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Abstract

The various molar concentrations of cobalt doped manganese dioxide (Co-MnO₂) nanostructures were synthesized by an hydrothermal technique for electrochemical supercapacitor application. The X-ray diffraction analysis showed that the samples were composed of multiphase of MnO₂ with dominant reflections of γ -MnO₂ structure of crystallization. The morphological studies displayed the existence of MnO₂ nanowires with the width of 10-20 nm and showing a good degree of crystallization. The electrochemical characterization was performed using cyclic voltammetry, galvanostatic charge/discharge test and impedance spectroscopy in 1 M Na₂SO₄ aqueous electrolyte. All the samples exhibit a typical ideal capacitive behavior with an increasing order of specific capacitance values with respect to the increase in the concentration of cobalt ions up to a certain limit. The specific capacitance of 415 F g⁻¹ was delivered by 5% Co-MnO₂ sample at 0.2 A g⁻¹ which was nearly double that of bare MnO₂ electrode of 231 F g⁻¹. Moreover, the Co-MnO₂ electrode shows an excellent capacitance retention (97.3%) after 5000 charge and discharge cycles.

Keywords

electrochemical, properties, enhanced, nanowires, cobalt, dioxide, manganese, doped

Disciplines

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Enhanced electrochemical properties of cobalt doped manganese dioxide nanowires

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Abstract

The various molar concentrations of cobalt doped manganese dioxide (Co-MnO₂) nanostructures were synthesized by an hydrothermal technique for electrochemical supercapacitor application. The X-ray diffraction analysis showed that the samples were composed of multiphase of MnO₂ with dominant reflections of γ -MnO₂ structure of crystallization. The morphological studies displayed the existence of MnO₂ nanowires with the width of 10-20 nm and showing a good degree of crystallization. The electrochemical characterization was performed using cyclic voltammetry, galvanostatic charge/discharge test and impedance spectroscopy in 1M Na₂SO₄ aqueous electrolyte. All the samples exhibit a typical ideal capacitive behavior with an increasing order of specific capacitance values with respect to the increase in the concentration of cobalt ions up to a certain limit. The specific capacitance of 415 Fg⁻¹ was delivered by 5% Co-MnO₂ sample at 0.2 Ag⁻¹ which was nearly double that of bare MnO₂ electrode of 231 Fg⁻¹. Moreover,

the Co-MnO₂ electrode shows an excellent capacitance retention (97.3%) after 5000 charge and discharge cycles.

Keywords: Electrode materials; Energy storage materials; Nanostructured materials; Electrochemical impedance spectroscopy; Oxide materials

1. Introduction

Supercapacitors (SCs) are excellent power sources for electronic devices and automotive application due to their high power density, better energy density and durability[1]. Based on the charge storage mechanism, the SCs have been classified into two categories; one as electrochemical double layer capacitors (EDLCs) that use double-layer capacitance arising from the separation of charge at the interface between the solid electrode/electrolyte, and the other as pseudocapacitors which utilize fast faradaic redox reactions that occur near the electrode surface or takes place inside the bulk of the materials [2, 3]. In recent years the pseudocapacitance materials like metal oxides, sulfides, hydrides and conducting polymers received considerable attention in energy storage applications [4-10]. The large specific capacitances and high energy density of these materials can meet the demand of high power and energy density in modern devices than that of carbon based electric double-layer capacitors. The metal oxides such as RuO₂, NiO, Co₃O₄, MnO₂ etc., have been considered as better candidates for pseudocapacitance electrode materials[11-14]. Among these MnO₂ is of particular interest due to its low cost, low toxicity, high theoretical capacitance, and excellent capacitive performance in aqueous electrolytes, which adds more potential towards supercapacitor electrodes [15-17]. The charge storage mechanism of MnO₂ is based on fast faradaic redox reactions either that occur near the

electrode surface or takes place inside the bulk of the materials over an appropriate range of potentials [18-20]. In order to achieve high capacitive performance, a large surface area and a fast ion/electron transport by the electrode material are required.

Generally, MnO_2 was the most studied material due to its promising electrochemical properties; but its specific capacitance values are still far below the theoretical value. The poor electronic conductivity and limited surface area are responsible for low specific capacitance values in MnO_2 based SCs [21, 22]. Several attempts have been made to improve the capacitive performance of MnO_2 by the addition of conductive additives like carbon nanotubes, polymers, graphene and other composites to enhance the electron transport properties to attain a reasonable capacitance value [23-27]. Moreover, various transition metal oxides such as Ni, Pb, Mo and V oxides [28-31] that have been incorporated with MnO_2 show considerable improvement in the specific capacitance and overall performance of the SCs. Cobalt oxide is another excellent material for supercapacitor electrode, whereby addition of cobalt ions to MnO_2 shows a reasonable improvement in pseudocapacitive performances [32, 33]. Pramod [34] et. al., reported the doping of Co ions into the layered alkali MnO_2 that showed a considerable improvement in the conductivity of the electrodes, and following this work a series of reports have been published on Co- MnO_2 showing it to be a promising supercapacitor electrode material[35, 36].

Apart from the conductivity and transport properties, the specific capacitance mainly depends upon the surface area of the materials. Various morphological structures of MnO_2 including nanorods, nanowires, nanosheets, nanoflakes, and nanoflowers[37-40] have been synthesized and effectively studied for their electrochemical performance. Mostly an hydrothermal method was adopted for the synthesis of the above mentioned MnO_2 nanostructures. In general, the hydrothermal technique is a simple and effective green synthesis

technique to fabricate nanomaterials with different morphologies by optimizing the reaction temperature, time, pH and the active fill level or solvent used in the reaction. Large surface area nanostructures can be effectively synthesized on a large scale using this simple solution based hydrothermal technique [41, 42]. In this work we report the hydrothermal synthesis of Co-MnO₂ nanocomposites for electrochemical supercapacitor. Cobalt of various molar percentage (1, 2, 5, 10 %) were incorporated in MnO₂ and their electrochemical properties were studied extensively using cyclic voltammetry, galvanostatic charge/discharge tests and electrochemical impedance spectroscopy. Furthermore, the structural and morphology of synthesized nanoparticles were characterized by XRD, SEM, TEM, EDAX, and their surface area and pore size distributions were analyzed using a nitrogen physisorption technique.

2. Experimental Methods

2.1 Synthesis of Co doped MnO₂ nanomaterial

Manganese(II) sulfate pentahydrate (MnSO₄ · 5H₂O), Cobalt (II) sulfate heptahydrate (CoSO₄ · 7H₂O) and Potassium persulfate (K₂S₂O₈) were used as precursors for the hydrothermal synthesis of MnO₂ and Co-MnO₂ nanocomposites. The process was begun by dissolving MnSO₄ · 5H₂O (5 mM), K₂S₂O₈ (5 mM) and required mol percentage of CoSO₄ · 7H₂O (0, 1, 2, 5, 10 mol%) into 75 mL of double distilled water under vigorous stirring at room temperature until the formation of an homogeneous solution. Finally, the mixture was transferred into a 100 mL Teflon-lined stainless autoclave and maintained at 160 °C for 3 h in a hot air oven. Then the autoclave was cooled naturally to room temperature. The obtained precipitate was washed several times in double-distilled water by repeated centrifugation and ultrasonication. Finally, the product was dried in oven at 80 °C for 12 h and used for further characterization.

2.2 Characterization

The crystalline structure of the synthesized samples were identified by using GBC MMA XRD (Australia) with Cu K α radiation ($\lambda=1.540598\text{\AA}$) operated at 30 kV and 20 mA in the 2θ range 20° - 80° . Morphologies were characterized by field emission scanning electron microscope (JEOL-7500FA field emission SEM (Japan)). Transmission electron microscopy (TEM) images and EDS measurements were performed using a JEOL (Japan) model JEM-2100F at an accelerating voltage of 200 kV. The nitrogen absorption/desorption measurement was carried out using a Quantachrome surface analyzer at 77.35°C employing the volumetric method. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) technique. The pore size distribution was estimated from the desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method.

2.3 Electrode fabrication and electrochemical measurements

The bare and Co-MnO₂ electrodes were fabricated by mixing the active materials (70 wt%), acetylene black (20 wt%) and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP). The obtained paste was coated over a stainless steel substrate of exposed geometric area 1 cm^2 and dried at 100°C for 12 h in a vacuum oven. The mass of the active material present in the electrodes was determined to be $\sim 0.6\text{ mg}$. Electrochemical studies such as cyclic voltammetry, galvanostatic charge/discharge and impedance measurements were performed at room temperature ($\sim 20^\circ\text{C}$) using ZIVE - SP2 (Korea) electrochemical workstation in a three electrode arrangement, including a working electrode of bare or Co-MnO₂ electrodes, a platinum sheet counter electrode and a Ag/AgCl reference electrode in 1M Na₂SO₄ aqueous

electrolyte. The electrochemical impedance spectra (EIS) of the electrodes were measured in the frequency range of 0.01 Hz - 100 kHz at an equilibrium open circuit potential 0 V with an AC perturbation of 5 mV in 1M Na₂SO₄ electrolyte.

3. Results and Discussion

3.1 Structural analysis

Fig. 1 shows the XRD patterns of the bare MnO₂ and 1, 2, 5, 10 mol% of Co-MnO₂ samples. All the samples show the same trend of diffraction pattern with multiple crystalline phases with a dominant diffractions of γ type MnO₂ phase. The corresponding strong peaks of each sample can be indexed as the orthorhombic phase of γ -MnO₂ (JCPDS 44-0140). Moreover, the broad diffraction peaks at $\sim 18^\circ$ and 50° correspond to the peaks of tetragonal phase of α -MnO₂ (JCPDS 44-0140). The formation of this type of α , γ -MnO₂ mixed phase has been reported by Hill et. al.[43]. Apart from this, a few more diffraction peaks were observed nearly at 28.5, 37 and 65 which can be clearly identified as the K-birnessite type of layer structured MnO₂ phase (JCPDS 80-1098). Rapid hydrothermal growth of MnO₂ using the same combination of MnSO₄. 5H₂O and K₂S₂O₈ [39] at the same reaction temperature shows formation of pure K-birnessite phase of MnO₂. But in our case the mixed phase of MnO₂ nanostructure was formed by the same mixture and reaction temperature. This phase transformation might be due to long duration hydrothermal reaction than the reported reaction time (30 min); since a duration dependent hydrothermal reaction can easily affect the MnO₂ phase of crystallization or transfer to other phases as reported by Wang and Li [44]. Even though no additional peaks related to the Co oxide

phase appeared, in the Co-MnO₂ sample the intensity of peak at 18° shows improvement with respect to the increase in concentration of Co doping; especially higher for 10% Co-MnO₂ sample. This might be due to the presence for Co(OH)₂, since the peak corresponds to the (001) diffraction of Co(OH)₂; similar to that observed in bare Co sample prepared by this same route.

3.2 Morphological and surface area analysis

Fig. 2 a, b and c, d show the different magnification SEM images of bare and 5% Co-MnO₂ samples. From these images, both the samples show the morphology of agglomerated microsphere with diameter ranges from 1 to 3 μm. At a high magnification, it can be observed that the MnO₂ microspheres are composed of a large number of tiny nanowires in the order of a few nanometers. The TEM images (Fig. 3 a, b, c and d) further reveal that each MnO₂ microspheres is made up of MnO₂ nanowires with diameter ranging from 5 to 20 nm and a length of about a few micrometers. The high resolution TEM image (Fig. 3 b) of MnO₂ nanowires shows clear lattice fringes of the nanowires thus confirming the well crystalline nature of the nanowires. The TEM image of the 5% Co-MnO₂ sample has some agglomeration of short nanorods with the nanowires, which might be due to the presence of some impurity phase due to cobalt ions. In addition, the HRTEM image (Fig. 3 d) shows high crystallinity of the short nanorods over the surface of MnO₂ nanowires. The EDS analysis of the samples shown in Fig. 4 a and b clearly indicates the composition and the incorporation of Co ions in MnO₂ nanostructure. Additionally a small amount of the K⁺ is present in both the samples. Based on the XRD results, the presence of K ions can be concluded to be due to the existence of K-birnessite type of MnO₂ structure in the synthesized samples.

The specific surface area and pore size distribution of the MnO₂ and 5% Co-MnO₂ nanocomposite were obtained from an analysis of the desorption branch of N₂ gas isotherms method. Fig. 5 shows that the isotherms are typical for a slightly mesoporous material with a small hysteresis loop at high partial pressures. The BET surface area and corresponding pore volume of the samples were calculated to be 42.25 m² g⁻¹ and 0.258 m³ g⁻¹ for bare MnO₂, and 44.96 m² g⁻¹ and 0.295 m³ g⁻¹ for 5% Co-MnO₂ sample respectively. As shown by BJH analysis (inset in Fig. 5), both the samples have a narrow pore size distribution of around 3.7 nm. From this analysis, no considerable change in the surface area and pore size of MnO₂ samples due to the presence of cobalt ions is observed. The slight enhancement in the surface area of the Co-MnO₂ sample may be due to the influence of the impurities observed in the TEM images.

3.3 Cyclic voltammetry studies

The cyclic voltammograms (CV) of the MnO₂ and Co-MnO₂ electrodes measured in 1M Na₂SO₄ electrolyte at scan rates of 10 mVs⁻¹ are shown in Fig. 6. From the CV curves all the electrodes shows typical rectangular shapes, revealing the surface Faradaic reaction of the synthesized samples; that is, the surface electrosorption of Na⁺ cations and the fast reversible successive surface redox reactions of the electrode by means of interaction/extraction processes of the proton according to Equation (3.1) [3, 45] :

Moreover, no characteristic redox peaks were observed in all electrodes; indicating that the electrode is charged and discharged at a pseudo-constant rate over the complete voltammetric cycle. The specific capacitances (C_{sp} , Fg⁻¹) were calculated from the CV curve according to Eq. (3.2):

$$C_{sp} = \frac{\int i dV}{m \times s \times \Delta V} \quad (3.2)$$

where, m is the mass of active material on electrodes (g), s is the potential scan rate (mVs^{-1}), i is the voltammetric current (A), and ΔV is the potential window of CV curve. The estimated specific capacitance of the bare and 1, 2, 5, 10 mol% of Co-MnO₂ at the scan rate of 10 mVs^{-1} are 143, 180, 206, 302 and 234 Fg^{-1} respectively. The obtained values and the improved background current of the CV curves confirm the positive influence of Co ions in the supercapacitive performance of the MnO₂ nanostructure. The 5% Co-MnO₂ electrode exhibits the maximum specific capacitance value which is double that of the bare MnO₂ electrode. But 10 % Co-MnO₂ shows a decline in the capacitance value which reveals that Co ions doping have a positive effect up to a certain limit within the MnO₂ nanocomposite. Moreover the bare MnO₂ electrode exhibits higher specific capacitance value than that of γ -MnO₂ of nearly the same surface area and morphology [3, 46]. This might be attributed to the existence of other two highly electrochemical active systems of MnO₂ like K-birnessite and α -MnO₂ in the samples. Although these materials having low surface area, they can exhibit relatively high specific capacitances owing to their special type of layered structure with appropriate hydrate content and their promising Faradaic behavior[46, 47].

3.4 Galvanostatic charge/discharge measurements

The galvanostatic charge/discharge is an effective measurement technique to study more about the charge storage properties and stability of the electrodes. Fig.7 shows the charge/discharge profile of MnO₂ and various concentrations of Co-MnO₂ electrodes at 0.2 Ag^{-1} of constant discharge current density. All the electrodes show a linear variation of the potential during both the charging and discharging processes; with nearly triangular shape representing

excellent supercapacitor behavior. The specific capacitance (C_{sp}) of the electrodes measured by the galvanostatic discharge process can be calculated using Equation (3.3):

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m} \quad (3.3)$$

where I is the constant discharge current (A), Δt is the discharge time (s), ΔV is the potential window (V), and m (g) is the mass of the active material in the electrode. According to this equation, the specific capacitance (SC) of the MnO_2 and various concentration of Co- MnO_2 at the constant current density of 0.2 A g^{-1} are 231 (bare), 292 (1%), 325 (2%), 415 (5%) and 375 F g^{-1} (10%). From these values, it can be observed that the variation of C_{sp} values are nearly consistent with those obtained from the CV measurements. It is clear that all the Co- MnO_2 electrodes provide improved specific capacitances than that of bare MnO_2 , which may reflect an improved electrical conductivity caused by the incorporation of Co into the MnO_2 nanostructures[34, 48]. Even though 10% Co- MnO_2 shows better capacitance than bare MnO_2 electrode, the value is less compared to the 5% Co- MnO_2 electrode. This drop in C_{sp} value confirms that the Co ions can improve the specific capacitance MnO_2 up to a certain concentration of dopant [36, 48]. This depicts some constraints in the pseudocapacitance reaction of the electrode with excess Co ions in Na_2SO_4 electrolyte. Since, generally, cobalt based electrodes have a narrow operational potential window and require a basic electrolyte (KOH or NaOH) for supercapacitor applications compared with the MnO_2 based electrode materials, this might be the reason for the decrease in specific capacitance values in the case of higher concentrations of Co ions in MnO_2 electrode. Fig. 8a represents the relationship between the specific capacitance and current densities; all the electrodes show decay of C_{sp} with respect to the increase in current density. The drop in specific capacitance with increase in current densities is due to the less involvement of the active materials, whereas at low current densities the current

accumulation process is slow and all the active materials sites and pores are involved in the energy storage process [5, 39]. The cyclic stability of the MnO₂ and 5% Co-MnO₂ electrodes was also investigated by continuous charge/discharge measurements over 5000 cycles (Fig. 8b) at a constant current density of 5 Ag⁻¹. The 5% Co-MnO₂ electrode has superior cycling stability with 97.3% retention of initial specific capacitance after 5000 cycles, which is higher than the cyclic stability of bare MnO₂ electrode (92.8%). The better performance and stability of the 5% Co-MnO₂ electrode could be due to the Co species facilitating the electronic conduction within the metal oxide [11, 48].

3.5 Impedance spectroscopy

EIS analysis was performed for the electrodes to study the effect of Co species on the internal resistance, charge transfer and electrochemical kinetics of the electrodes. The obtained Nyquist plot for the MnO₂ and Co-MnO₂ electrodes are shown in Fig. 9a. Nyquist plots are composed of a spike in the low frequency region and an incomplete semicircle (inset of Fig. 9a) in the high frequency region indicating a pronounced capacitive behavior with a moderate resistance. The impedance spectra were analyzed by Zview software on the basis of the electrical equivalent circuit, as shown in the inset of Fig. 9a. The bulk solution resistance is represented as R_s , the double layer capacitance (CPE_{dl}) and charge transfer resistance (R_{ct}) across the electrode/electrolyte interface. The spike at lower frequency of the plots exhibits an angle between 45° to 90° relative to the real axis representing the diffusion control process of the electrode and it was fitted with an Warburg element Z_w . Additional RC components R_L and C_p were added to the circuit which represents the leakage resistance and pseudocapacitance of the electrodes. The fitting parameters of the electrodes are listed in Table 1. The overall resistance

values of the electrodes are the combination of R_s with R_{ct} values[49], which were found to decrease with increase in Co content in the electrodes and confirming the influence of Co ion in the improvement of conductivity of the electrode. The leakage resistance R_L is found to be larger for all the electrodes, indicating the negligible self-discharging property of the fabricated electrodes[50]. The low frequency pseudocapacitances (C_p) of the electrodes are similar to those values obtained from the CV measurements, which shows the reliability of the fitted values. In addition to this, the Bode plots (Fig. 9b) for MnO_2 and Co-MnO_2 electrodes were obtained from the change of phase angle degree with respect to the different frequencies from 10 mHz to 100 kHz. The phase angle degree of the MnO_2 electrodes with different concentration of Co species remained close to 90° even in the higher frequency range, indicating better capacitive behavior of the electrodes.

4. Conclusion

Cobalt doped MnO_2 nanocomposites were successfully synthesized by an hydrothermal method and used in the fabrication of supercapacitor electrodes. The MnO_2 electrodes exhibit highly reversible charge/discharge features with an excellent specific capacitance due to the presence of various electrochemically active phases of MnO_2 nanocrystals. Moreover, these experimental evidences confirm that the incorporation of certain amounts of Co ions in the MnO_2 sites strongly influence the properties of the electrode by increasing the conductivity and electrochemical properties of the electrode. Among the various concentrations of Co dopant added, the 5 mol % of Co doped MnO_2 electrode shows a very high specific capacitance (415 Fg^{-1}) at constant discharge current density of 0.2 Ag^{-1} and a superior cycling stability (97.3 %) over 5000 cycles. From this overall observation, the optimized hydrothermal growth condition and an

appropriate amount of Co ions in the MnO₂ nanocomposite affords an excellent electrode material for supercapacitor applications.

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Table 1. EIS fit parameters of MnO₂ and Co-MnO₂ electrodes

Fit parameters	MnO ₂	1%Co-MnO ₂	2% Co-MnO ₂	5% Co-MnO ₂	10% Co-MnO ₂
R _s (Ω)	3.67	3.1	2.5	2.7	3.7
R _{ct} (Ω)	11.19	5.25	4.94	3.99	4.05
C _{dl} (mF)	0.33	0.23	0.73	1.06	1.28
Z _w (Ω)	1.57	1.24	2.46	2.68	4.75
R _L (kΩ)	2.02	1.55	0.53	0.45	1.87
C _p (Fg ⁻¹)	124	170	227	294	180

Fig. 1 X-ray diffraction pattern of MnO₂ and Co-MnO₂ electrodes. **Fig. 2** FESEM image of a, b) bare MnO₂ and c, d) 5% Co-MnO₂ nanocomposites.

Fig. 3 TEM image of a, b) bare MnO_2 and c, d) 5% Co-MnO_2 nanocomposites.

Fig. 4 EDAX spectrum of a) bare MnO_2 and b) 5% Co-MnO_2 nanocomposites.

Fig. 5 N_2 adsorption/desorption isotherms and inset pore size distribution of the bare MnO_2 (open circle) and 5% Co-MnO_2 (bold circle) samples.

Fig. 6 Cyclic Voltammograms of bare MnO₂, 1%, 2%, 5% and 10% Co-MnO₂ electrodes in 1M Na₂SO₄ electrolyte at 10 mVs⁻¹ scan rate.

Fig.7 The charge/discharge curve for MnO₂, 1%, 2%, 5% and 10% Co-MnO₂ electrodes at a constant current density of 0.2 Ag⁻¹ in 1M Na₂SO₄ electrolyte.

Fig. 8 a) Variation of specific capacitance with discharge current density for bare MnO₂ and Co-MnO₂ electrodes and b) Cycle life of the MnO₂ and 5% Co-MnO₂ electrode at a constant current density of 5 Ag⁻¹.

Fig. 9 a) Nyquist plots for the MnO_2 and Co-MnO_2 electrodes, inset shows the equivalent circuit of fit and b) the Bode plots of MnO_2 and Co-MnO_2 electrodes .