Chapter 3

SYNTHESES AND CHARACTERIZATION OF \( \text{MnO}_2/\text{PEDOT-PSS} \) COMPOSITE CATHODES

3.1. INTRODUCTION

Manganese dioxide has been widely explored as an electrode material for supercapacitors and batteries because of its low-cost, abundance, non-toxicity and high theoretical specific capacitance (1370 F g\(^{-1}\)) [112, 113]. However, its practical specific capacitance is still low as compared with the high-cost \( \text{RuO}_2 \) [114, 115]. It is believed that the low energy density of \( \text{MnO}_2 \) is caused by its charge storage mechanism, which is based on ion adsorption or redox reactions on the surface layer[95, 116]. In a typical charge-discharge process, only the first few nanometers from the surface of the electrode can be utilized while no reactions occur in the bulk, resulting in limited energy densities[12, 117]. Therefore, improving the utilization of active materials is the key to enhance energy densities of these electrodes. Recently, porous electrodes, which can facilitate electrolyte ions to react with active materials more efficiently, have attracted a lot of attention[118, 119]. Previous studies have shown that \( \text{MnO}_2 \) based hybrid porous electrodes synthesized using CNT/conducting polymer have exhibited specific capacitance of 427 F g\(^{-1}\) [120] while flexible electrodes using \( \text{Zn}_2\text{SnO}_4/\text{MnO}_2/\) carbon have exhibited mass specific capacitance of 642 F g\(^{-1}\) [121]. Studies by Lang et al. have shown that electrodes based on \( \text{Au/MnO}_2 \) can offer high performance with a mass specific capacitance of 1145 F g\(^{-1}\)[76]. Although these studies have shown promising results, all these processing methods are complicated which can limit its scalability. Hierarchical macroporous structures like sponges are known for being strong absorbing media with significant internal surface area [122] giving it good accessibility and compatibility to aqueous solutions and electrolytes. Therefore, it is anticipated that a hybrid material with such sponge like structure exhibiting continuous conducting network of material like PEDOT: PSS (poly (3,4-ethylenedioxythiophene): poly(styrenesulfonate)) (~1000 S cm\(^{-1}\)) embedded with high capacitive material like \( \text{MnO}_2 \) could offer high storage performance. Besides, PEDOT: PSS polymers can also store charge; through electrical double layer mechanism and faradaic mechanism throughout its matrix. Thus, the
present study provides the preparation of a hybrid material with a 3D hierarchical porous network system, comprising of a conducting polymer (PEDOT: PSS) as matrix embedded with MnO₂ using a simple freeze drying process. The study also provides details on the physicochemical characterization of these hybrid sponges and investigates into its application for supercapacitor electrodes.

3.2. EXPERIMENTAL

3.2.1. PREPARATION OF SPONGY COMPOSITE ELECTRODE USING FREEZE DRYING METHOD

All the chemicals used in the present study were of analytical grade. 5 wt% PVA solution was mixed with polyethylene dioxythiophene- polystyrene sulphonate (PEDOT-PSS) (Alfa Aesar, India) for 30 min. Different amounts of MnO₂ (5, 10 and 20 wt%) nanoparticles (Nice chemical, India) were added to the above mixture and stirred overnight. This stirred solution was aged at 20°C for 24 hrs and then freeze dried (lyophilized) using a lyophilizer (ALPHA 2-4 LD plus) for 24 hrs. Depending on the amount of MnO₂ (diameter ~ 50 nm) embedded into the PEDOT: PSS as matrix material, these spongy samples were designated as PPM-5, PPM-10 and PPM-20, where PP and M denotes PEDOT: PSS and MnO₂ respectively. These nanoparticles were not characterized for this study. The number represents the amount of wt % of MnO₂ added to the PEDOT: PSS matrix.

3.2.2. MORPHOLOGY AND PHASE ANALYSIS OF SPONGY SYSTEMS

Morphological analysis was performed using scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. The crystalline phases of the samples were determined by X-ray powder diffraction method (XRD, X’Pert PRO Analytical) with Cu Kα radiations generated at 40 kV and 20 mA. Thermal stability of the PPM system was evaluated using thermo gravimetric-differential thermal analysis (TG-DTA) instrument (SII TG/DTA6200) in nitrogen atmosphere with a heating rate of 20 °C/min from room temperature to 400 °C. Surface area measurements were performed using BET method (Micromeritics Instrumentation, USA) (Sud Chemie, Kochi, India). Current profiles of PPM and PP samples were determined using scanning electrochemical microscopy (SECM, Nanotec, Munich).
3.2.3. **ELECTROCHEMICAL CHARACTERIZATION OF SPONGY ELECTRODE SYSTEMS**

Cyclic voltammetry (CV) and discharge studies (electrochemical workstation: Newport Model) were performed to evaluate the capacitance, energy and power density of the prepared electrode. For these studies, a three electrode setup consisting of lyophilized sponges, platinum and calomel electrode were used as a working, counter and reference electrodes respectively. KOH was used as an electrolyte.

3.3. **RESULTS AND DISCUSSION**

3.3.1. **EFFECT OF MNO$_2$ CONTENT ON THE MORPHOLOGY OF PPM ELECTRODES**

Fig. 3.1 shows the SEM image of PPM-10 samples under lyophilized condition. It was observed that the PPM samples exhibited interconnected macro-pores with sizes ranging from 100-150 μm (Fig. 3.1 (a—c)).

![SEM images of PPM-10 samples](image)

Fig. 3.1.SEM image showing the hierarchical mesoporous structure in PPM-10 hybrid sponges. SEM images (Fig.3.1 (d—f)) of these PPM-10 scaffolds at higher magnifications revealed a highly roughened surface exhibiting mesoporous structure. In case of PP samples the wall surface was found to be smooth in nature (see Fig. 3.2 (a-d)) as compared to PPM-10 samples, thus we did not characterize PP samples at higher magnification.
Both samples showed similar size macropores. The formation of these roughened surfaces seemed to increase with increase in wt% of MnO$_2$ in PEDOT: PSS (see Fig.3.3 and Fig.3.4). Unlike PPM-10 sponges, PPM-5 sample did not show any mesoporous structure. The lower magnification SEM images of PP, PPM-5 and PPM-10 sample showed similar microporous structures. But the higher magnification images of these 3 samples showed different morphologies. In the case of PP sample it does not show any mesoporous structure (see Fig.3.2(d)) and the surface seemed to be smooth. Unlike PP samples, PPM-5 samples showed roughened morphology but it does not show any mesoporous structure (see Fig.3.3(d) and inset of Fig. 3.3 (d)).
However, as the amount of MnO$_2$ increased beyond 10 wt % (i.e. for PPM-20 samples); the samples seemed to lose the sponginess. SEM images (Fig.3.4) of PPM-20 showed deficit of macro-pores as compare to PPM-10 samples. The reason for the deficit of macro-pores in PPM-20 sample is mainly because of the excess amount of MnO$_2$. In this composite the spongy nature and the macropore are given by the PEDOT: PSS. It was observed that the PPM-20 sample have lost its spongyness. The higher magnification image of Fig.3.1, Fig.3.3 and Fig. 3.4 represents a roughened morphology. We believe that the roughness is mainly due to the presence of MnO$_2$ particles, however due to the poor phase contrast MnO$_2$ particle could not be distinctly identified from the PEDOT PSS matrix even under field emission scanning electron microscopy. Thus, inorder to verify the presence of MnO$_2$ in the PEDOT PSS matrix, EDAX mapping was carried out (please see Fig. 3.7) for PPM-5 samples (minimum weight percentage of MnO$_2$), which
confirmed the presence of MnO₂ in the PEDOT PSS matrix.

![SEM images showing the porous structure in PPM-20 samples at various magnifications.]

Fig. 3.4. SEM image showing the porous structure in PPM-20 samples at various magnifications.

### 3.3.2. MECHANISM OF FORMATION OF PORES IN PP AND PPM ELECTRODES

The schematic representation of pore formation in PP and PPM sponges is shown in Fig. 3.5.

![Schematic illustration showing the mechanism of formation of hierarchical pores in a) PP b) PPM-10 samples and c) PPM-20.]

Fig. 3.5. Schematic illustration showing the mechanism of formation of hierarchical pores in a) PP b) PPM-10 samples and c) PPM-20.
The formation of macro-pores in PP samples can be attributed to sublimation of water from the PP matrix during the freeze drying (Fig 3.5a). MnO₂ being hydrophilic in nature ensures nano-islands of entrapped water in PP matrix being sublimated during freeze drying resulting in mesopores (Fig.3.5b). However as the amount of MnO₂ increases in the PP matrix the concentration of these nano-islands also increases preventing the formation of any macro-sized water enclaves as seen in case of PP electrodes. This can create deficits of macropores as seen in case of PPM-20 composites (Fig.3.5c).

3.3.3. ELEMENTAL AND PHASE ANALYSIS OF PP AND PPM ELECTRODES

Fig. 3.6. Typical XRD spectrum of PPM sponges.

Fig. 3.6 shows the characteristic XRD spectrum of spongy composite electrode (PPM) where the diffraction peaks of MnO₂ corresponded to tetragonal phases (JCPDS 72-1984). The roughness of this plot is mainly because of the presents of PEDOT:PSS polymer. But using XRD spectrum
the presence of PEDOT: PSS is not possible to find out. Since it was difficult to phase contrast MnO₂ nanoparticle in PPM samples (Fig.3.1, Fig.3.3 and Fig. 3.4) even under field emission scanning electron microscopy, the dispersion of MnO₂ in the spongy PPM was confirmed by elemental analysis of Mn using EDAX (See Fig.3.7). The EDAX analysis shows the uniform distribution of sulfur and nitrogen in the PPM matrix. Moreover the EDAX analysis also indicates uniform dispersion of MnO₂ in the polymer matrix.

![EDAX analysis](image)

**Fig. 3.7.** EDAX analysis showing the elemental distribution of N, O, S and Mn in PPM-5 sample.

BET analysis of the PPM samples showed that addition of MnO₂ into the PP matrix seems to increase the surface area (see Fig.3.8).

### 3.3.4. THERMAL STABILITY ANALYSES

Thermo gravimetric analysis performed from room temperature to 400°C under nitrogen atmosphere illustrate the alteration in thermal stability of PPM sample caused by the addition of MnO₂ (Fig. 3.9). In PP onset of thermal degradation occurs at around 30°C. Elevated degradation rate and pronounced increase in slope of thermal degradation were found in PP system whereas,
incorporation of MnO$_2$ seemed to augment the thermal stability of the composite. The PPM material showed a reduced degradation profile and better thermal stability. PPM material lost ~30 wt% when compared to 70 wt% loss in PP system. Thermal stability in PPM can be attributed to the presence of MnO$_2$ which acts as heat sink material creating a thermal resistance against heat transfer. Since both polymer and metal oxide exhibit different thermal conductivity, the thermal energy that is transferred from a localized site (in present case MnO$_2$) to a larger area (polymer matrix) does not distribute uniformly along the matrix. This thermal resistance causes a large temperature gradient between the matrix and the heat sink resulting in lower temperatures at the surrounding area. It is anticipated that such thermal gradient can increase the thermal

![BET analysis of PPM-10 and PP sponges](image)

Fig. 3.8. BET analysis of PPM-10 and PP sponges
3.3.5. THE ROLE OF MNO₂ ON THE ELECTROCHEMICAL PERFORMANCE OF THE PPM ELECTRODE

In order to determine the optimal wt % of MnO₂ in the composite for electrode applications, cyclic voltammetry (CV) tests at a scan rate of 10 mV s⁻¹ were performed using standard calomel electrode (SCE) and platinum as reference and counter electrode respectively in KOH electrolyte. The working electrodes comprised of PP, PPM-5, PPM-10 and PPM-20 electrode systems. Traditionally reports have shown that electrolytes like LiClO₄ are more suitable for PEDOT: PSS based supercapacitor system. But in the present study, PPM samples in KOH electrolyte showed better results (see Fig.3.10). This could be primarily attributed to the
presence of MnO$_2$ on the surface of PP and its electrochemical affinity towards KOH as shown in the previous chapter.

![Fig. 3.10. CV curves of PPM-10 in a) LiClO$_4$ and b) KOH electrolytes.](image)

It was found that for concentration $>1$ M the dissolution of the electrode in KOH was observed. At lower concentrations $<0.1$ M the current response obtained from CV studies were lower compare to 0.1 M KOH. On comparing the CV performance of stand alone MnO$_2$ and PP (Fig.3.11); the current response at a given potential of MnO$_2$ in KOH was found to be higher as compare to PP.

![Fig. 3.11. CV curves of a) PP and MnO$_2$ in 0.1 M KOH electrolyte.](image)

This is indicative of the fact that MnO$_2$ electrodes in KOH shows combined effects of high mass transfer rates and low depletion rate of the K$^+$ from the electrolyte in the diffusion layer as
compare to PP. Further the low hydrated radius of K$^+$ (0.25 nm) can have enhanced ionic mobility and better interaction with MnO$_2$ as compared to Li$^+$ (0. 42 nm) [125] resulting in better CV performance. However CV performance of PPM-20 was found to be lower as compare to PPM-10 samples which could be attributed to lower electrolyte percolation resulting from macropore deficits (see Fig.3.12 (a&b)). Unlike PPM-20, PPM-5 showed macropores but the reduction in capacitance in this case could be due to the absence of mesopores (see Fig.3.4). The best CV performance was observed for PPM-10 electrodes. Thus in order, to complement best of the electrical, electrochemical and mechanical properties of these porous structures, the further characterizations was performed on PPM-10 electrodes in 0.1M KOH.

![Fig.3.12. a) CV curves PPM-5, PPM-10 and PPM-20 electrodes at 10 mV s$^{-1}$ scan rate and b) plot showing the relation between specific capacitance and wt% of MnO$_2$ in PPM. SECM analysis showed that the current profile at the surface of PPM-10 did not alter much after the addition of MnO$_2$ (see Fig. 3.13(a&b)).](image-url)
Fig. 3.13. SECM spatial analysis of a) PPM and b) PP systems.

This meant that PP can act as an effective current collector in such hybrid electrode systems. That is the poor conductivity of MnO$_2$ did not affect the final conductivity of the PPM spongy samples. The analysis was carried out under constant height mode condition where changes in current as a function of distance between electrode tip and substrate surface was used to image the insulating and conducting surfaces for topology information by moving the tip across the surfaces and measuring tip current. The micro-probe comprises of a vacuum sealed platinum wire interacting with the KOH electrolyte using Ag/AgCl$_2$ as the reference electrode. The surface of horizontally placed substrate is immersed into the KOH electrolyte and scanned across the surface in the x-y plane which called as the spatial resolution and this depends on specification of the equipment. The maximum possible spatial resolution of the current device is 100 µm$^2$. The fluctuation in the current is due to the fact that device attempts to maintain a constant current by changing the substrate to tip distance, d, and recording the change in d. If the surface under consideration is smoother and dense then the fluctuation in the current is minimal as seen in PPM-10 samples.

The mass specific capacitance was calculated using the following equation:

$$C = \frac{1}{M \times \Delta V \times s} \int_{v_1}^{v_2} IdV$$

(1)

Where C is the mass specific capacitance (F g$^{-1}$), M is the mass of the active electrode, $\Delta V$ is the voltage window, s is the scan rate and I represent the current.

The Faradaic reactions occurring on the surface of both PP and MnO$_2$ are the major charge storage contributors resulting from the intercalation/de-intercalation process of K$^+$ at the electrode/KOH interfaces.

For different scan rates, it was observed that the specific capacitance value for these composites decreased from 1068 to 206 F g$^{-1}$, as the scan rate increased from 1 to 100 mV s$^{-1}$ (see Fig. 3.15). The specific capacitance value of PP system was found to be 772 to 97 F g$^{-1}$, as the scan rate increased from 1 to 100 mV s$^{-1}$ (see Fig. 3.16). The reason for this lower specific capacitance could be a) the less number of active sites on PP electrode as compared to PPM-10 electrode due to its comparatively lower surface area (see Fig. 3.8). This meant that the increased surface area
can indeed increase K\textsuperscript{+} intercalation/ deintercalation mechanism in the electrode, contributing more in the total capacitance of the composite electrode, b) the low reactivity of PP in KOH electrolyte as compared to PPM-10 samples (see Fig.3.11).

Fig.3.14. Typical CV pattern of PPM-10 at different scan rates.
3.3.6. CYCLING AND CONSTANT CURRENT DISCHARGE BEHAVIOR OF PPM-10 ELECTRODE

The cycling stability was determined using CV tests for both PPM-10 and PP electrodes for 1000 cycles at a scan rate of 100 mV s\(^{-1}\) (see Fig.3.16 (a)). Large capacitance fading (67\%) was observed in the case of PP electrode system at the end of 1000\(^{th}\) cycle (Fig.3.16(a)). But for PPM-10 electrodes there was no such capacitance fading observed even at the end of 1000\(^{th}\) cycle. The large fading could be attributed to the formation of C: PSS as shown in the scheme

\[
\text{PEDOT: PSS + M}^+ + e^- \leftrightarrow \text{PEDOT + M: PSS}
\]  

Where M\(^+\) denotes the positively charged ion and e\(^-\) represents the electron. Oxidation of PP films promotes expulsion of M\(^+\) towards the solution and film shrinking. The reduction promotes
insertion of $M^{+}$ from the solution; it leads the swelling of film. But in the case of PPM-10 system the more active sites are contributed by MnO$_2$ that was uniformly coated on the PP matrix.

These reactions can be shown as

$$\text{MnO}_2 + yM^{+} + \text{e}^- \leftrightarrow y\text{MnOOM}^+ + (1-y)\text{MnO}_2 + \text{e}^- \tag{3}$$

Here $y$ represents the total number of active sites present on the surface of the MnO$_2$ structure.

![Fig.3.16. a) Cycling stability studies of PPM-10 and PP samples at 100 mV s$^{-1}$ and b) discharge profile of PPM-10 electrode at different discharging currents.](image)

During redox reaction these mesoporous metal oxide film acts as active electrode layer and actively participate in the intercalation/ deintercalation mechanism. This protects the PP layer by reducing the swelling and shrinkage. Another reason for capacitance reduction in the case of PP electrode could be attributed to the dissolution of PP material into the electrolyte, due to the dimensional or structural variations within an electrode during the cycling [100]. The constant current discharge curves of lyophilized PPM-10 composite electrode at different discharge currents are shown in Fig.3.16 (b). From these discharge curves, the energy density, power density and capacitance values were derived. The capacitance values were obtained using the following equation:

$$C = \frac{I \times \Delta t}{M \times \Delta V} \tag{4}$$

Where $C$ is the specific capacitance, $I$ is the discharge current, $\Delta V$ is the potential window, $\Delta t$ is the discharge time, $m$ is the mass of the active material.
The energy and the power density was calculated using the following equations (3) and (4):

\[ P_{\text{max}} = \frac{V^2}{4R} \times \frac{1}{M} \]  

(5)

\[ E = \frac{1}{2} \frac{CV^2}{M} \]  

(6)

Where R=equivalent series resistance (ESR), V=maximum charged voltage (V), \( P_{\text{max}} \)=maximum specific power density (W kg\(^{-1}\)), E=energy density (Wh kg\(^{-1}\)), C=capacitance (F), M= mass of the active material (Kg) The value of ESR was calculated from the charge discharge curve. The capacitance reduction at higher discharging currents can be assigned to many factors like large voltage drop, pore resistance distribution and redox reactions on the electrode surface [103]. The non-linear behavior of the discharge curve indicates the redox nature of the material. This variation could be attributed to either of the following factors or its combinations i.e. a) change in the equivalent series resistance, b) the redistribution of charges within the pores of the material structure during the discharging cycles and c) pseudocapacitive behavior of the material [104-106]. The maximum energy density of \(~78\) Wh kg\(^{-1}\) at 5 mA and power density of \(~6\) kW kg\(^{-1}\) were achieved for the PPM-10 system using a three electrode setup (see Fig. 3.16 (b)).

3.3.7. IMPEDANCE STUDIES

Fig. 3.18 compares the Bode plots of MnO\(_2\) and PPM-10 electrodes tested in 0.1 M KOH to detect the solution resistance\( (R_s) \) and response time. On the whole, the Bode plots of both MnO\(_2\) sample and PPM-10 sample showed similar trends, but displayed slightly different values of \( R_s \) on the Y-axis. An \( R_s \) of \(~4.3\)Ω and 3.8 Ω was deduced for MnO\(_2\) and PPM-10 samples respectively, indicating that PPM-10 electrode with lower \( R_s \) had more affinity towards the electrochemical reaction on the electrode–electrolyte interface which is seen as an increase in the overall capacitance values. The response time of these samples were calculated from the phase curves and it was found to be 12.5 ms and 10 ms for MnO\(_2\) and PPM-10 systems respectively.
3.4. SUMMARY

In summary, the present study investigates the performance of PPM hierarchical spongy composite electrodes for supercapacitor electrode applications. The addition of MnO$_2$ to PP has shown to increase the surface area. This hybrid porous morphology shows advantages especially from points of better surface area and mass specific capacitance. The mean mass specific capacitance value was found to be 1068 F g$^{-1}$ from CV studies. These electrodes exhibited energy and power density values of 78 Wh kg$^{-1}$ and 6 kW kg$^{-1}$ respectively. The superior performance of these hierarchical spongy PPM-10 composite electrode as makes them promising systems for rechargeable energy units for battery applications.