Electrochemical Energy Storage Performance of Electrospun CoMn₂O₄ Nanofibers

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Abstract:

Nanofibers of cobalt manganese oxide (CoMn₂O₄) were grown using an electrospun technique. Structural and microstructural characterizations confirm the formation of phase pure CoMn₂O₄ with high porosity. The potential application of CoMn₂O₄ nanofibers as an electrode material for energy storage device was studied using cyclic voltammetry and galvanostatic charge-discharge measurements. A specific capacitance of 121 F/g was observed with enhanced cyclic stability. Furthermore, an energy storage device was fabricated by sandwiching two electrodes separated by an ion transporting layer. The device showed a specific capacitance of 241 mF/cm² in 3M NaOH electrolyte. The effect of temperature on the charge storage properties of the device was also investigated for high temperature applications. The device showed about 75% improvement in the charge storage capacity when the temperature was increased from 10 to 70 °C. This research suggests that nanofibers of CoMn₂O₄ could be used for fabrication of energy storage devices which could operate in a wide temperature range with improved efficiency.

KEYWORDS: Electrospun, CoMn₂O₄, cyclic voltammetry, energy storage device

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1. Introduction

Electrochemical energy storage devices are gaining interest due to their high power densities, fast charge-discharge process and long term cyclic stability than batteries[1-6]. Because of these unique features, they can be especially found in applications where sudden power delivery is needed[7-10]. In general, electrochemical energy storage devices are operated based on two distinguishable charge storage mechanisms. The first group of device stores energy by accumulating electrostatic charge at the electrode/electrolyte interface. This type of energy device is called electrical double-layer capacitors (EDLCs). The other group is called pseudocapacitors where energy is stored due to a reversible redox reaction at the electroactive material surface[1, 11]. With the ever increasing demand for smaller but more powerful energy storage devices, pseudocapacitors can play an important role. Due to the chemical reaction based charge storage process, pseudocapacitors pose higher specific charge storage capacity compared to the EDLCs.

Till date, several oxides and sulfides of redox active metals such as iron oxide, nickel oxide, ruthenium oxide, cobalt oxide, manganese oxide, molybdenum sulfide and cobalt sulfide have been utilized in pseudocapacitors[12-27]. In recent times, nanofibers have attracted considerable attention of scientists due to their unique characteristics such as high porosity and large surface area which make them an ideal candidate for energy storage applications[28]. There are different ways to fabricate nanofibers. Among them, electrospinning technique is a low cost and versatile method on offer[29]. The properties such as porosity, thickness, surface area and dimensions of nanofibers could be easily controlled by varying experimental conditions. In the literature, there are several efforts to fabricate metal oxide nanofibers using electrospinning. Wee *et al* fabricated the vanadium pentoxide (V_2O_5) nanofibers using electrospinning and obtained

moderate capacitance values of 190 F/g in 2 M KCl electrolyte[30]. Lee *et al* synthesized the nanofibers with mixed phases of manganese oxide such as Mn_3O_4 and Mn_2O_3 using the electrospinning process[31]. They observed the highest specific capacitance of 361 F/g at a current density of 1 A/g. Moreover, the electrospinning method has been utilized to fabricate the metal oxide/carbon combine electrode materials. For example, Ren *et al* fabricated the hollow nickel oxide nanofibers modified with citric acid[32]. They reported a capacitance value of 336 F/g which was 2.5 times higher than unmodified nickel oxide.

Lee *et al* have decorated MnO_2 on hierarchical porous carbon nanofiber/graphene in one-step electrospinning process [33]. The supercapacitor electrode prepared using 5 wt% graphene showed a specific capacitance of 210 F/g in a 6M KOH aqueous solution. The enhanced electrochemical performance was explained based on the synergistic effect between carbon nanofiber/graphene and MnO_2 particles. Xu *et al* synthesized lotus root-like CoMoO_4 @graphene nanofibers using electrospinning method and used it for lithium ion batteries [34]. These nanofibers showed a reversible capacity of 735 mAh/g at 100 mA/g. Hierarchical NiCo_2O_4 @ MnO_2 composites with ultrathin MnO_2 nanosheets were grown on NiCo_2O_4 nanotubes by an electrospinning method [35]. The composite electrode displayed a specific capacitance of 706.7 F/g at 3 A/g with about 85% retention of the initial capacitance. Recently, Nilmounget *al* have used electrospun carbon/ CuFe_2O_4 composite nanofibers for electrochemical energy storage applications. Specific capacitances of carbon/ CuFe_2O_4 composite nanofibers in both Na_2SO_4 and KOH showed higher than those of carbon nanofibers and CuFe_2O_4 nanoparticles [36].

In this work, we present the detailed synthesis process of cobalt manganese oxide (CoMn_2O_4) using an electrospinning technique and study of their electrochemical properties. The

effect of temperature on the charge storage capacity of the device based on CoMn_2O_4 nanofibers has been reported for the first time. A specific capacitance of 121 F/g was observed with enhanced cyclic stability. An energy storage device was fabricated which showed a specific capacitance of 241 mF/cm^2 which is among the highest reported values. In addition, the device showed about 75% improvement in charge storage capacity on increasing temperature from 10 to 70 °C.

2. Experimental Details

2.1. *Synthesis of CoMn_2O_4 nanofibers*

CoMn_2O_4 nanofibers were synthesized using an electrospinning process followed by calcination in air. The solution for the electrospun was prepared by dissolving 0.25 g of polyvinylpyrrolidone (PVP) and 0.25 g of polyacrylonitrile (PAN) in 5 mL of N,N-dimethylformamide (DMF). The solution was stirred for 1 hour to obtain a homogeneous solution. To this solution, 0.5 mmol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 1 mmol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were added and stirred at room temperature for 24 hours to obtain a homogeneous solution for the electrospun. Next, the homogeneous solution was loaded into a plastic syringe which contained a stainless steel needle. A voltage of 18 kV was applied between the tip of the stainless steel needle and aluminum foil collector plate. The distance between tip of the needle and the collector plate was 16 cm and spinning rate was set to 1 mL/h. Finally, nanofibers obtained were calcinated at 600° C (3 °C/min) for 8 hours in air.

2.2. *Structural Characterization*

Structural characterizations of the prepared nanofibers were carried out using X-ray diffractometer (XRD), scanning electron microscope (SEM) and X-ray energy dispersive

spectrometer (EDX). The XRD spectra of the sample was taken using Shimadzu X-ray diffractometer using the 2θ - θ scan with $\text{CuK}_{\alpha 1}$ ($\lambda=1.5406 \text{ \AA}$) radiation. The morphology of the synthesized nanofibers was investigated using a JEOL JSM-840A scanning electron microscope (SEM) equipped with an Oxford INCA 250 silicon drift X-ray energy dispersive spectrometer (EDX). Transmission electron microscopy (TEM) analysis was performed using a FEI-Tecnai, 200 kV transmission electron microscope equipped with a CCD camera for STEM, HAADF detector, and EDX. TEM image non-linear processing was carried out using Gatan digital micrograph version 3.4. The powdered sample of CoMn_2O_4 was analyzed using a Thermo Scientific K-Alpha XPS system equipped with a monochromatic X-ray source at 1486.6 eV, corresponding to the Al K_{α} line. The X-ray power of 75 W at 12 kV was used for the experiment with a spot size of $400 \mu\text{m}^2$. The base pressure of the instrument was at $1.0 \times 10^{-9} \text{ mBar}$. The K-Alpha was calibrated to give a binding energy of 84.0 eV for $\text{Au } 4f_{7/2}$ and 284.8 for the C1s line of adventitious (aliphatic) carbon present on the nonsputtered samples. Photoelectrons were collected from a takeoff angle of 90° relative to the sample surface. The survey spectra were taken at a pass energy of 200 eV, an energy step size of 1.0 eV, an using an average of 20 scans, while the high resolution (HR) core-level spectra of C 1s, O 1s, Mn 2p and Co 2p were taken at a 40 eV pass energy, an energy step size of 0.1 eV, and using an average of 20, 50, 40 and 40 scans respectively. The XPS data acquisition was performed using the “Avantage v5.932” software provided with the instrument.

2.3. Electrochemical Characterization

Electrochemical properties of the synthesized nanofibers were studied using Versastat4-500 electrochemical workstation (Princeton Applied Research, USA). For electrochemical investigation, a conventional three electrode system was used. A platinum wire, saturated

calomel electrode and nanofibers on nickel foam were used as a counter electrode, a reference electrode and a working electrode, respectively. 3M NaOH was used as an electrolyte. The working electrode was prepared using 80 wt.% of the nanofibers, 10 wt.% of acetylene black and 10 wt.% of polyvinylidene difluoride (PVdF) in N-methyl pyrrolidinone (NMP). The mixture was dispersed and a pre-cleaned nickel foam was dipped into the dispersion to get an even coating. The coated nickel foam was dried in a vacuum oven at 60°C overnight. An energy storage device (capacitor) was fabricated by sandwiching the ion transporting layer between two working electrodes. Electrochemical properties of the electrode and device were investigated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) methods.

3. Results and Discussion

3.1. Structure and Morphology of the CoMn_2O_4

X-ray diffraction patterns of nanofibers revealed the detail crystal structure and phase purity of the prepared sample. Fig. 1 shows the XRD patterns of the synthesized nanofibers in the range of 10-70 degree. The originated diffraction peaks could be assigned to the (101), (112), (200), (103), (211), (004), (220), (204), (105), (312), (303), (321), (224) and (400) planes of CoMn_2O_4 (JCPDS card no. 77-0471). No extra peaks other than peaks due to CoMn_2O_4 were observed in the XRD patterns indicating high phase purity of the CoMn_2O_4 nanofibers. The XRD data was used to evaluate the crystallite size of the synthesized CoMn_2O_4 nanofibers. The average crystallite size (t) was calculated using the Debye Scherrer equation [19]:

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad \dots(1)$$

where λ is the X-ray wavelength, β is the full width at half maximum of the diffraction line, and θ is the diffraction angle of the XRD spectra. The average crystal size was estimated to be 21.4 nm.

Morphology and microstructure of the CoMn_2O_4 nanofibers were studied using scanning electron microscopy and transmission electron microscopy. SEM image of the CoMn_2O_4 nanofibers are shown in Fig. 2. As seen in the image, CoMn_2O_4 nanofibers are porous in nature. The porous structure originates during calcination of the nanofibers in air. The fabricated nanofibers contain PVP and PAN and during the calcination process PVP decomposes first and creates a porous structure in the nanofibers. Energy-dispersive X-ray spectroscopy (EDS) was further used to confirm the composition of synthesized CoMn_2O_4 nanofibers. The EDS image of the CoMn_2O_4 nanofibers are shown in Fig. 3. As seen in the EDS image, the presence of Co, Mn, O, and C are quite evident. Elemental ratio of Co, Mn and O was observed to be 1:2:4 confirming formation of CoMn_2O_4 . The presence of a small amount of carbon could be from PVP and PAN. The size of crystallite and its morphology was further investigated using TEM. TEM image in Fig. 4 shows nearly uniform structures that are composed of nanocrystals. The chemical composition of the CoMn_2O_4 was analyzed using X-ray photoelectron spectroscopy (XPS). Fig. 5a shows survey scan spectrum of the CoMn_2O_4 , which clearly exhibits the presence of Co, Mn and O elements in CoMn_2O_4 . The chemical states of Co and Mn in the CoMn_2O_4 sample were analyzed using XPS high-resolution Mn 2p and Co 2p and O 1s core-level spectra (Fig. 5a, b). The oxidation state of cobalt was deduced from the deconvoluted XPS spectra of Co 2p. The deconvoluted Co 2p_{3/2} peaks were assigned to Co^0 (780.5 eV), Co^{3+} (782.1 eV) and Co^{2+} (783.8 eV) from low to high binding energy [37, 38]. While oxygen O 1s deconvoluted peaks show O- Co^{3+} (530.1 eV) and O- Co^{2+} (531.5 eV) along with presence of OH (532.7 eV). The

peaks at 641.06 and 642.28 eV corresponds to Mn^{3+} and Mn^{4+} , respectively, while a small peak at 644.8 eV corresponds to the satellite peaks of Mn^{4+} [39]. The Mn 2p orbital region exhibits the binding energies of Mn 2p_{3/2} and Mn 2p_{1/2} peaks at 641.7 eV and 653.8 eV, respectively. The binding energy separation of ~12 eV is a typical value for Mn^{3+} [40]. Thus, it is reasonable to conclude that Mn exists as Mn^{3+} in CoMn_2O_4 .

3.2. Electrochemical properties of CoMn_2O_4 nanofibers based electrode

Electrochemical properties of CoMn_2O_4 nanofibers as an electrode material for energy storage application were studied using cyclic voltammetry and galvanostatic charge-discharge measurements at room temperature. Fig. 6a shows the cyclic voltammograms of CoMn_2O_4 nanofibers at various scan rates in 3M NaOH electrolyte. All the CV curves showed a pair of redox (anodic and cathodic) peaks which indicated the pseudocapacitor behavior of CoMn_2O_4 nanofibers. In addition, shape of the CV curves was observed to be retained even at higher scan rates, suggesting high electrochemical stability of the CoMn_2O_4 nanofibers. The specific capacitance (C_{sp}) of the CoMn_2O_4 nanofibers was calculated using the following equation[41]:

$$C_{sp} = \frac{Q}{\Delta V \times \left(\frac{\partial v}{\partial t}\right) \times m} \quad \dots(2)$$

Where Q is the area under the CV curve, $\frac{\partial v}{\partial t}$ is the scan rate, ΔV is the potential window and m is the mass of the CoMn_2O_4 nanofibers. The effect of scan rate on the charge storage capacity of CoMn_2O_4 nanofibers is shown in Fig. 6b. Specific capacitance of the CoMn_2O_4 nanofibers was observed to decrease with increase in the scan rates which could be due to insufficient time for the electrolytes to adsorb and desorb on the electrode surface[42]. The CoMn_2O_4 nanofibers showed the maximum specific capacitance of 121 F/g in 3M NaOH electrolyte. As observed in the CV curves, the peak current increases with increase in scan rate. A linear relationship was

observed between the peak currents (anodic as well as cathodic) and the square root of the scan rate (Fig. 7). The linear behavior between the peak current and the square root of the scan rate indicates that the reaction kinetics during the redox process was likely controlled by diffusion processes. Ghouriet *al* synthesized Fe/CeO₂ decorated carbon nanofibers using the electrospun process [43]. Electrochemical characterization of the synthesized nanofibers revealed a specific capacitance of 56 F/g. Vanadium pentoxide (V₂O₅)/carbon nanofiber composites were prepared for supercapacitor applications [44]. It was observed that loadings of V₂O₅ affects the microstructures of the nanofibers and thus the electrochemical properties. The nanofibers based capacitors delivered a high specific capacitance of 150 F/g. Wang *et al* have fabricated supercapacitors based on carbon and carbon-MnO₂ nanofiber synthesized using electrospun technique [45]. A maximum specific capacitance of 57 F/g at 5mV/s was observed in their studies.

The charge storage capacity of the CoMn₂O₄ nanofibers was further investigated using galvanostatic charge-discharge methods. The galvanostatic charge-discharge characteristics of CoMn₂O₄ nanofibers are shown in Fig. 8a at various current densities. All the measurements were performed using constant charging current and various discharging currents. It is observed that CoMn₂O₄ nanofibers take longer time to discharge at lower discharge current indicating higher charge storage capacity. The specific capacitance of the CoMn₂O₄ nanofibers from galvanostatic charge-discharge measurements was calculated using the equation given below [46]:

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m} \quad \dots (3)$$

where, I is the discharge current (A), Δt is the discharge time (s), ΔV is the potential window (V), and m is the mass (g) of the CoMn₂O₄ nanofibers. The effect of applied current on the charge storage capacity of the CoMn₂O₄ nanofibers is shown in Fig. 8b. Specific capacitance

was observed to decrease with increasing current density which could be due to insufficient time for the electrolyte ions to diffuse into the inner pores of the CoMn_2O_4 nanofibers. The electrochemical stability of the CoMn_2O_4 nanofibers was also tested using galvanostatic charge-discharge technique. Gao *et al* have prepared porous carbon/nickel nanofibers for supercapacitor applications [47]. They also observed a decrease in specific capacitance with increase in discharge current, e.g. the specific capacitance was decreased from $\sim 104 \text{ F/g}$ to 38 F/g with increasing current density from 0.5 A/g to 25.0 A/g , respectively. Electrospun NiO/RuO_2 composite carbon nanofibers fabricated from 5 wt% nickel (II) and 15 wt% ruthenium (III) precursors showed a capacitance up to $\sim 60 \text{ F/g}$ after 30 cycles of measurement at 30 mA/g . Galvanostatic charge/discharge measurements on carbon nanofibers containing MnO_2 showed a specific capacitance of $\sim 56 \text{ F/g}$ at 0.2 A/g which decreased to $\sim 32 \text{ F/g}$ when the current density was increased to 30 A/g [45]. Fig. 9, shows the capacitance retention of the CoMn_2O_4 nanofibers as a function of number of galvanostatic charge-discharge cycles. The specific capacitance was observed to be increasing with increasing charge-discharge cycles which could be due to electrochemical activation of the CoMn_2O_4 nanofibers. Wu *et al* have also observed improvement in charge storage capacity in electrospun NiO/RuO_2 composite carbon nanofibers [48]. On the other hand, electrospun vanadium pentoxide/carbon nanofiber composites fabricated for supercapacitor electrodes showed decrease in charge storage capacity with increase in number of charge discharge cyclic study [44]. They observed a decrease in the capacitance of about 18% of the initial value after only 100 cycles. In general, decrease in the capacitance in cyclic (stability) measurement could be due to dissolution of active materials in electrolytes, problems in electrode (such as corrosion, expansion, loss of active materials due to weak binding).

3.3. Electrochemical properties of CoMn_2O_4 nanofibers based energy storage device

A symmetrical capacitor device was fabricated by assembling the CoMn_2O_4 nanofibers as the electrode materials separated by ion transporting layer. The performance of the device was investigated in detail at different temperatures. The CV curves of the device were studied at room temperature at various scan rates (Fig. 10a). It can be seen that CV curves even at higher scan rates are identical and nearly rectangular in shape which suggest high electrochemical stability and near ideal behavior of our fabricated device using CoMn_2O_4 nanofibers. Calculated specific capacitance of the device was plotted as a function of scan rate (Fig. 10b). The highest capacitance of about 241 mF/cm^2 was observed at 5 mV/s for the CoMn_2O_4 nanofibers based device. It is further observed that the specific capacitance of the device decreases with increasing scan rate, which could be due to insufficient time for the electrolyte ions to complete the electrochemical reaction at higher scan rates.

The effect of temperature on electrochemical performance of the device was studied. Fig. 11a shows the CV curves of the device at 100 mV/s scan rate at various temperatures. As seen in the CV curves, the shape is rectangular which indicate near ideal behavior of the capacitor. In addition, the shape of the CV curves was retained even at elevated temperature, suggesting high thermal stability of the device and its suitability to operate in wide temperature range. It is further evident from CV curves at various temperatures that there is a progressive improvement of the area under the CV curves with increase in temperature, suggesting improvement in charge storage capacity. In addition to the cyclic voltammetry studies, temperature dependence of the charge storage capacity was investigated using galvanostatic charge-discharge measurements. Potential vs time curves measured at various temperatures at constant charge discharge (1 mA/cm^2) are shown in Fig. 11b. The discharge time increases with increase in temperature

indicating improvement in charge storage capacity. This interesting behavior is plotted as a percentage change in the capacitance with varying temperature (Fig. 11c). The energy device showed about 75% improvement in charge storage capacity when temperature increased from 10 to 70 °C. Temperature dependence study suggests that CoMn₂O₄ nanofibers based device can be used in wide temperature range without suffering any failures in charge storing capability. The increase in the charge storage capacity of the device with increasing temperature can be explained using electrochemical impedance spectroscopy (EIS). The variation of real and imaginary impedance of the device at several temperatures can be seen in the Fig. 11d. According to our studies, the equivalent series resistance (ESR) of the device decreases with increasing temperature. ESR value might be reduced due to the enhanced kinetic activity of the electrolyte ions with the increasing temperature. Hence, electrolyte becomes more conductive and this improves the overall charge storage capacity of the device. The impedance plot was fitted using the circuit given in inset of Fig. 11d. In the fitting circuit, R_s , CPE1, R_{ct} , W and C_p are the solution resistance, electric double layer constant phase element, charge-transfer resistance, Warburg resistance and pseudocapacitive element. The bottom inset figure of Fig. 11d shows the measured and fitted data of the device at 70 °C. It is observed that the solution resistance decreases from 0.43 to 0.26 Ω with increase in temperature from 10 to 70 °C. The semicircle at high frequency region is related to the charge transfer resistance (R_{ct}) which is due to the Faradic redox reaction of the electrode. The R_{ct} value of the device was observed to be decreasing with increasing temperature indicating enhanced electrochemical activity at higher temperature.

4. Conclusion

CoMn₂O₄ nanofibers were successfully fabricated via an electrospinning technique. The structural characterizations confirm the formation of phase pure CoMn₂O₄ nanofibers.

Electrochemical properties of CoMn_2O_4 nanofibers material were investigated and a charge storage capacity of 121 F/g was observed with enhanced cyclic stability. In addition, an energy storage device was fabricated and tested at various temperatures. The highest specific capacitance of the CoMn_2O_4 nanofibers based supercapacitor device was observed to be 241 mF/cm^2 in 3M NaOH electrolyte. The device showed about 75% improvement in the charge storage capacity when temperature increased from 10 to 70 °C. In summary, CoMn_2O_4 nanofibers were prepared using a facile technique to fabricate highly stable energy storage device which could be operated in wide temperature range.

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Fig. 1: XRD patterns of CoMn₂O₄ nanofibers.

Fig. 2: SEM images of CoMn₂O₄ nanofibers.

Fig. 3: EDS patterns of CoMn_2O_4 .

Fig. 4: (a) TEM image of CoMn₂O₄.

Fig. 5: (a) XPS survey scan spectrum of CoMn_2O_4 , (b) XPS spectra of Co 2p and (c) Mn 2p for CoMn_2O_4 .

Fig. 6: (a) CV curves at various scan rates, and (b) effect of scan rate on charge storage capacity of CoMn₂O₄ nanofibers.

Fig. 7: Variation of anodic and cathodic peak currents as a function of square root of scan rate.

Fig. 8: (a) Galvanostatic charge-discharge characteristics at various currents, and (b) effect of discharge currents on the specific capacitance of CoMn_2O_4 nanofibers.

Fig. 9: % change in the specific capacitance verse number of charge-discharge cycles.

Fig. 10: (a) CV curves at various scan rates, and (b) effect of scan rate on charge storage capacity of the device.

Fig. 11: (a) CV curves at various temperatures, (b) galvanostatic charge-discharge characteristics at various temperatures, (c) change in capacitance with temperature, and (d) Zreal vs Zimp plots at various temperature for the device (top-left inset is the fitted circuit of Nyquist plot; bottom-right is the measured and fitted plot for the device at 70 C.