Electrodeposited MnO_2-Carbon Cloth Supercapacitor Electrode Material for High Power Applications

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Abstract

Carbon cloth is a promising new material for the electrodes of supercapacitors, owing to their high surface area, flexibility, high conductivity with chemical stability. In this work, MnO_2 was electrodeposited on a commercially available post treated carbon cloth. The MnO_2 deposited carbon cloth was examined using HRSEM, which reveals the formation of nanosized irregular structure of MnO_2 over the carbon cloth. Electrochemical study was performed which revealed the specific capacitance of 483 Fg^{-1} at a scan rate of $10mVs^{-1}$. The fabricated device exhibited good electrochemical performance with energy density of $22WKg^{-1}$ at a power density $330KWKg^{-1}$. The results were convincing to use this material for high power applications.

Keywords: Supercapacitors; carbon cloth; high power applications; nanostructured electro-active materials; electrodeposition of MnO_2

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Introduction

Ease Smaller, slimmer and lighter is today's trend of electronics. Compaction of the energy storage device is highly recommended that is the size of the energy storage device must be smaller than the entire device. It also demands large energy density with low specific loss to maintain the energy requirement to run the device. Batteries are no longer compatible due to its number of issues/limitations. Supercapacitor emerges as a solution for this problem. It has many advantages such as fast recharge, large energy density, low manufacture cost, low per charge cost, longer life time, and eco- friendly, etc., [1,2]. In today's market, the most powerful supercapacitor has an ED (energy density) of 30wh/kg. Supercapacitors (double-layer capacitors or ultracapacitors) are electronic devices which are used to store extremely large amounts of electrical charge. It offers a promising alternative approach to meet the increasing power demands of energy storage systems. Supercapacitors rely on a physical charge storage mechanism by establishing an electrical double layer at the interface of the electrode and electrolyte.

Supercapacitors can be charged/discharged within seconds and can quickly respond to power fluctuations at the grid scale and provide high power for vehicle electrification. However, the energy density of supercapacitors is still too low. Integrating the new generation pseudo-capacitance materials with nanoscale hierarchical structures are obligatory to enable high energy density supercapacitors during high power operations. In electronic industries, the device used to store energy must also have a good power transform rate. But nature prohibits this, and they exhibit a mutually exclusive type principle that a good energy storage device has poor power transform rate. For example, batteries & fuel cells have good energy density but poor power density. Similarly, capacitance has good power transform rate with poor storage density. So far, the most effective available electrochemical energy conversion and storage devices are batteries, fuel cells, and electrochemical supercapacitors (ES).

In recent years, the electrochemical supercapacitors have gained attention due to its advantages including high-power density, long lifecycle etc., power- energy gap linking function for the traditional dielectric capacitors because of its high-power output and batteries /fuel cells for its high energy storage. Due to this, supercapacitors are encouraged for high power applications in future energy storage devices [3]. Recent years have yielded major progress in the theoretical and practical research and development of ES, as evinced by many research articles and technical reports [4–12]. At the same time, the disadvantages of supercapacitors—including low energy density and high production cost—have been identified as major challenges for the furtherance of technologies. Recently, great efforts have been made to increase the energy and power densities of micro-supercapacitors via the fabrication of nanostructured electro-active materials. MnO_2 honey-bee like structure over nanoporous gold have been developed with high specific capacitance [13]. Herein we develop a simple, cost-effective MnO_2 electrodeposition over carbon cloth as electrode material for supercapacitor and studied its electrochemical performance.

Materials and Methods

All chemicals used were of analytical grade, purchased from Sigma-Aldrich, India. Carbon cloth was purchased from sainergy fuel cell India, pvt limited. The electrodeposition was carried out to deposit MnO_2 over the carbon cloth, using the standard three electrode electrochemical workstation. Here, Ag/AgCl (saturated KCl) reference electrode and platinum wire counter electrode was used for the electro deposition process. 0.1 M Na_2SO_4 and 0.1 M manganese acetate were dissolved in the 100ml distilled water, to prepare the electrolyte solution. Carbon cloth electrode was immersed in ethanol for one hour. After this process, the carbon cloth electrode was washed thoroughly with deionized distilled water and used as a working electrode for the electrochemical deposition process.

Pre-treated carbon cloth electrode has been immersed in the mixture of 0.1 M Na_2SO_4 and 0.1 M manganese acetate solution. Here, the electrochemical deposition of MnO_2 over the pre-treated carbon cloth electrode has been performed with the cyclic voltammetry (CV) technique. The potential window for the CV analysis has been fixed from -0.3 to 0.5 V with varying scan rates from 10 to 60 mV/s. Electrochemical impedance spectroscopy (EIS) measurement was carried out with an AC perturbation of 0.5V over the frequency range from 0.01Hz to 100 kHz. The morphology of MnO_2 deposited carbon cloth was analysed using HR Scanning Electron Microscope (HRSEM) at 20 kV. Electrochemical characterizations were performed using CHI 600 series Electrochemical Analyzer/Workstation.

Results and Discussion

The image of the MnO_2 deposited carbon cloth is presented in the Figure 1 (carbon cloth initially grey in color later changed to black after deposition). The growth mechanism of MnO_2 over carbon cloth was shown in the Figure 2. The mixture of Na_2SO_4 and $(CH_3COO)_2$ $Mn.4H_2O$ was used as electrolyte for the electro deposition process. Here, the function of Na_2SO_4 is to enhance the mobility of the Mn^{2+} ions towards the carbon cloth working electrode. At suitable voltage, the Mn^{2+} ions forms $Mn(OH)_2$ and oxidizes to MnO_2. The electro deposition was the result of the below mentioned chemical reactions. At first, water electrolysis occurred at the carbon cloth electrode surface generating OH^- ions. This generated OH^- ions bonds with Mn^{2+} ions causing the deposition of MnO_2 over the electrode surface.

Fig. 1. Photo image of MnO_2 deposition over carbon cloth. Black color shows the deposition MnO_2 over grey color carbon cloth.

$$Mn(CH_3COO)_2 \Longrightarrow Mn^{2+} + (CH_3COO)^-$$
$$2H_2O + 2e^- \Longrightarrow H_2 + 2OH^-$$
$$Mn^{2+} + 2OH^- \Longrightarrow Mn(OH)_2$$
$$2\,Mn(OH)_2 \Longrightarrow 2MnO_2 + 2H_2O$$

Figure 3a,b show the typical HRSEM of MnO_2 deposited carbon cloth electrode. We can see that the carbon cloths are densely packed but randomly oriented to form a macroscopically open structure. This kind of open structure can offer better accessibility to the electrolyte. Furthermore, the carbon cloth of high conductivity can also be used as flexible electrodes. The electro deposited MnO_2 was clearly seen in 4 µm resolution. It shows the electro deposited MnO_2 over the individual fiber in carbon cloth. MnO_2 are grown the carbon cloth quite uniformly forming Mesoporous structure. As it can be seen from the image, MnO_2 are irregular and have size varied from 100 to 300 nm and lengths in the range 0.5 to 2 µm. Thus, this type of mesoporous MnO_2 structure over carbon cloth forms an ideal structure with high surface area for ion absorption facilitating the electrochemical performance.

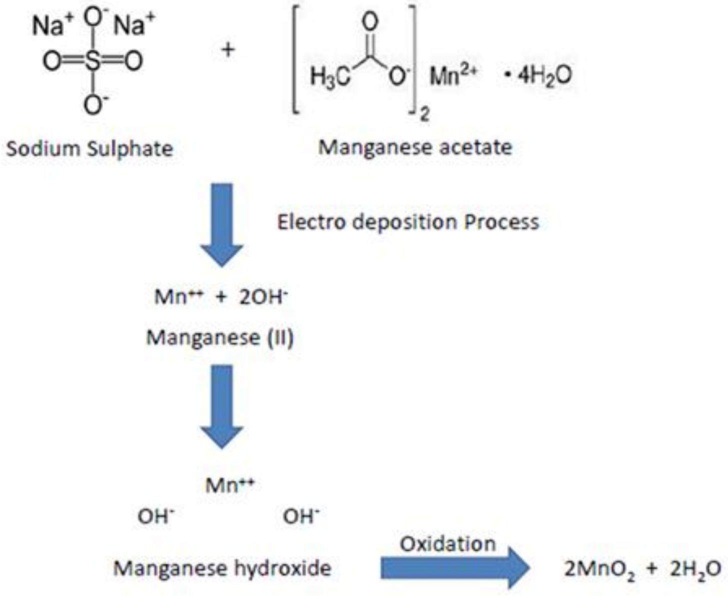

Fig. 2. Reaction mechanism for electrodeposition of MnO_2 over the carbon cloth electrode.

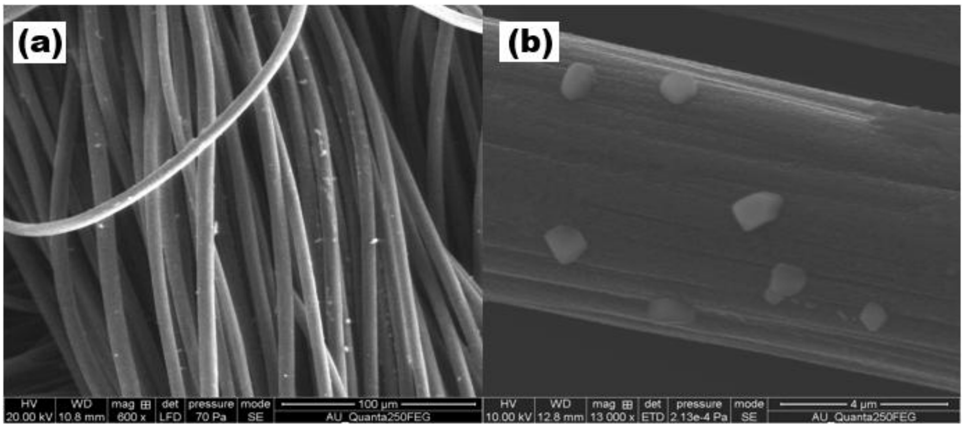

Fig. 3. HRSEM image of electrodeposited MnO_2 over carbon cloth.

To evaluate the power capability of our electrode, cyclic voltammetry (CV) experiments were performed at scan rates ranging from $10 mVs^{-1}$ to $60 mVs^{-1}$. Figure 4 shows the CV performance for the electrode at different scan rates. This electrode exhibited an exceptionally enhanced electrochemical performance with asymmetric curve pattern of charge/discharge behavior. The potential window was from –0.3 to +0.5 V. From the CV plot, the electrode while forward scan, remain in the steady value of current and reaches maximum while discharging. I_{max} was found to be 2.218 mA at voltage 0.2 V. Beyond this voltage, current decreases linearly up to maximum potential window 0.5V. In the reverse scan, it exhibits similar pattern during discharging and charging. This behavior of symmetric in charging and discharging cycles helps to use it in high power applications. The capacitance values were calculated from CV data according to the following equation,

$$C_{device} = \frac{1}{v(V_f - V_i)} \int_{Vi}^{Vf} I(V)dV$$

where v is the scan rate, V_f and V_i are integrated potential limits of voltammetry curve and I(V) is the voltammetry discharge current. Specific capacitance of the electrode is calculated by the relation,

$$C = \frac{C_{device}}{m}$$

where m is the active mass of the electrode material. We obtained a specific capacitance value of 483 Fg^{-1} at a scan rate 10 mVs^{-1}. The variation of specific capacitance for different scan rates were presented in the Figure 5. It reveals that constant value of specific capacitance at higher scan rates, which is the potential significance of the supercapacitor materials.

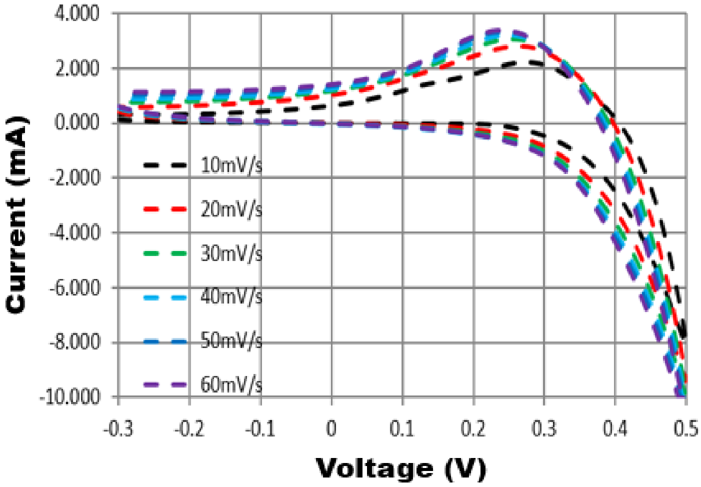

Fig. 4. CV curves at different scan rates for MnO_2 deposited carbon cloth.

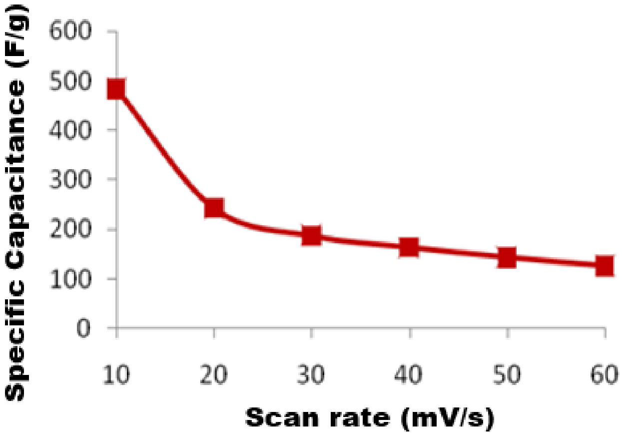

Fig. 5. Variation of specific capacitance with different scan rates.

The Ragone plot in Figure 6 shows high power-energy characteristics of MnO_2 electrodeposited carbon cloth. The high-power density of 330$KWKg^{-1}$ and the maximum energy density of 22WKg^{-1} were achieved and much higher than other carbon-based electrodes [14–17]. An electrochemical impedance test was carried out at the frequency of 0.1MHz to further evaluate the electrochemical behavior of the MnO_2 electrodeposited carbon cloth electrode. As shown in the Nyquist plot in the Figure 7, the almost straight line parallel to imaginary axis shows the ideal capacitor behavior of our electrode. The intercept of Nyquist curve on real axis is only 2.91Ω, indicating the good conductivity of the electrode with very low internal resistance. The knee frequency of the supercapacitor is about 6.9 Hz, showing that pure capacitive behavior can be obtained and most of its energy stored is accessible below this frequency [18].

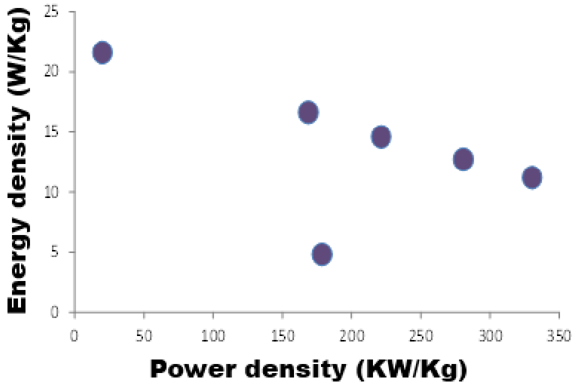

Fig. 6. Ragone plot for MnO_2 electrodeposited carbon cloth.

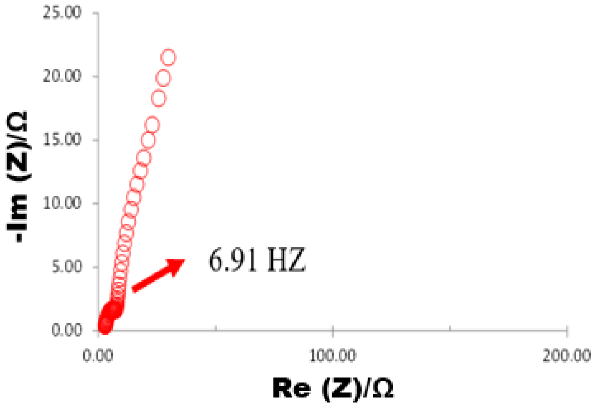

Fig.7. Nyquist plot for MnO_2 electrodeposited carbon cloth with knee frequency labelled in the plot.

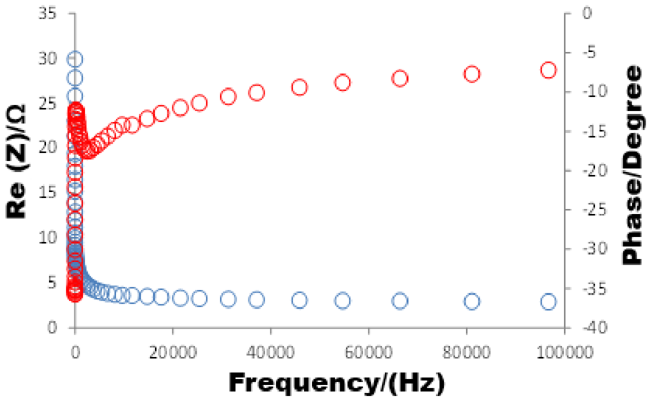

Fig. 8. Bode plot for our electrode showing the frequency response of impedance and phase.

Figure 8 displays the Bode plot of our electrode. The capacitive response frequency at the phase angle –37° is about 6 Hz and is comparable to the values for super capacitors with other electrolytes. The phase angle of the supercapacitor was about 35° at the frequency of 1 Hz, which is about 40% of ideal supercapacitor.

Conclusions

Supercapacitor based on a MnO_2 electrodeposition over carbon cloth is fabricated using a simple cost-effective method. The device exhibited good electrochemical performance with an energy density of $22WKg^{-1}$ at a power density of $330KWKg^{-1}$. Hence, the electrodeposited MnO_2 over carbon cloth exposed the possibility of developing the new generation energy storage devices in the field of energy management for flexible and lightweight electronic applications.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

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