Original Research Paper

Mixed Nickel Cobalt Manganese Oxide Nanorods for supercapacitor application

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Abstract: Mixed Nickel Cobalt Manganese oxide (NiCoMn-Oxide) is a new class of excellent material for supercapacitor application. Here, hydrothermal synthesis technique has been employed to prepare mixed NiCoMn-Oxide nanorods. The elemental composition and morphology of this material were validated by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and EDX techniques. To analyze the capacitive performance of this material, cyclic voltammetry and galvanostatic charge-discharge tests were performed. A maximum specific capacitance of ~500 F/g was obtained for the mixed NiCoMn-oxide material within a potential range of -0.5 to 0.5 V (Vs. Ag/AgCl) in 2 M aqueous KOH solution.

Keywords: Supercapacitor, Hydrothermal Synthesis, Elemental Composition, Morphology, Capacitive Performance

Introduction

Now civilized and industrialized world demands more and more energy but the resources of energy like fossil fuels (coal, petroleum etc.) are limited in storage and also very alarming for our environment. So, some new renewable (Tian *et al*., 2007; Chan *et al*., 2008) non-toxic green energy sources are urgently required in place of all the traditional non-renewable fossil fuels without any compromise in performance. The supercapacitor (Conway, 1999; Miller and Burke, 2008; Jayalakshm and Balasubramanian, 2008) is an electrochemical device that has emerged as a very promising energy storage device (Pushparaj *et al*., 2007; Zhang *et al*., 2013) with almost zero environmental hazards. Supercapacitors have very large capacitance than any other normal capacitor mainly because of the large effective surface area of the electrode and electrochemical reactions involved during the charging processes. Different nanostructured and highly porous morphology (nanorods, nanotubes etc.) has been employed for the fabrication of supercapacitor device. These highly porous structures effectively enrich the surface area as well as the capacitance. People are also trying to combine a battery and a supercapacitor to make a hybrid device which will provide both high power density as well as high energy density. Depending on the working procedure supercapacitor is mainly two types- (a) Electric Double Layer Capacitor (EDLC) (Wang and Zhang, 2012; Sharma and Bhatti, 2010) and (b) Pseudocapacitor (Augustyn *et al*., 2014; Simon and Gogotsi, 2008; Huang *et al*., 2013; Zhou *et al*., 2014). EDLC is a non-faradic electrochemical capacitor i.e., no transfer of charge occurs between electrode and electrolyte. It stores energy and capacitance via electric double layer on the electrode surface. Mainly carbon based materials are helpful for EDLC application. In contrast to EDLC, pseudocapacitor works on the principle of faradic reaction (Electrosorption, REDOX-reaction etc.) between electrode and electrolyte and providing higher capacitance than EDLC (Sarangapani *et al*., 1996). Metal oxides and conducting polymers help to achieve very high capacitance via pseudocapacitance effect. Punching both the EDLC and pseudocapacitor properties of another hybrid supercapacitor has been made and which is a major research area of supercapacitors (Conway and Pell, 2003). Materials used for supercapacitor electrode have a lot of importance. Different carbon based materials (Zhu *et al*., 2011; Wang *et al*., 2009) are very useful for supercapacitor for their high conductivity and surface area. Recent research in supercapacitor materials showed that nanostructured transition metal oxides (Lokhande *et al*., 2011; Chen *et al*., 2010; Wu *et al*., 2015; Ponrouch *et al*., 2013; Liu and Anderson, 1996; Srinivasan and Weidner, 2000; Lu *et al*., 2011; Xu *et al*., 2009; Reddy and Reddy, 2004; Xie *et al*., 2011) are also attractive material for supercapacitor application because of their high specific surface area, high ionic conductivity and fast redox reactions. These materials show pseudocapacitive effect.

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Ruthenium oxide (RuO_2) (Ponrouch *et al*., 2013) is a capable material for supercapacitor electrode for its high specific capacitance (1585F/g)and high conductivity. But this material is expensive and toxic. So, people are searching for new transition metal oxides like NiO (Liu and Anderson, 1996; Srinivasan and Weidner, 2000), MnO_2 (Lu *et al*., 2011; Xu *et al*., 2009; Reddy and Reddy, 2004) and Co_3O_4 (Xie *et al*., 2011) etc. Recently, it has been observed that mixed transition metal (Ni, Co, Mn and Fe etc.) oxides (MTMOs) also show very good performance for supercapacitor application. Particularly, metal oxides containing transition metal elements like Ni, Co and Mn, provide higher redox state than carbonaceous material. Hydrothermally synthesized (Byrappa and Adschiri, 2007) mixed NiCoMn-oxide has all the potentials for supercapacitor application. The outstanding supercapacitive behavior of NiCoMn-oxide is attributed to the unique homogeneous structure with uniform distributions of Ni, Co and Mn elements, enhanced oxidation states and synergistic effects of multi-metal components in the electrodes.

In this report, a facile hydrothermal synthesis technique of NiCoMn-oxide is reported. Morphology and composition of the material is validated by XRD, SEM and EDX techniques. A maximum capacitance of 500 F/g is obtained from the electrochemical test at current density 1 A/g in 2 M aqueous KOH solution with excellent cycling stability.

Experimental Section

Chemicals Used

Nickel nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$, 98% Merck specialties privatelimited (INDIA)], cobalt nitrate hexahydrate [$Co(NO_3)_2.6H_2O$, 97% Merck specialties private limited (INDIA)], Manganese chloride tetrahydrate [$MnCl_2.4H_2O$, Himedia Pvt. Ltd.], Urea [CH_4N_2O, 99.5% Sisco research laboratories private limited (India)] and DI water are used for (mixed NiCoMn-oxide) synthesis.

Synthesis Procedure of Mixed NiCoMn-Oxide Nanorods

To prepare mixed NiCoMn-oxide nanorods facile hydrothermal technique has been performed. This is a very well-known technique for preparing crystals with full control over the elements. In this method, all precursors are dissolved in DI water and then heated in high pressure. For preparing mixed NiCoMn-oxide nanorods, 0.7275 g $Co(NO_3)_2,6H_2O$, 0.725g $Ni(NO_3)_2,6H_2O$, 0.630 g $Mncl_2,4H_2O$ and 0.45 g urea were dissolved in 80 ml DI water to make a light pink solution. The solution was transferred in two 40 ml Teflon lined stainless steel autoclave and maintained at 150ºC for 10 hours in an electric oven. Then the autoclave was cooled at room temperature, precipitated solution was separated and rinsed several times. After that precipitated solution was dried at 100°C for 24 hours and followed by annealing at 400°C for 6 hours. Here, urea was used as a nutrient medium and all the precursors get nucleated in presence of urea.

Material Characterization

The elemental composition and morphology of the mixed NiCoMn-oxide material was characterized by X-ray diffraction (Bruker D8 advanced diffractometer) method with Cu Kα radiation (λ = 0.154184 nm), EDX and FESEM (MERLIN Compact with GEMINI I electron column, Zeiss Pvt. Ltd., Germany) analysis.

Preparation of Electrode and Electrochemical Characterization

The working electrodes were prepared by mixing the electrode material with ethanol and then drop casting it on nickel foam. The mixture of electrode material and the Ethanol were sonicated for almost 30 min to make an homogeneous mixture and then coated on a nickel foam strip for two times to have a uniform coating. Then the coated nickel foam was dried at room temperature in a vacuum container for almost 24 h followed by pressing. Weight measurement was done before the coating and after the coating to know how much active material was loaded. It has been found that almost 5 mg sample was loaded on each nickel foam. The electrochemical performance of the mixed NiCoMn-oxide material was obtained by a three electrode electrochemical test using a Potentiostat (PG-16125, Techno science instrument, Bangalore, India) in 2 M aqueous KOH solution. The Cyclic voltammetry and Charge-discharge tests were carried out at room temperature within a potential range between -0.5 to 0.5 V Vs. Ag/AgCl electrode. The coated nickel foams were used as a working electrode and Pt coil as counter electrode in this three electrode test. Specific capacitance (C_s) of a material obtained from the cyclic voltammetry curves at different scan rates by using the Equation 1:

$$C_s = \frac{\int_{V_i}^{V_f} I(V)\,dV}{m.s.[V_f - V_i]} \tag{1}$$

where, $[V_f\text{-}V_i]$ is called the potential window, m is mass loaded on the electrode and s is the scan rate. In the above formula the numerator gives the area under the CV curves.

The specific capacitance also obtained from the charge-discharge curves by using Equation 2:

$$C_m = \frac{\mathrm{I}}{m.\frac{dV}{dt}} \tag{2}$$

where, I is the discharge current density and dV/dt is the slope of the discharge curve.

Result and Discussion

Composition and Morphology

Figure 1 shows XRD pattern of mixed NiCoMn-oxide. From XRD pattern it is conformed that mixed NiCoMn-oxide is composed of $NiCo_2O_4$ (JCPDS no.-20-0781) and Mn_2O_3 (JCPDS no.-89-4836). All peaks for $NiCo_2O_4$ are present in the XRD pattern and two peaks at 2θ values of 33.4° and 58.7° can be seen due to Mn_2O_3 phase. Elemental composition of the material is verified by EDX image shown in Fig. 2. The EDX images clearly show that the material is composed of Ni, Co and Mn with ratio of almost 3:3:1. The peak obtained at 1.5 KeV is due to the Au particles deposited on the sample. Prior to the FESEM characterization of the NiCoMn-Oxide sample, Au was sputtered on the sample to avoid charging effect. Figure 3 and 4 show the elemental mapping of NiCoMn-oxide. FESEM image shown in Fig. 5 confirms that nanorods of diameter 20-40 nm are formed. This nanorod type structure is very helpful for supercapacitor performance because it provides lot of surface area when dipped in electrolyte.

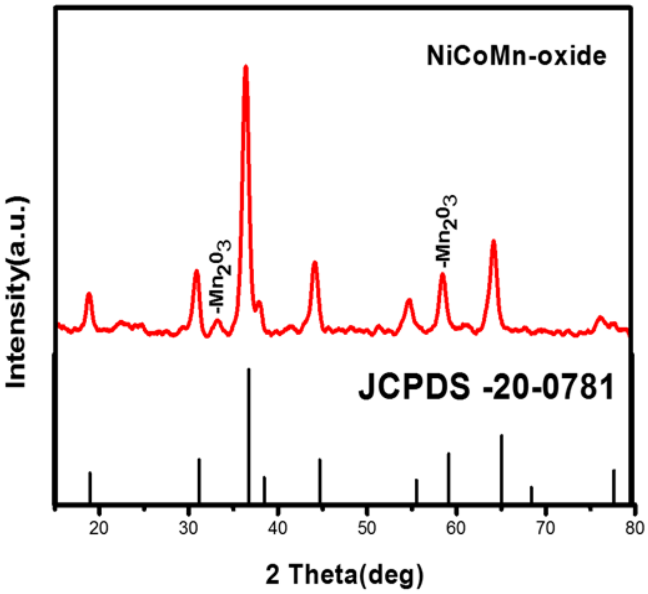

Fig. 1. X-ray diffraction pattern of mixed NiCoMn-oxide and comparison with JCPDS card -20-0781

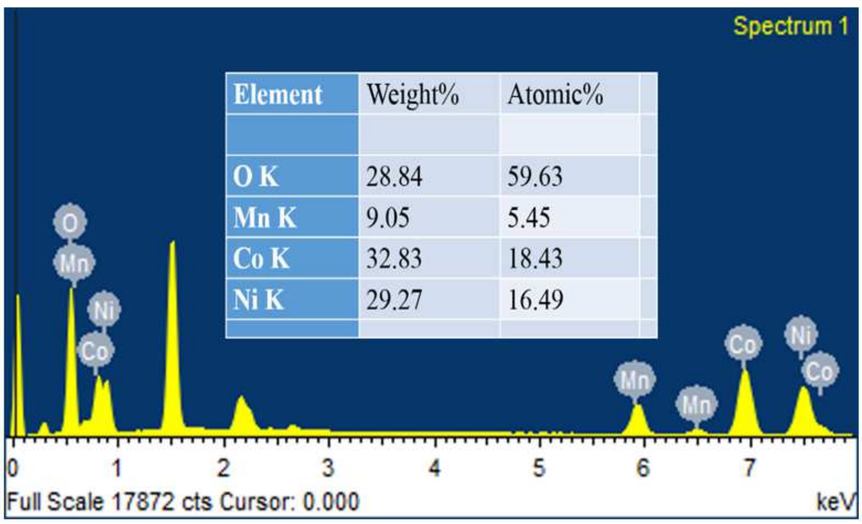

Fig. 2. EDX spectrum of mixed NiCoMn-oxide with inset showing the composition of materials

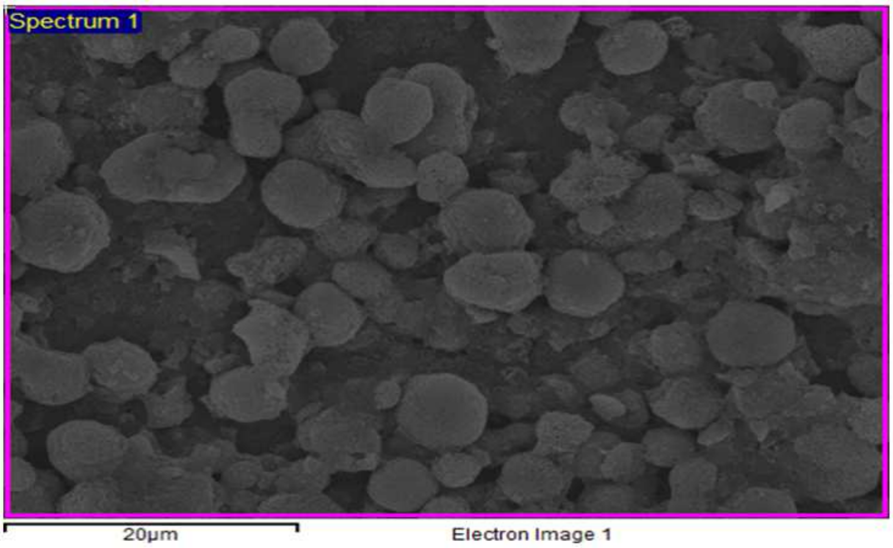

Fig. 3. Electron image over which elemental mapping was determined

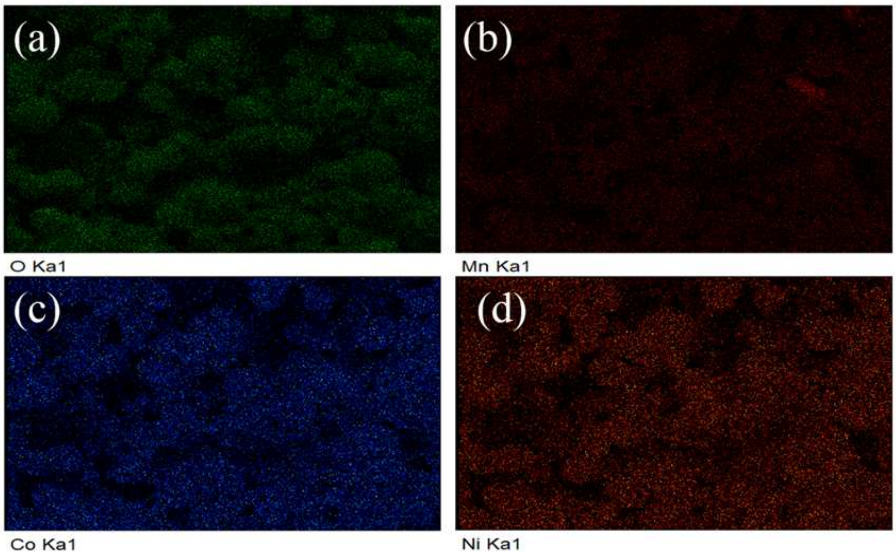

Fig. 4. Elemental mapping of mixed NiCoMn-oxide (a) presence of oxygen (b) manganese(c) cobalt(d) and nickel is confirmed from the mapping data

Supercapacitive Performance

Supercapacitive performance of the mixed NiCoMn-oxide material was obtained by three electrode cyclic voltammetry and charge-discharge test in an aqueous KOH solution. The potential window for these tests were -0.5 to 0.5 V. Figure 6a shows the cyclic voltammetry curves of the NiCoMn-oxide material at different scan rates. Specific capacitances obtained from these graphs are 208.75, 203.08 and 153.33 F/g for scan rate of 1, 2 and 4 mV/s respectively. It is clearly seen that specific capacitance is decreasing with increasing scan rate because at higher scan rate electrolyte ions do not get sufficient time to diffuse deep into the pores of the materials. At higher scan rate it only accumulates on the outer surface of the material so capacitance decreases. To get further detail about specific capacitance of the mixed NiCoMn-oxide material galvanostatic charge-discharge tests were carried out at same potential range between -0.5 to 0.5 V in aqueous KOH solution. Figure 6b shows the charge-discharge graphs of the material at different current densities. From charge-discharge graphs, specific capacitance of about 500, 334.44, 301.50 and 250 F/g estimated at different current densities 1, 2, 3 and 5A/g respectively. It is clear that specific capacitance is decreasing with the increasing current densities. The variation of specific capacitance with current density is shown in the Fig. 6c. At higher current densities potential drop across the internal resistance increases and that increase dV/dt value which may be a cause of decrease in capacitance. The Long cycling stability performance of the supercapacitor electrode is a basic requirement for a material used for practical application of energy storage devices. Figure 6d displays the capacitance retention curve of NiCoMn-oxidenanorods over 1000 charge-discharge cycles at a constant current density of 10 A/g. We observed that Ni foam supported NiCoMn-oxide exhibit an approximately 11% reduction in specific capacitance after 1000 charge-discharge cycles. Overall performance of this mixed NiCoMn-oxide nanorods show that nanorod type morphology of this mixed oxide is very helpful for supercapacitor device.

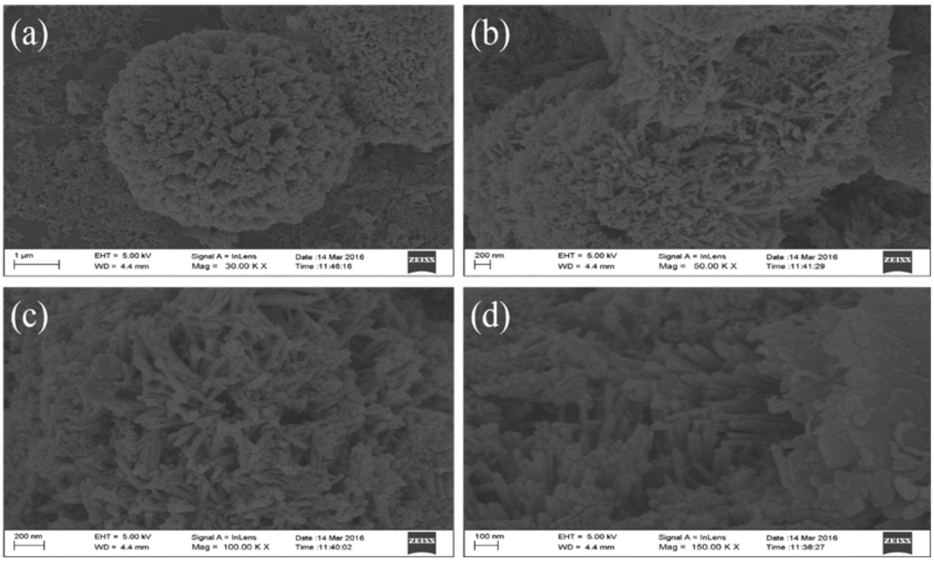

Fig. 5. FESEM image at different magnification

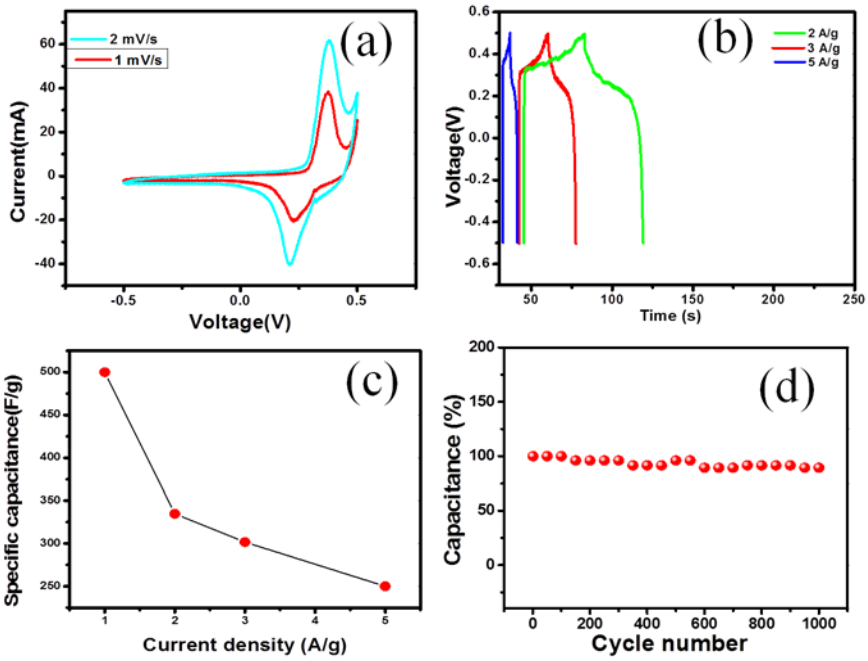

Fig. 6. Capacitive performance of NiCoMn-oxide (a) cyclic voltammetry curves at different scan rates (b) charge-discharge curves at different at different current densities, (c) Current density (A/g) Vs Specific Capacitance (F/g) curve, (d) Long cycling performance

Conclusion

This report emphasizes on synthesis procedure for mixed NiCoMn-oxide via a facile hydrothermal technique and their electrochemical capacitive properties. XRD and SEM characterization of the material have been illustrated in this report. Capacitance measurement by cyclic voltammetry and charge-discharge technique shows that this material has great potential to be used as excellent electrodes for the supercapacitor devices. In charge-discharge method, maximum specific capacitance shown by mixed NiCoMn-oxide sample was almost 500 F/g at current density 1 A/g also having excellent long cycling stability performance. The raw materials used for the synthesis of mixed NiCoMn-oxide are abundant and can be extracted in a cost-effective method. So, mixed NiCoMn-oxide is promising material for large scale practical application as supercapacitor electrodes.

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Author's Contributions

Rajat Mondal: Performed the experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

Surjit Sahoo: Performed the experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

Chandra Sekhar Rout: Proposed the idea, initiated the research, guided the student in performing the experiments, performed the experiments and contributed to the writing of the manuscript.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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