Conducting Polymer based Manganese Dioxide Nanocomposite as Supercapacitor

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Abstrct:

Polyaniline (PANI) and Poly 3, 4-ethylenedioxythiophene (PEDOT)-based MnO_2 conducting nanocomposites were synthesized and their electrochemical properties were studied in order to find out their suitability as electrode materials for supercapacitor., Structural morphology and characterization of the nanocomposite with nanorods of δ-MnO_2 (having~20 nm diameter) materials were studied using XRD, XPS and TEM. Electrochemical measurements of these electrode materials have been carried out using cyclic voltammetry and galvanostatic charge–discharge at different constant current densities (0.5–10mA/cm^2). Contribution of pseudocapacitance (CFS) in the composite materials has also been investigated through the measurement of AC impedance in the frequency range 10 kHz–10 mHz with potential amplitude of 5 mV.

1. Introduction

In recent years it is well known that Electrochemical Capacitor (EC) or supercapacitor is one of the very good candidates to provide high power and long cycle life, essential for new energy devices such as hybrid electric vehicles, and uninterrupted power supplies [1]. Therefore, finding new electrode materials for supercapacitor to meet the requirements of high power density and long durability devices is extremely important as energy storage device. Depending on the charge storage mechanism, electrochemical capacitors are categorized as Electrochemical Double Layer Capacitors (EDLC) and pseudocapacitors. The origin of capacitance in the EDLC is the charge separation at the electrode-electrolyte interface, whereas pseudocapacitance arises from fast, reversible faradic redox reactions taking place on or near the surface of the electrode.

Electronically Conducting Polymers (ECPs) have advantage as an electrode material for supercapacitor, as they have both electrochemical double layer capacitance and pseudocapacitance arising mainly due to the fast and reversible oxidation and reduction processes related to the π- conjugated polymer chain [2-3]. Among various conducting polymers, poly 3, 4-ethylene dioxythiophene (PEDOT) has recently attracted interest due to its environmental stability and controllable electrical conductivity. Polyaniline is also very interesting and well studied conducting polymer. However, PEDOT like other ECPs also suffers a serious problem of typical volumetric swelling and shrinkage during the

insertion and ejection of counter ions [4-8]. In order to solve this problem, nanocomposite comprising of PEDOT or Polyaniline and inorganic transition metal oxide nanoparticles acting as filler, has been considered as the electrode materials for supercapacitor where a synergistic effect of composite formation plays a significant role to increase the capacitance value. Moreover, transition metal oxides have generally been reported to be suitable as electrode material for pseudocapacitors because of their large capacitance and fast redox kinetics [9].

Manganese dioxide (MnO_2) is one of the promising candidates as an electrode material for supercapacitor due to its low cost, natural abundance, environmental friendliness having very high specific capacitance value. But, intrinsically poor electronic conductivity of the manganese dioxide limits its practical capacitance value to a very low level. Conducting polymer based MnO_2 nanocomposites have been investigated to increase its conductivity and hence supercapacitive properties.

In the present work, the electrochemical performances of nanorods based PEDOT- MnO_2 and Polyaniline-MnO_2 nanocomposite as electrode for supercapacitor using 1M $LiClO_4$ in acetonitrile solution was investigated and compared them for the first time. Structural morphology and characterization were carried out by XRD, and TEM studies. The electrochemical performances of the supercapacitors were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge cycling and electrochemical impedance spectroscopy (EIS) studies.

2. Experimental:

2.1. Synthesis of materials

2.1.1 Synthesis of δ- MnO_2

Nanorods of δ- MnO_2 were synthesized by redox reaction between stoichiometric quantities of $MnSO_4$ and $KMnO_4$ in aqueous medium. In a typical synthesis in aqueous medium, 10 mL of 0.2 M $KMnO_4$ solution was mixed with 10 mL of 0.15 M $MnSO_4$ solution and stirred continuously for 6 h. A dark-brown precipitate thus formed and was washed several times with Milipore water, centrifuged, and then dried at 70°C in vacuum drier for 12 h. [10]

2.1.2 Synthesis of PEDOT and PEDOT–δ-MnO_2 nanocomposite in n-Hexane medium

A reverse microemulsion was first prepared by dissolving 19.12 mM sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in 70 ml of n-hexane. 10 mM $FeCl_3$ in 1.0 mL distilled water was added to it and the mixture was gently stirred for 5 min. Previously distilled 3.52 mM EDOT monomer was added to the reaction mixture followed by slow addition of 100mg δ- MnO_2 and kept for 3 hour under gentle magnetic stirring. The blue-black precipitate of PEDOT- δ-MnO2 was filtered and washed with methanol followed by acetonitrile. Composite was dried under vacuum for 12 hour at 60°C. Pure PEDOT polymer in n-hexane medium was synthesized applying similar procedure in absence of any metal oxide nanoparticles [11,12]

2.1.3. Synthesis of Polyaniline and Polyaniline –δ-MnO_2 nanocomposite in aqueous medium

The PANI-MnO_2 nanocomposite was chemically synthesized by oxidative polymerization of aniline using ammonium peroxydisulfate [$(NH_4)_2S_2O_8$)] under controlled conditions. Ammonium peroxydisulfate (APS) (0.025M) was dissolved in 200mL of 1M HCl solution, and the solution was pre-cooled to 4°C. Later, 1ml Aniline was slowly added to the APS in 1M HCl solution. Further, 100mg of δ-MnO_2 was added to the solution and the reaction was continued for 12h[13]. The dark precipitate of the PANI-MnO_2 nanocomposites recovered from the reaction vessel was filtered, and washed using deionized water, methanol, acetone, and diethyl ether for the elimination of the low molecular weight polymer and oligomers. Further, this precipitate was heated at 100°C in a temperature-controlled oven.

2.2. Sample Characterization

Phase identification and morphological characterizations of MnO_2 was carried using powdered X-Ray Diffractrometer (Philips PW 1710) with Cu Kα (λ = 1.5406 Å) radiation and Transmission Electron Microscope (FEI model Tecnei G2 20S with 200 kV accelerating voltage and resolution of 0.2 nm). XPS core-level spectra were taken with an Omicron Multiprobe (Omicron NanoTechnology GmbH., UK) spectrometer fitted with an EA125 hemispherical analyzer. A monochromated Al Kα X-ray source operated at 150W was used for the experiments. The analyzer pass energy was kept fixed at 40 eV for all the scans.

2.3. Electrochemical measurements

Electrodes for supercapacitor were prepared using following procedure**:** 85 wt % electroactive materials (i.e pure PEDOT, Polyaniline and its composite containing 20% δ-MnO_2 nanoparticles**)** were mixed with 10wt % acetylene black (AB) and 5wt% polytetrafluoroethylene (PTFE) to form a thick paste. The paste was then pressed into a thin sheet of ~ 100 μm thickness using mortar & pastel. Finally, the sheet was compressed on a stainless steel mesh having the surface area around of 1 cm^2. The prepared electrodes were dried at 60^0C for 6 hour under vacuum. The total weight of the active material in the electrode is usually ~ 5mg.

Electrochemical behavior of the samples through cyclic voltametry (CV) measurement was investigated with AUTOLAB-30 potentiostat/galvanostat. A platinum electrode and a saturated Ag/AgCl electrode were used as counter and the reference electrodes respectively. Cyclic voltammograms were recorded between -0.6 to 0.6 V with respect to reference electrode at a different scan rate (5mV/s to 50 mV/s). Galvanostatic charge-discharge cycling and electrochemical impedance studies both were performed with two-electrode system having identical electrodes made of same active electrode materials (i.e Type-I symmetry supercapacitor). Constant current density ranging from 0.5 to10 mA/cm^2 have been employed for charging/discharging the cell in the voltage range 0 to 1 V. The discharge capacitance (C) is estimated from the slope (dv/dt) of the linear portion of the discharge curve using the expression.

$$C = \frac{I}{(dv/dt)} \qquad (1)$$

$$C_s = \frac{2C}{m} \qquad (2)$$

where m is the active mass of the single electrode Cs represents specific capacitance.

Electrochemical impedance spectra (EIS) were taken at open circuit potential (OCP) over the frequency range 10 kHz to 10 mHz with a potential amplitude of 5mV. All the electrochemical experiments (i.e CV, Charge-discharge, EIS) were carried out in an electrolyte containing 1M $LiClO_4$ in acetonitrile.

3. Result and Discussion

3.1. X-ray Diffraction, TEM studies

X-ray diffraction patterns of MnO_2 nanoparticles. In this figure, all the characteristic peaks (including the hundred percent intensity peak at $2\theta = 38^0$) of single-phase spinel structure of MnO_2 were observed.

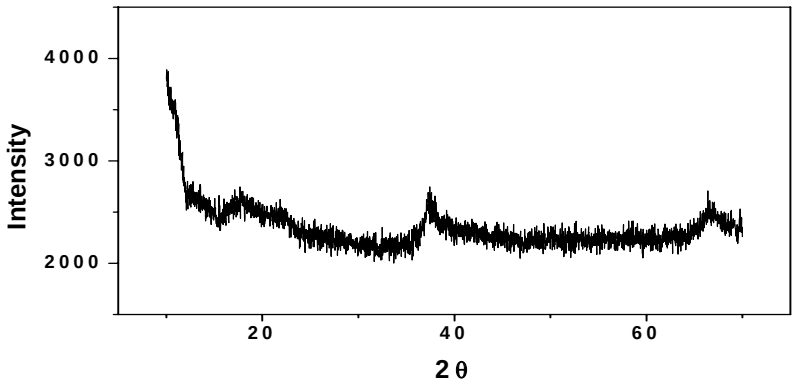

Figure.1 XRD picture of δ-MnO_2

The TEM picture (Fig.2) of manganese dioxide nanorods suggests that they are in crystalline state having clear lattice fringe. The diameter of the rods is in the range of 10-20 nm. The structural morphology of Polyaniline-MnO_2 composite synthesized in aqueous medium (Fig.2b) shows no signature of formation of any mesoporous/microporous structure.

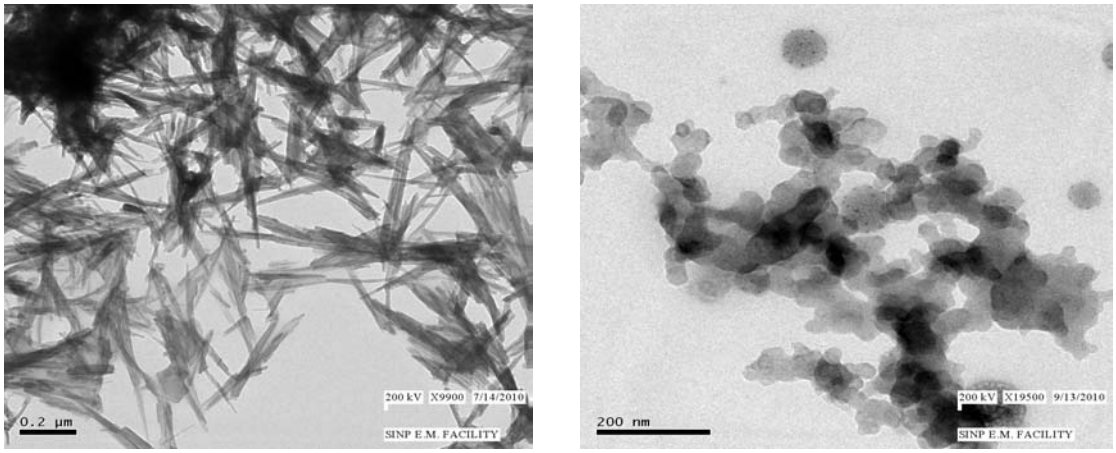

Figure 2. TEM images of MnO_2 and Polyaniline MnO_2 nanocomposites

3.2 XPS analysis of the CP and its nanocomposites:

In order to have a precise knowledge about different oxidation states of Mn in the nanocomposite samples, essential for assessing the overall contribution towards their pseudocapacitance, X-ray Photoelectron Spectroscopy studies were carried out.

In Fig 3(a), 3(b) and 3(c) the Mn 2p $_{3/2}$ XPS data for PANI-MnO_2 and PEDOT-MnO_2 samples are shown respectively. The fitting of the data shows there are two chemical environments in both the materials. The lower energy peak at 641.3 eV for PANI-MnO_2 sample and 640.8 eV for PEDOT-MnO_2 sample corresponds to Mn in 2+ valance state. Whereas the higher energy peak at 642.9 eV for PANI-MnO_2 sample and 642.4 eV for PEDOT-MnO_2 sample corresponds to Mn in 4+ valance state.

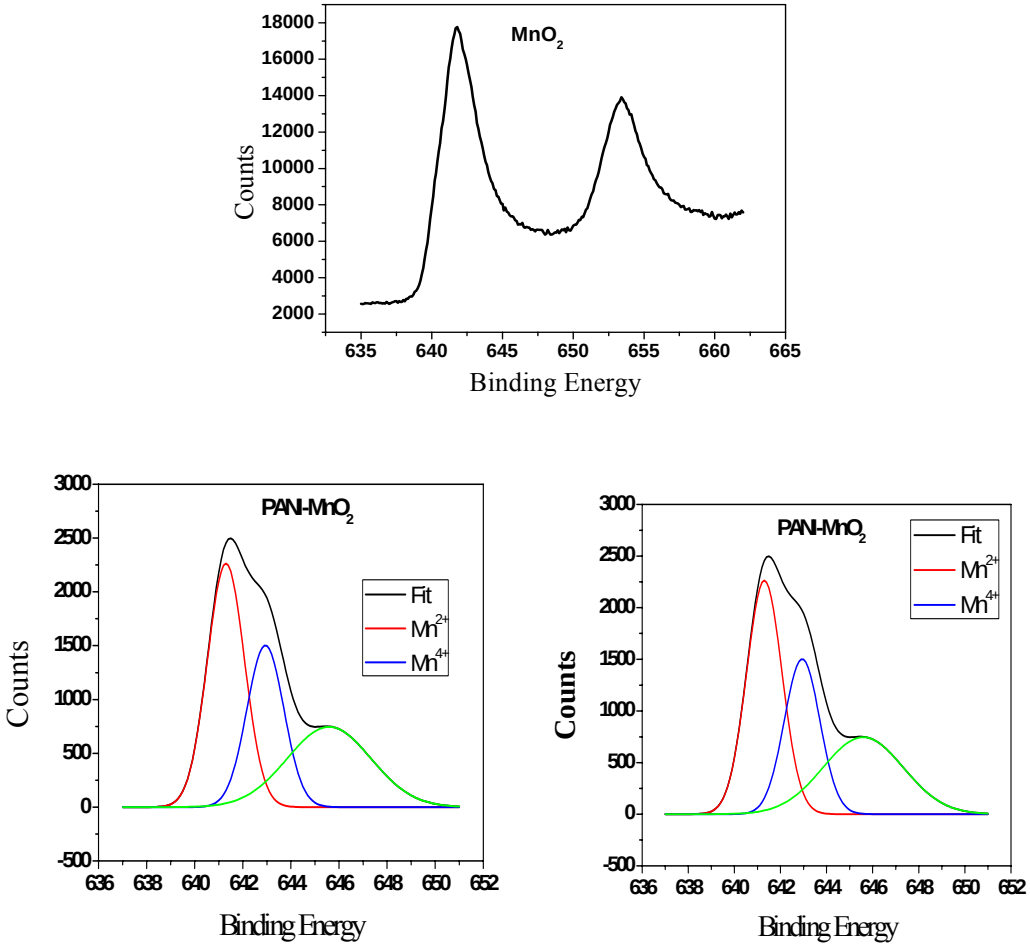

Figure.3. XPS data for pure MnO_2,PEDOT- MnO_2 and Polyaniline- $MnO_2$is shown. The position of the 2p $_{3/2}$ peak at 641.8 ev indicates the material to be MnO_2

3.3 Electrochemical Characterization:

CV, EIS and Charge-discharge

In order to determine the capacitance values of conducting polymer-MnO_2 nanocomposites and pure polymers, CV, charge-discharge studies and impedance spectroscopy were carried out.

For typical cyclic voltammograms (CV) a scan rate of 2mV/s between 0 to 1V in acetonitrile containing 1M $LiClO_4$ electrolyte, were used. Cyclic voltammograms of different samples are nearly semi rectangular in shape, which indicates the good capacitative behaviour of the electrodes suitable for charging and discharging at a constant rate over the voltage range of 0 to 1 V.

The applicability of the supercapacitor has been directly evaluated by means of galvanostatic charge-discharge studies. Specific capacitances of different electrode materials were compared at a constant current density of $\pm$ 1mA/cm^2.

Electrochemical impedance spectroscopy is a powerful technique for investigating the capacitative behaviour of electrochemical cells. Typical Nyquist impedance spectra of conducting polymer and its composites over a frequency range of 10 kHz to 10 mHz with a potential amplitude of 5mV are carried out. The impedance spectra shows a single semicircle in the high frequency region and nearly vertical line in the low frequency region, which indicates that the electrode process is controlled by electrochemical reaction at high frequencies and by mass-transfer at low frequencies.

Details of the results of capacitance determination for different samples will be shown at the presentation during the conference. It was found that PEDOT-MnO_2 nanocomposite has the highest value of specific capacitance (~250 F/g) among the different samples. Partial change in oxidation state of Manganese in MnO_2 from four to two (observed in the XPS data) during composite formation is suggested to be one of the reasons for possessing high capacitance value in the nanocomposite.

4. Conclusion

Sol-gel method has been adopted for the preparation of MnO_2 nanorods having diameter in the range of 10-20nm. TEM images of PANI-MnO_2 nanocomposite synthesized in aqueous medium reveals the formation of polyaniline over the surface of MnO_2 nanoparticles, PEDOT-MnO_2 nanocomposite exhibits highest specific capacitance value (~251F/g**),** where introduction of MnO_2 having lower value of specific capacitance is playing a role of synergystic agent. The small decrease in specific capacitance value over 500 cycles compared to first cycle suggests PEDOT-MnO_2 nanocomposite as a promising candidate for future development of safe and cost effective electrochemical supercapacitors.

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