Effect of Redox Additive Electrolyte on the Electrochemical Performance of MnO_2 Nanorods for Supercapacitor Application

S. Arunpandiyan, C. Selvameenakshi, S. Ezhil Arasi, P. Devendran, A. Arivarasan

Abstract*: Pure MnO_2 nanorods were synthesized by hydrothermal method and characterized by different techniques to analyze their crystalline nature, surface morphology, functional groups, and optical properties. XRD analysis confirms that the prepared nanorods possess a tetragonal crystalline structure. The occurrence of nanorods was confirmed by SEM analysis and its elemental composition was studied by elemental mapping. MnO_2 nanorods modified working electrode was fabricated by the deposition of prepared nanorods on nickel foil. Electrochemical performance of the MnO_2 nanorods modified working electrode was studied using redox additive based electrolyte containing 0.1M $K_4[Fe(CN)_6]$ in 1M KOH solution. The maximum specific capacitance of the prepared nanorods in 1M KOH electrolyte was 89 Fg^{-1} and it is greatly enhanced by the addition of 0.1M $K_4[Fe(CN)_6]$ redox additives (634 Fg^{-1}).

Keywords*: MnO_2 nanorods, Supercapacitor, Redox-additive electrolyte.

I. INTRODUCTION

The supercapacitor is one of the energy storage devices with high specific power, faster charge-discharge rate, long life cycle with wide operating temperature [1]. Supercapacitors are widely used in some hybrid vehicles, electronic devices, trains, smartphones, etc. The efficiency of the supercapacitors are based on the electrode material and electrolyte. Generally, carbon-based materials, metal oxides, and some conducting polymers are used in a supercapacitor electrode. In recent trends, metal oxide based pseudocapacitive materials is attracted much more attention because of their superior capacitive behavior.

Commonly pseudocapacitor electrodes are made up of metal oxides such as NiO [2], RuO_2 [3], Co_3O_4 [4], MnO_2 [5], TiO_2 [6], CeO_2 [7] etc. Among the various transition metal oxides, manganese oxide has gained great deal of attention as a pseudocapacitor electrode material due to its superior supercapacitor performance, low-cost and environmental compatibility [8]. Normally, one-dimensional nanorod possess high surface area than other types of nanomaterials and it is a key component to achieve high specific capacitance. Recently, redox additive based electrolytes are used to improve the performance of supercapacitor electrode materials by enhancing faradaic redox reactions inside the electrolyte. From previous reports, the addition of 0.1M $K_4[Fe(CN)_6]$ to the usual KOH electrolyte will enhance the specific capacitance tremendously [9].

In this present study, we have synthesized 1-D MnO_2 nanorods with the high surface area through a one-step hydrothermal method. Prepared nanorods were analytically characterized to confirm its crystalline structure and its surface morphology. MnO_2 nanorods modified working electrode was fabricated using nickel foil and its electrochemical performance was studied by using 0.1M $K_4[Fe(CN)_6]$ redox additive based electrolyte.

II. MATERIALS AND METHODS

A. Precursors

All the precursors were purchased in analytical grade and used without further purification. Manganese sulphate monohydrate ($MnSO_4.H_2O$) and potassium permanganate ($KMnO_4$) were used as starting materials for the synthesis of MnO_2 nanorods and procured from SRL chemicals, India. Potassium hydroxide (KOH) and potassium ferrocyanide ($K_4[Fe(CN)_6]$) was purchased from Reachem chemicals, India and used for electrolyte preparation.

B. Preparation of MnO_2 Nanorods

MnO_2 nanorods were prepared by the simple hydrothermal method under ambient atmosphere. In a typical synthesis, 0.05 M of $MnSO_4.H_2O$ solution was prepared in 120 ml of D.I water. One gram of $KMnO_4$ was added to the above solution and stirred for 30 mins. Then it was transferred to a 150 ml Teflon lined autoclave and reacted for 24 h at 160 °C. The resultant solution was filtered and extensively washed using D.I water, ethanol and air dried at 80 °C for overnight.

Then the crystallinity of the prepared sample was improved by the calcination process at 300

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°C for 3 h.

C. Material Characterization

The prepared samples were characterized by X-Ray diffractometer (BRUKER-D8 Advance Eco XRCD) systems with SSD 160 1D Detector for structural confirmation. Surface morphology was analyzed by Scanning Electron Microscope (EVO18 CARL ZEISS). Functional groups present in the prepared sample were analyzed by Fourier Transform Infrared Spectrophotometer (IR Tracer 100) by applying the frequency from 400 to 4000 cm^{-1}. The optical absorption of the prepared MnO_2 nanorods was studied by UV-Vis spectrophotometer (Shimadzu UV-1800) in the wavelength range of 190-800 nm.

D. Electrode Preparation and Evaluation

The calcinated sample was well ground and mixed with activated carbon (for enhancing the conductivity) in 85:15 weight ratio. Then, one drop of Nafion solution (binder) was added to the above mixture to make slurry. The obtained slurry was pasted on the Ni-foil (1 cm^2) and dried at 80 °C for overnight. The total active mass pasted on to the substrate is about 1 mg/cm^2. The electrochemical performances of the prepared modified working electrode were evaluated by electrochemical workstation in the three-electrode system (CH instrument CHI6008e, USA). For this purpose, platinum wire and Ag/AgCl is used as the counter and reference electrodes respectively. The electrochemical analysis was carried out in two different electrolytes, such as bare KOH and redox additive based electrolyte. First, 1M KOH electrolyte solution was used as the bare KOH electrolyte. Then, 0.1M $K_4(Fe[CN]_6)$ redox additive was added in 1M KOH solution, to prepare redox additive based electrolyte. The potential window for electrochemical measurements was optimized and fixed as 0 to 0.6 V and Cyclic Voltammetry (CV) measurements were performed at different scanning rate, such as 5, 10, 15, 25, 50, 75 and 100 mVs^{-1}. Galvanostatic Charge Discharge (GCD) was performed at varied current densities to study the charge storage capacity of the electrode. Electrochemical Impedance Spectroscopy (EIS) techniques were performed to analyze the ionic movement between the electrodes through the electrolyte. The EIS measurements were carried out in the frequency range between 1Hz to 100 KHz.

III. RESULTS AND DISCUSSION

A. Powder X-Ray Diffraction (XRD) Analysis

The powder X-ray diffraction (XRD) pattern of calcinated MnO_2 nanorods was as shown in Fig. 1. The diffraction peaks were observed at the diffraction angles (2θ) of 12.78, 18.10, 28.84, 37.52, 39.01, 41.96, 49.86, 56.37, 60.27, 65.10, 69.71, 72.71° corresponding to the crystalline planes of (110), (200), (310), (211), (330), (301), (411), (600), (521), (002), (541), (312) respectively. The observed were indexed to tetragonal α-MnO_2 in bulk form (JCPDS No. 44-0141) with lattice constants a = b = 9.785 Å, c = 2.863 Å. Sharp diffraction peaks with high intensity reveal that the prepared MnO_2 nanorods were well crystallized in the corresponding lattice plane. Absence of other impurity peaks confirms that the prepared MnO_2 nanorods possess high purity in nature.

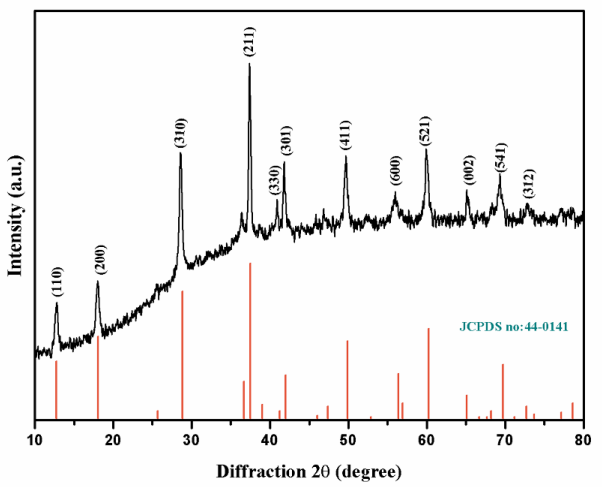

Fig. 1.XRD pattern of MnO_2 nanorods.

B. Scanning Electron Microscope (SEM) Analysis

The surface morphology of the MnO_2 nanorods was examined by SEM analysis. Fig. 2 (a, b), shows the SEM images of MnO_2 nanorods at different magnification. The images showed that the obtained products have rod like morphology. The EDAX spectrum as shown in Fig. 2 (c), shows the presence of only Mn, O elements, which confirms that there were no impurities were present in the sample. The mapping of Mn and O elements were shown in Fig. 2(e, f). The overall mapping (Fig. 2(d)) reveals that more than 40% oxygen was present on the surface of the MnO_2 nanorods.

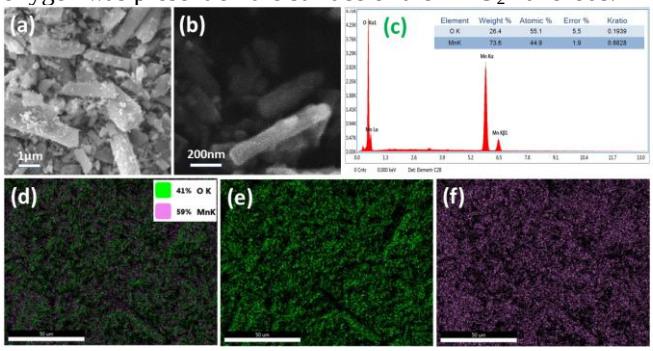

Fig. 2.(a, b) SEM images of MnO_2 nanorods at different magnifications, (c) EDAX spectrum, (d) overall mapping and (e, f) mapping of O, Mn.

C. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis was performed to study the presence of functional groups and metal-oxygen vibrations of the prepared nanorods. The FTIR spectrum of the prepared MnO_2 nanorods was shown in Fig. 3. The peaks appeared at 523, 574 cm^{-1} were attributed to the Mn-O stretch vibrations. And the peak appeared at 666 cm^{-1} is due to the C-OH stretch vibration. All the peaks were appeared at low-frequency region (below 1000 cm^{-1}) due to the presence of metal-oxygen stretching vibrations. It reveals the presence of pure metal oxides in the prepared sample.

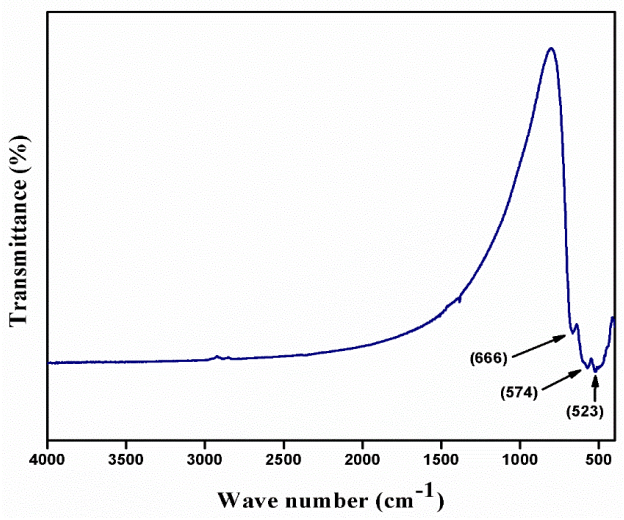

Fig. 3.FTIR spectrum of MnO_2 nanorods.

D. UV-Vis Analysis

The optical absorption of the prepared sample was studied by UV-Vis absorption spectrometer. Fig. 4 show the absorption spectrum of MnO_2 nanorods. UV-Vis absorption spectrum was recorded in absorption mode and it can be clearly seen that there is a broad absorption peak observed in the visible region. The spectrum illustrates that the sharp peak occurred at ~ 305 nm was attributed to the quantum confinement effect and broad absorption peak observed at ~ 450 nm related to the absorption behavior of MnO_2 nanorods. The bandgap energy was calculated by tauc plot using (1) as shown at the inset of Fig. 4.

$$E = hc/\lambda \ (eV) \qquad (1)$$

where h is Planck's constant (6.626×10^{-34}Js), c is the velocity of light (3×108 ms^{-1}), λ is the wavelength corresponding to the sharp absorbance. The average band gap energy calculated was about 2.36 eV.

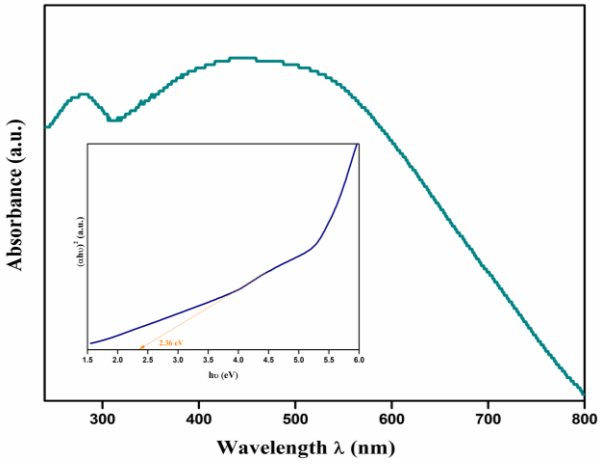

Fig. 4.UV-Vis absorption spectrum of MnO_2 nanorods.

E. Cyclic voltammetry

The cyclic voltammetry was performed using two different electrolytes (1M KOH and 1M KOH with 0.1M $K_4(Fe[CN]_6)$) and the corresponding voltammograms were shown in Fig. 5 (a,c). A pair of redox peaks was observed in the CV curve corresponding to the oxidation and reduction of manganese oxide. Similar kinds of CV curves were observed in both the electrolytes. But the integral area of the curve was increased in redox additive based electrolyte. It reveals that the prepared MnO_2 nanorods show better electrochemical performances in redox additive based electrolyte. Galvanostatic charge-discharge curve for MnO_2 nanorods in KOH and redox additive electrolyte were shown in Fig. 5 (b,d). In pure KOH electrolyte MnO_2 nanorods showed a potential drop at the staring stage of discharging. This is due to the self-discharging of electrolyte and this potential drop gets expanded in terms of redox additive based electrolyte. It reveals that the self-discharge of electrolyte gets increased by the addition of redox additive. The specific capacitance achieved for each electrolyte at various scan rate was calculated and the relation between the specific capacitance and scan in different electrolytes were displayed in Fig. 6. The maximum specific capacitance achieved for MnO_2 nanorods modified working electrode in redox additive based electrolyte was about 634 Fg^{-1}.

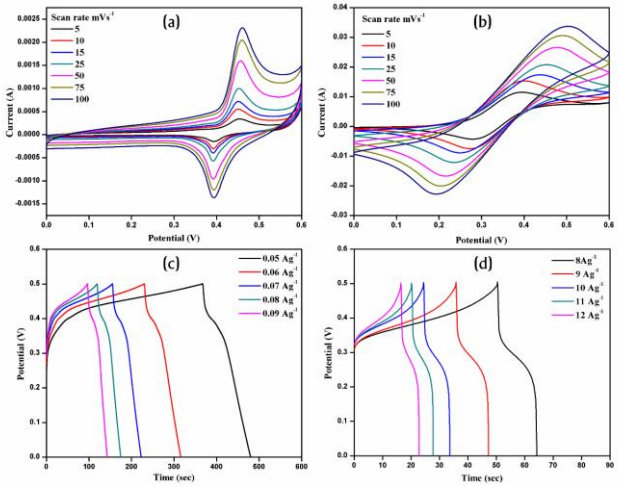

Fig. 5.(a,c) Cyclic voltammogram and Galvanostatic charge discharge of MnO_2 nanorods in 1M KOH, (b,d) Cyclic voltammogram and Galvanostatic charge discharge of MnO_2 nanorods in redox additive electrolyte.

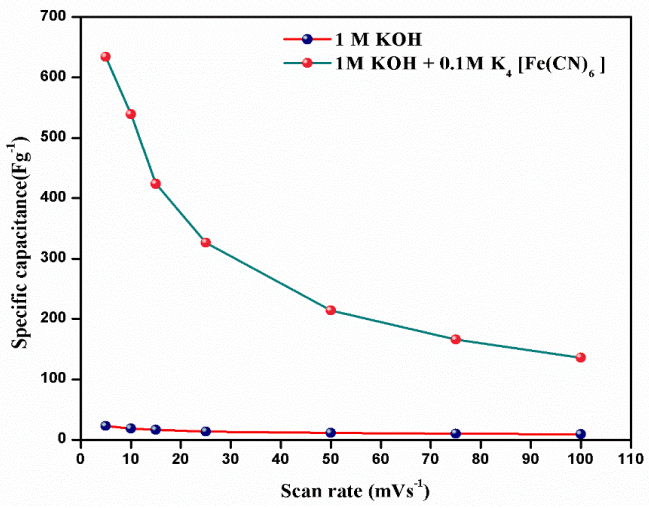

Fig. 6.Specific capacitance at various scan rates in different electrolytes.

F. Electrochemical Impedance Spectroscopy

The impedance spectrum of MnO_2 modified working electrode in bare KOH and redox additive electrolyte were displayed in Fig. 7. In both the electrolytes, a small semicircle was observed in high-frequency region due to the combinational effect of capacitance and resistance. In bare KOH electrolyte, a straight line was observed at lower frequency region due to the effect of Warburg resistance. But in redox additive based electrolyte, the straight line in low-frequency region was transformed into a small semi-circle like curve, which shows the parallel combination of capacitor and resistor behavior. It confirms that the addition of redox additive into 1M KOH electrolyte increases the resistivity of the electrode through electrode-electrolyte interactions.

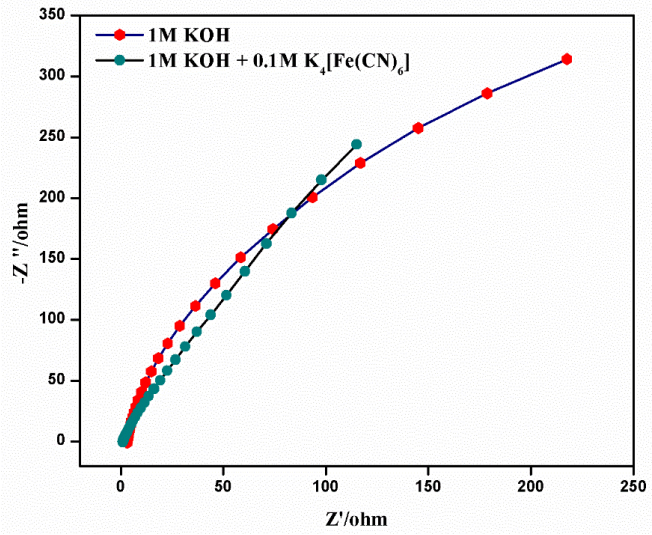

Fig. 7.Electrochemical Impedance Spectrum of MnO_2 nanorods modified working electrode.

IV. CONCLUSION

Pure MnO_2 nanorods were successfully synthesized using one-step hydrothermal method. Tetragonal structure of the prepared MnO_2 nanorods was confirmed by the XRD analysis and the appearance of nanorods was confirmed by the SEM analysis. MnO_2 nanorods modified working electrode was fabricated by using nickel foil and their electrochemical performances were studied. MnO_2 nanorods modified working electrode showed better electrochemical performances compared with bare KOH electrolyte. The specific capacitance values of the fabricated working electrode were increased by adding 0.1M $K_4(Fe[CN]_6)$ into the 1M KOH electrolyte. By enhancing redox reactions between electrodes and electrolyte, the supercapacitor performances were comparatively increased. The prepared MnO_2 nanorods show superior electrochemical performances under redox additive based electrolytes. So, it can act as a potential candidate for supercapacitor electrodes.

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