Chapter 2

MORPHOLOGICAL EFFECT ON CYCLING STABILITY AND OVERALL PERFORMANCE OF MnO₂ BASED SUPERCAPACITOR

2.1. INTRODUCTION

High power density, energy density and durability are the three attributes which make an energy storage device (supercapacitor/battery/fuel-cell) a promising power source for any portable electronic device and automotive application [12, 75]. In order to maximize the performance of these devices, several approaches have been applied (e.g., modulating the pore sizes, introducing secondary phase in the form of metallic particles and conducting polymers, fabricating tandem hybrid-type cells, etc.) [76-79]. MnO₂ as cathode material for supercapacitors and batteries has been widely investigated because of its low-cost, abundance, non-toxicity and high theoretical specific capacitance of 1380 F/g [35-37]. However, its practical specific capacitance is low compared with the high-cost RuO₂. It is believed that the low energy density of MnO₂ is caused by its charge storage mechanism, which is based on ion adsorption or redox reactions on the surface layer [38, 39]. In a typical charge discharge process, only the first few nanometers from the surface can be utilized while no reactions occur in the bulk of active material, resulting in low utilization and limited energy densities [40, 41]. Therefore, improving the utilization of active material is the key to enhance energy and power density of the electrode material. Consequently, porous thin film electrodes which can facilitate electrolyte ions to react with active materials more efficiently, have attracted great interest [41-43]. Studies have shown that employing MnO₂ porous dip coated thin film coatings spread over an area can exhibit high specific capacitance of 698 F/g at a small loading of 1.05 μg/ cm² [36] with almost complete utilization of active material. Among the different types of electro active nanostructures, wire-based MnO₂ are of great potential since they can impart flexibility and structural stability when applied as thin film providing large surface area. Amongst the polymorphs, α-MnO₂ is widely used as electrode material in energy storage devices due to its larger pore size [80-82]. This property makes α-MnO₂ a desirable material for electrode fabrication in storage devices like supercapacitors/batteries.
2.2. EXPERIMENTAL

2.2.1. NANO-WIRE PREPARATION

The chemicals used in the present study were of analytical grade obtained from Sigma Aldrich. 0.1M MnSO$_4$ and 0.1M KMnO$_4$ were dissolved in 30 mL distilled water. To this 1mL of H$_2$SO$_4$ (60 % concentration) was added under vigorous stirring conditions for 30 mins. The prepared solution was transferred to a 100 mL Teflon-coated container and autoclaved at 150 °C for different time intervals ranging from 30 mins to 36 h. The resultant solution was centrifuged for 30 mins and the obtained precipitate was thoroughly washed using distilled water and dried at 60 °C for 4 h.

2.2.2. ELECTROPHORETIC DEPOSITION AND SURFACE CHARACTERIZATION

Morphology and phase analysis were performed using transmission electron microscopy-selective area energy dispersive X-ray (TEM, Model: JEOL, JEM-2100F) and X-ray diffraction analysis (XRD, X’Pert PRO Analytical) (KAUST, South Korea), respectively. Image J software was used to determine the diameter size distribution of the nanowires. The resultant nanowires and nanoparticles were electrophoretically [36] deposited onto a titanium substrate. Figure 2.1 shows the simple schematic representation of the electrophoretic deposition, where titanium (Ti) foil (1cm × 1cm × 0.2 mm) was used as substrate (cathode) and platinum wire as an anode. Isopropanol solution was used as the electrolytic solvent. To this electrolyte, 5 mg of MnO$_2$ nanowires/nanoparticle were dispersed uniformly under constant stirring. The pH of the prepared dispersion was found to be ~ 5.5. Since the pH value is above the point of zero charge (PZC ~4) of the MnO$_2$, it will be negatively charged which will ensure the deposition of the MnO$_2$ nanostructure onto the Ti substrate. The deposition was carried out at 40 V for 1 h at room temperature, resulting in a thin uniform porous layer of MnO$_2$ nanowires and a dense nanoparticulate film. The active weight of the material for the nanowire system was found to be ~1.1±0.3 mg/cm$^2$ and for nanoparticulate system was found to be ~1.5±0.5 mg/cm$^2$. This was used to normalize the capacitance data and was expressed as specific mass capacitance. The surface porosity was determined by quantitative image analysis (using GMDH software, Charlottesville, VA) from the SEM images Atomic force microscopy (AFM) (JEOL SPM 5200)
NIT Calicut) and Profilometer (Veeco Dektak 150) were used to measure the surface roughness and thickness of the deposited layer. Surface area measurements were obtained using BET analyzer (Nova Quantachrome, USA) (Sud Chemie, Kochi, India).

![Electrophoretic deposition diagram](image.png)

Fig. 2.1. Electrophoretic deposition

### 2.2.3. ELECTROCHEMICAL CHARACTERIZATION

Cyclic voltammetry (CV) and constant current charge-discharge were performed to evaluate the capacitance. Electrochemical impedance spectroscopy (EIS) (electrochemical workstation: Newport Model) was performed under a biased potential of 0.2V to measure the charge transfer resistance of the prepared electrode. For the above electrochemical studies, a three electrode setup consisting of electrophoretically deposited MnO$_2$ nanowires, platinum and calomel electrode were used as working, counter and reference electrode respectively. Different electrolytes comprising of KOH, Na$_2$SO$_4$ and LiClO$_4$ in different concentrations of 0.001-1M were used.
2.3. RESULTS AND DISCUSSION

2.3.1. PHASE AND MORPHOLOGICAL ANALYSIS

2.3.1.1 NANOWIRE

Fig. 2.2. (a-d) shows the TEM images displaying the morphology of hydrothermally synthesized MnO$_2$ at different processing times of 30 mins, 1h, 24 h and 36 h. It was observed that, as the processing time increases from 30 mins to 36 h the morphology changes from nanorods to nanowires.

![TEM images of MnO$_2$ nanowires](image)

The variation in the diameter and aspect ratio with respect to different processing times is shown in Fig 2.3. It was observed that at the end of 24 h there was not much variation in diameter and aspect ratio of MnO$_2$ nanowires. BET surface area of MnO$_2$ nanowires was found to be 44 m$^2$/g.
Fig. 2.3. Plot showing the variation in the aspect ratio and diameter at different processing times.

Fig. 2.4 shows the XRD pattern of the synthesized nanowires where the diffraction peaks corresponded to pure tetragonal phases of $\alpha$-MnO$_2$ (JCPDS 44-0141). From high-resolution (HR)-TEM images, (Fig. 2.5(a)) the inter-planar spacing was measured as $\sim$0.31 nm along the diameter, which is consistent with the (310) lattice spacing, respectively. This was confirmed by Fast Fourier Transform (FFT) analysis (Fig. 2.5(b)).

The possible formation of $\alpha$-MnO$_2$ nanowires can be shown from the following reaction:

$$3\text{MnSO}_4 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 2\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$$  (1)

This reaction could initiate the nucleation of $\alpha$-MnO$_2$ crystallites. The growth of $\alpha$-MnO$_2$ wires could be attributed to the relative specific surface energies linked with the different planes of $\alpha$-MnO$_2$ crystal that determines the growth direction. For a specific plane, the formation of
Fig. 2.4. XRD pattern of the synthesized nanowires.

A nanowire can be described by agglomeration of crystallites at a specific plane by molecular attractions thereby causing surface free energy minimization [83, 84]. For further characterization 24 h hydrothermally synthesized MnO$_2$ nanowires were used as electrode material. Fig. 2.6(a) shows the wire diameter size analysis for these nanowires, which showed a narrow skewed distribution. The diameter was found to be in the range of 5-40 nm centered at ~20 nm.
Fig. 2.5. a) HR-TEM showing inter-planar spacings along the growth direction and diameter and b) FFT analysis.

Fig. 2.6(b) reveals the SEM image of electrophoretically deposited layer of α-MnO₂ nanowires. It was observed that these wires were randomly oriented and exhibited a highly porous network-like structure. Image analysis of this layer revealed an average surface porosity of 75 ± 8 %. The image also shows particle-like morphologies after the deposition; this could be attributed to the aggregation of these nanowire tips after the annealing process, which may result in alignment distortion and lump formation. Furthermore, the used nanowires may also contain some short nanorods. These smaller particles move faster than the longer nanowires and easily form aggregates and deposited onto the Ti plate. Fig. 2.6(c&d) shows the cross-sectional SEM and AFM image of the MnO₂ nanowire on Ti foil showing a coating thickness of 60-80 µm and the mean roughness (Ra) of 350 ± 21 nm was obtained using surface profilometer. The active electrode surface area determined from AFM was found to 1.89 cm².
Fig. 2.6. a) The wire diameter size analysis and b) SEM image of eletrophoretically deposited layer of α-MnO₂ nanowires c) cross-sectional and d) AFM image of α-MnO₂ nanowires layer.

2.3.1.1 NANOPARTICLE

Fig. 2.7 (a) shows the TEM image of the commercially obtained nanoparticles. The diameter was found to be in the range of 15-30 nm. Fig. 2.7 (b) reveals the XRD pattern of the nanoparticle where the diffraction peaks corresponded to pure tetragonal phases of α-MnO₂ (JCPDS 44-0141). Fig. 2.7 (b) represents the SEM image of eletrophoretically deposited layer of α-MnO₂ nanoparticle. It was observed that these particles showed a dense surface. The mean surface roughness was found to be 110 ±16 nm using a surface profilometer. The similar diameter size and the XRD pattern of this nanoparticulate system gave us an ideal platform to compare the
electrochemical performance of this nanoparticulate system with the hydrothermally synthesized nanowire system.

Fig. 2.7. a) TEM image and b) XRD spectrum of commercially obtained MnO$_2$ nanoparticle and c) SEM image of electrophoretically deposited nanoparticle.

### 2.3.2. ELECTROCHEMICAL CHARACTERIZATION

In order to evaluate the electrochemical performance of these thin film electrodes in different electrolytes with varying concentrations; CV tests at a scan rate of 50 mV/s were performed using standard calomel electrode (SCE) and platinum, as reference and counter electrode respectively (see Fig. 2.8 (a-c)).

### 2.3.3. INFLUENCE OF DIFFERENT ELECTROLYTES
Several early works have shown that neutral electrolytes like Na₂SO₄ are more suitable for MnO₂ system when it comes to supercapacitors [85-87] while, MnO₂ in combination with KOH electrolyte has been widely employed for the alkaline battery application [86] In the present study, for a given concentration, the symmetrical redox patterns were quite prominent in KOH electrolyte (Fig. 2.8 (a)) but were strongly limited in Na₂SO₄ and LiClO₄ electrolytes (Fig. 2.8 (b&c)).

![CV curves recorded at 50 mV s⁻¹ for nanowire-based MnO₂ in different electrolytes](image-url)

Fig.2.8. CV curves recorded at 50 mV s⁻¹ for nanowire-based MnO₂ in different electrolytes a) KOH, b) Na₂SO₄ and c) LiClO₄.

The reasons for this could be mainly attributed to the low hydrated radius of K⁺ ions (0.25 nm) compare to Na⁺ (0.36 nm) and Li⁺ (0. 42 nm) ions [87] and the high basicity of the KOH electrolyte. The hydrated radius and the atomic radius of an ion are not the same, because the hydrated radius will not only depend on the ionic radius but also depend on the charge density of
the ions. That means for a smaller ion the charge will be concentrated in a smaller volume as compared to the larger ion, thus its charge density will be higher and hence it exerts stronger attractive forces on the opposite polar end of the water molecules, which causes the formation of a larger hydration shell. In the present study the Li$^+$ and Na$^+$ ions attract more water dipoles and forms a larger hydration shell resulting in larger hydrated radius than K$^+$ ions which has a larger atomic radius than Li$^+$ and Na$^+$ ions. So this smaller hydrated size of the K$^+$ ions facilitate intercalation and deintercalation of this K$^+$ ions through the 2×2 tunnel of α-MnO$_2$ which has an inner diameter ~0.38 nm [86, 87]. Also this lower hydrated radius of K$^+$ can enhance the ionic mobility and its interaction with the electrode, resulting in better electrochemical performance [88]. For a given electrolyte, as the concentration increased to 1M, peeling off of the thin film coating was observed. For low concentrations of 0.01M, the current values were found to be lower which could be mainly attributed to the lower concentration of ions participating in the redox reactions. Thus, further electrochemical studies were done using 0.1 M KOH electrolytes. Fig. 2.9 (a&b) shows the CV curves of the nanowire and nanoparticulate electrode at different scan rates. Fig. 2.9 (c&d) represents the capacitance Vs scan rate curve of nanowire and nanoparticulate system respectively. Here we have observed a decrease in capacitance as the scan rate increased from 1 to 50 mV/s for both the nanowire and nanoparticulate system. The reason for this could be attributed to the kinetically slow Faradaic reactions on the electrode surface. This results a decrease in capacitance at higher scan rates. For example, if a slow surface reaction is present in the electrode system then the faster scan will over before this slow reaction starts which results lower current and hence lower capacitance. In the case of slow scan rate the slow faradic reaction will get enough time to complete resulting in better current and hence capacitance. The ESR values also have an impact on this dependence of scan rate on capacitance that is an electrode surface which is having high ESR value will not respond to the voltage changes during a higher scan rate. In effect, the reaction kinetics and the electronic and ionic conductivity of the material will depend on the net capacitance of the electrode at different scan rates. Interestingly, for lower scan rates, a more prominent redox pattern was observed. Although, at these lower scan rates a slight asymmetry in redox pattern was observed indicating a battery like behavior, however unlike a battery, this system showed high cycling stability even at the end of 3000 cycles (see Fig. 2.11 (c)) which is typical to a supercapacitor behavior.
Fig. 2.9. CV curves recorded for a) nanowire-based MnO$_2$ and b) nanoparticulate MnO$_2$ at different scan rates and c&d) capacitance Vs scan rate curve of MnO$_2$ nanowire and nanoparticle respectively.

The redox peaks of MnO$_2$ nanowire electrodes (Fig. 2.10 (a)) in KOH can be attributed to the intercalation and de-intercalation of K$^+$ ions from the electrolyte into the pores of wire-based network.

### 2.3.4. ROLE OF SURFACE MORPHOLOGY ON ELECTROCHEMICAL AND STABILITY PERFORMANCE

For further understanding on the role of surface area, nanowire-based electrodes were compared with electrodes prepared using a commercially available MnO$_2$ powder (Nice Chemicals, India, particle size: ~ 50-80 nm). This powder was used for fabricating a nanoparticulate-based MnO$_2$
electrode by electrodepositing nanosized MnO\(_2\) particles under similar electrophoretic deposition conditions. However unlike MnO\(_2\) nanowires, these particles on electrophoretic deposition under similar conditions formed a relatively dense, aggregated layer of coating. The porosity of this layer was found to be 20 ± 5 \% with an average thickness value of 22 ± 6 μm, mean roughness (Ra) of 110 ± 16 nm and active surface area of 0.93 cm\(^2\). Capacitance fading was observed in nanoparticulate electrode at the end of 1000th cycle (Fig. 2.10(b)).

![CV curves](image)

**Fig.2.10.** CV curves recorded for a) nanowire MnO\(_2\) at 1\(^{st}\) and 3000\(^{th}\) cycle b) nanoparticulate MnO\(_2\) at 1\(^{st}\) and 1000\(^{th}\) cycle.

The mass specific capacitance was calculated using the following equation [89]:

\[
C = \frac{1}{M} \int I dV/(M \times \Delta V \times s) \tag{2}
\]

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 represents the current. It is quite known that the Faradaic reactions occurring on the surface of MnO\(_2\) are the major charge storage contributors resulting from the intercalation/de-intercalation process of K\(^+\) at the MnO\(_2\)/KOH interface [90-94] and can be shown as:

\[
\text{MnO}_2 + y \text{K}^+ + e^- \leftrightarrow y\text{MnOOK}^+ (1-y) \text{MnO}_2 + e^- \tag{3}
\]
Here \( y \) represents the total number of active sites present on the surface of the MnO\(_2\) structure. The above reaction shows that only a fraction of the active manganese sites are involved in the redox reaction (i.e., when \( y = 1 \); all the manganese sites have actively participated in the redox reaction). The value of \( y \) for both samples was calculated using the following equation [95].

\[
y = C \times M \times \Delta V / F
\]  

(4)

Where \( C \) is the mean mass specific capacitance (F g\(^{-1}\)), \( M \) is the molecular weight (86.9 g mol\(^{-1}\)), \( \Delta V \) is the potential window of the CV curve and \( F \) is the faradic constant (96500 C mol\(^{-1}\)). The specific capacitance value decreased from 1050 to 347 F g\(^{-1}\), as the scan rate increased from 1 to 50 mVs\(^{-1}\). For different scan rates, nanowire electrodes (\( y = 0.18 \) - 0.8) showed 2-3 times more active sites as compared to nanoparticulate electrode (\( y = 0.09 \) - 0.3). For nanoparticulate electrode, the specific capacitance values at 1 mV s\(^{-1}\) and 50 mV s\(^{-1}\) were found to be 513 and 126 F g\(^{-1}\) respectively. This meant that the increased surface area can indeed increase K\(^+\) adsorption/desorption reactions contributing an increase in the total capacitance of the nanowire electrode. The decrease in specific capacitance at faster scan rates can be attributed to the fact that the ions from the electrolyte can reach only at the electrode surface with limited entry into the deeper pores of the electrode overlay which is reflected as lower capacitance values. As mentioned earlier, the cycling stability was determined using CV tests which were performed for 3000 cycles (scan rate: 100 mVs\(^{-1}\)) and the area under the curve was used to determine the specific capacitance change for both nanowire and nanoparticulate electrodes as shown in Fig. 2.11 (c). Large capacitance fading was observed in the nanoparticulate system at the end of 1000th cycle. The redox peaks become more prominent (at higher current values) in nanowire-based electrodes, which mean that the increased surface area indeed increases K\(^+\) intercalation/de-intercalation reactions contributing to the overall capacitance [96]. For nanowire-based electrode at the end of 3000\(^{th}\) CV cycle, an increase in capacitance was observed. It has been shown that the porous microstructure is electrochemically favorable since it can provide substantially larger spatial clearance for electrode expansion and contraction during cycling [97]. Upon prolonged cycling, expansion and contraction of the electrode overlay opens new active sites within the porous structure which participates in the charge-transfer mechanism and increases the capacitance values. Similar phenomenon has been reported earlier in a
literature where MnO$_x$ nanostructures in the form of thin film nanoporous electrodes in combination with 1M Na$_2$SO$_4$ electrolyte have been used wherein the mass specific capacitance increased by 27% [98]. Similar trend has been also observed in case of vanadium oxide supercapacitor, wherein, an increase in capacitance over the first few thousands of cycles has been observed and after which they have got a stable performance [99, 100].

The reason for the increase in capacitance over the cycle number was attributed to the participation of increasing number of active sites due to better electrolyte electrode interaction after the prolonged cycling resulting from the morphological and crystal structural changes of the electrode surface which eventually changes the electron transport behavior. However, the exact mechanism behind this phenomenon is stated to be unclear [99]. However as mentioned earlier
for nanoparticulate electrode capacitance fading was observed, as the specific capacitance values at the end of 1000\textsuperscript{th} cycle was found to be \(\sim 40\%\) lower than the first cycle. Capacitance reduction and fading could be attributed to the dissolution of the oxide film into the electrolyte. Any dimensional or structural variations within an electrode during the cycling can play a significant role in determining the final stability. During the cyclic volumetric expansion/contraction, nanowire matrix tends to be stretched and relaxed, leading to submicronic tensile and compressive stresses on the entire electrode overlay. Since the nanowires are deposited in 3-dimensional stacked plane, the electrode overlay can distribute these microscopic stresses isotropically along the porous wire matrix. The bridging of these wires over each other could increase shear strength of the electrode structure, which in turn may help to prevent crack formation thereby preventing any peeling or delamination under cycling. It was observed that no such crack formation took place at the end of the 3000\textsuperscript{th} cycle (Fig. 2.11(a)). However, in case of particulate structure during the expansion/contraction phase of a cycle, the particles tend to oscillate relative to their original positions. Since the stress distribution in such particulate electrode matrix depends on the particle coordination number, the tendency for such electrode to gradually become fatigued or mostly likely to be de-bonded; as a result these particles lose electric contact between each other leading to cracks as seen in Fig. 2.11(b).

2.3.5. ROLE OF SURFACE MORPHOLOGY ON THE CHARGE TRANSFER RESISTANCE

Fig. 2.12 compares the Bode plots of MnO\textsubscript{2} nanowires and nanoparticulate electrodes tested in 0.1M KOH to detect solution resistance \((R_s)\) and response time \([100]\). On the whole, the bode plots of both MnO\textsubscript{2} electrodes in the electrolyte tends to show similar patterns, but displayed different values of \(R_{ct}\) and \(R_s\) values (Fig. 2.12) on the Y-axis. These values were used to obtain information on the solution resistance \((R_s)\) which provided an index of the electrode’s internal resistance in the electrolyte. An \(R_s\) of \(\sim 4.3\ \Omega\) \& \(\sim 5.4\ \Omega\) was deduced for nanowire and nanoparticulate electrode samples respectively, indicating that, nanowire electrodes 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 for the nanowire and nanopariculate system was found to be 12.5 ms and 18 ms.
The constant current discharge curves of porous MnO$_2$ nanowire thin film electrode and nanoparticulate electrode at different discharge currents are shown in Fig. 2.13 (a & b) using a 3 electrode setup. The charging was carried out using constant voltage. The fully charged system then kept for constant current discharge at different discharge currents. From these discharge curves, the energy and power density values were derived using the following equation:

\[
E = \frac{1}{2} \frac{CV^2}{m} \quad (5)
\]

\[
P = \frac{V^2}{4 \times ESR \times m} \quad (6)
\]

Where E is the energy density; P is the power density; C is the capacitance; V is the peak voltage; m is the mass of the active material; ESR is the solution resistance obtained from Bode plot. The IR drop indicates (Fig.2.13 inset) that the nanowire system showed better power performance than nanoparticulate system which validate the low ESR value of the nanowire system. The obtained energy and power density values are 31 Wh Kg$^{-1}$ and 4 KW Kg$^{-1}$ for nanoparticulate system and 71 Wh Kg$^{-1}$ and 6 KW kg$^{-1}$ for nanowire system. This increase in energy and power density values of nanowire system as compared to the nanoparticulate system is mainly because of the large number of active sites and low ESR value of nanowire system.
The decrease in energy density with increase in applied current from 5 mA to 20 mA is a commonly reported phenomenon for transition metal oxide systems [101, 102]. The fading of energy density value of both particulate and nanowire systems at higher current densities can be attributed to an amalgamation of multiple factors like large voltage (IR) drop, distributed pore resistance and severe redox reactions on the electrode surface [103].

Fig. 2.13. Discharge behaviour of a) MnO$_2$ nanoparticulate and b) nanowire at different discharge currents of 5 mA and 20 mA respectively using a 3 electrode system and inset shows the IR drop of both nanoparticulate and nanowire systems.

The non-linear characteristic of the discharge curve indicates redox behavior. This variation could be attributed to either of the following factors i.e. a) change in the direct equivalent series resistance, b) redistribution of charges within the pores of the material structure during the discharging cycles and c) pseudocapacitive behavior of the material [104-106].

However, the individual or the combined influence of the above mentioned factors affecting the electrode’s performance need to be investigated. The maximum energy density of ~71 Wh kg$^{-1}$ at and power density of ~6 kW kg$^{-1}$ was achieved at 5 mA discharge current. We believe that such a nanowire electrode system can be beneficial both in terms of energy and power density if used in combination with appropriate secondary phases.
2.3.7. SELF DISCHARGE BEHAVIOR OF THE NANOWIRE BASED CYLINDRICAL STORAGE UNIT

As a preliminary study, for the given concentration of KOH electrolyte, the application of these nanowires was explored in a fully functional cylindrical energy storage unit (Fig. 2.14(a)).

![Image of cylindrical energy storage unit made from thin film MnO₂ nanowire electrode and b) Self-discharge- behaviour of MnO₂ nanowires thin film electrode](image)

Fig. 2.14. a) Image of cylindrical energy storage unit made from thin film MnO₂ nanowire electrode and b) Self-discharge- behaviour of MnO₂ nanowires thin film electrode

Fig.2.14 (b) shows the self discharge behaviour from 1.8 V to 1.6 V the discharge at given period of ~28 h indicating low self discharge property.

2.4. SUMMARY

The present study investigates the performance of high aspect ratio MnO₂ nanowire-based electrodes for high performance rechargeable energy storage device. This nanowire morphology shows advantages especially from the point of reduced internal resistance. The introduction of this wire layer over titanium substrate helps in improving the redox reaction with the electrolyte and enhancing cycling performance. High surface area of these nanowires in the electrode system enhances the mass specific capacitance values to as high as 1050 F g⁻¹ and 750 F g⁻¹ recorded in CV tests and constant current discharge studies, respectively. The energy and power
density values of nanoparticulate (31 Wh/Kg and 4 KW/Kg) and nanowire system (71 Wh/Kg and 6 KW/Kg) have compared with other literature values. Additionally, a working model of an energy storage unit in cylindrical form was fabricated with a low self discharge behavioural trend. The efficiencies reported for these MnO₂ nanowire systems are promising because of their reduced cost and facile fabrication. At this juncture, it was realized that particle morphology not only plays an important role in improving the capacitance and cycling stability but also plays a critical role in reducing the solution resistance associated with the electrode surface. In order to further improve the power and energy performance of these electrodes’s it was mandatory to further reduce the internal resistance for which an appropriate current collector was sort. The attempt was to introduce an architecture where appropriate current collectors that participate in the redox reactions along with the MnO₂ powder can be made thereby improving the energy and power density of the system. The motivation was to introduce a porous composite scaffold where MnO₂ active material could be blended with stable conducting polymers like PEDOT-PSS to achieve this objective. The subsequent chapter introduces this approach and discusses its merits and de-merits.