supercapacitors in aqueous electrolyte

Supercapacitor Type	Supercapacitor Electrode Materials in Aqueous Electrolyte	Energy Density Wh kg ⁻¹	Power Density kW. Kg ⁻¹	Ref
Symmetrical	PEDOT Nanotube	5.6	25	45
	Carbon Fibers	8.1	2.98	46
	Single Wall Carbon Nanotube	10	20	47
	Carbon Nanotube	7	20	48
Asymmetrical	Polyaniline/Graphene/CNT – Graphene	20.5	25	51
	Graphene -MnO ₂ Ni Foam	14.9	10.0	49
	Polypyrrole nanowire-CoO	5.5	11.8	50
	Polypyrrole-MnO ₂	7.4	62.8	10
	PEDOT-MnO ₂	13.5	120.1	10
	Polypyrrole- Carbon Maxsorb	7.64	48.3	10
	PEDOT - Carbon Maxsorb	3.82	54.1	10
	PEDOT- Carbon Nanofoam-PEDOT	13.6	19.0	This work

Figure Captions

- Fig .1 SEM images of porous carbon nanofoam electrode (a) carbon struts anchoring carbon nanofoam platelets, (b) nanofoam platelets showing 50-70 nm size pores, (c) Nanofiber morphology conformal PEDOT film.
- Fig .2 SEM images of PEDOT film on graphite, (a) thin wrinkly flakes forming clusters with ridges, (b) cluster conjoined with multiple PEDOT bundled fibers forming deep voids.
- Fig .3 Electrochemical characterization of mesoporous carbon nanofoam-fibrous PEDOT composite electrode (A) CV plots at scan rates of 5, 10 and 20 mV s^{-1} in the potential range -0.8 to +0.2 V, (B) CV plots at 20 mV s^{-1} scan rate in the potential range curve (a) -0.8 to 0 V, curve (b) -0.8 to +0.2 V and curve (c) -0.8 to +0.5 V (C) Nyquist plot with inset showing high frequency region, (D) CD plots at current densities, (a) 1.17, (b) 2.35 and (c) 3.53 A g^{-1} .
- Fig .4 Electrochemical characterization the microporous PEDOT/graphite electrode (A) CV plots at different scan rates in the potential range -0.8 to 0.2 V, (B) specific capacitance as a function of scan rates, (C) CD plots at current densities 1.1, 2.2, and 3.3 A g^{-1} , (D) Nyquist plot with inset showing high frequency region

- Fig .5 Randles–Sevcik plots for anodic and cathodic peak currents (A) microporous PEDOT film over graphite as positive electrode and (B) mesoporous carbon nanofoam-fibrous PEDOT as negative electrode.
- Fig .6 Schematic of the asymmetric supercapacitor assembly with components marked in the diagram
- Fig .7 Integrated CV plots of carbon nanofoam-fibrous PEDOT composite and microporous PEDOT/ graphite electrodes at 10 mV s^{-1} scan rate in the voltage range -0.8 to +0.2 and -0.2 to +0.8 V .
- Fig .8 CV plots of the supercapacitor cell measured in different voltage ranges at scan rates, (a) 50 mV s^{-1} , (b) 20 mV s^{-1}
- Fig .9 Dependence of specific capacitance of the supercapacitor cell on the potential range as calculated from the CV plots at scan rates 20 and 50 mV s^{-1} .
- Fig .10 CV plots of the supercapacitor cell at different scan rates in potential range (a) -0.8 to +0.8 V, (b) 0 to +1.0 V and (c) 0 to 1.2 V. Fig (d) specific capacitance dependence on scan rates for different potentials used in CV plots.
- Fig .11 Charge-discharge characteristics of supercapacitor cell, (A) at different current densities at cell voltage 0.8 V, (B) at current density of 1.5 A g^{-1} at different cell voltages, 0.5, 0.8 and 1 V.

- Fig .12 Nyquist plot supercapacitor cell, curve (a) without bias, curve (b) with +0.4 V bias. Inset shows high frequency region of the Nyquist plot and electrical equivalent circuit.
- Fig .13 Ragone plot showing energy density-power density relationship for supercapacitor cell based on charge-discharge characteristics at different voltage ranges.
- Fig .14 Long-term cycling performance of the supercapacitor cell measured at current density of 1 Ag^{-1} showing on the average 14% reduction in specific capacitance after 10,000 charge-discharge cycles. Inset shows charge-discharge characteristics after 1, 400, 3 k, 6 k, 8 k and 10 k cycles.

Figure 1

Figure -2

Figure 3

Figure 4

Figure -5

Figure -6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14