Investigation of structural electron density distribution and enhanced electrochemical properties of spinel structured MnCo_2O_4 /polyaniline nanocomposite prepared by facile and economical method

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Abstract

A nanocomposite of AB_2O_4 structured binary metal oxide and conducting polymer was synthesized by cost effective procedure. The procedure for synthesis of chosen MnCo_2O_4 was solution combustion method and the composite MnCo_2O_4 /polyaniline was obtained by physical blending. The procedure involved was very simple, speedy and inexpensive. The derived results from Scherrer and size strain plot methods showed good concurrence. The Strain value of the composite from Scherrer was 0.3406 and from SSP was 0.3332. Lattice parameter revealed in Rietveld method also matched well with Scherrer. The observations of functional groups through FT-IR confirmed the purity of the samples and presence of polyaniline and metal oxide. The morphological changes examined through High Resolution Scanning Electron Microscopy, favored enhanced conductivity in the composite showed that the changes occurred have facilitated more conductivity in the MnCo_2O_4 /polyaniline composite. The size of the nanoparticle revealed by High Resolution Transmission Electron Microscopy (HR-TEM) was 8–50 nm, showing good concurrence with the size observed in XRD which was 10–65 nm and shape in SEM. Selected Area Electron Diffraction patterns were also in confirmation of crystallinity of the samples and planes revealed by XRD. The variations in bond length and electron density distribution investigated by MEM technique, a unique report in this work also assured the improved energy storage potential of the nanocomposite material. The electro chemical analyses viz., cyclic voltammetry, chronopotentiometry and Electrochemical Impedance Spectroscopy by a three electrode assemblage with 6 M KOH as electrolyte have supported the above findings by confirming higher specific capacitance and low resistance. In the nanocomposite material synthesized. The maximum specific capacitance of the MnCo_2O_4 /polyaniline nanocomposite was 875 F/g and, the pure MnCo_2O_4 was 713 F/g at the scan rate 5 mV/s. The ESR value for pure was 4.07 Ω and that of the composite electrode was 2.75 Ω .

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Graphic abstract

Keywords Charge density distribution · Electrolyte · Spinel structure · Bond length · Energy storage · Nanocomposite

1 Introduction

In a highly energy dependent technological advancements and futuristic aspirations of humanity, supercapacitors in recent decades have been the breakthrough innovation in the field of energy storage devices [1]. In a scenario of fast depleting energy reserves across the world, high energy storage devices are expected to offer a technological solution. In spite of fulfilling the needs of the energy driven techno-centric societies for a great period of time, the batteries and capacitors are losing their grip as storage devices for their own shortcomings. Batteries offer good energy density [2] but fall short of power density [3] whereas capacitors provide good power density but fall short of energy density. Inheriting the combined advantages of both and succeeding over the challenges, supercapacitor proves its significance by unique capabilities [4]. They have extraordinarily fast charge/discharge [5] process bringing down to just milliseconds compared to hours of time in batteries. The ability to store more energy and deliver very high capacitance than ordinary capacitors [6], long life [7] with high cyclic stability, enormous power density are their special features. Exploring high efficient materials with excellent electrochemical potential to use

as electrodes in the supercapacitors, with feasible, simple and economical synthesis process has been the central focus of researches in energy storage field. This work aims an enhanced material for pseudocapacitance type supercapacitor that works by the faradic process, storing charge by redox reactions.

Metal oxides such as V_2O_5 [8], MnO_2 [9], CoO_3 [10], SnO_2 , CeO_2 [11], Fe_3O_4 [12] etc. and conducting polymers such as polyaniline [13], polypyrrole (PPy) [14], PEDOT [15] are generally used as electrode materials in Pseudocapacitors and ideal for faradic reaction. Ruthenium oxide (RuO_2) is one of the most commonly used metal oxide as pseudocapacitance electrode [16]. It possesses as large potential window and high specific capacitance, but the shortcomings are its less abundance [17], hazardous nature and expensiveness [18]. The other feasible options are NiO [19], CuO [20], MgO and ZnO. But they possess low conductivity [21], low theoretical capacitance [22] and cycle stability. In this context, binary metal oxides, such as $FeCo_2O_4$ [23], $MnCo_2O_4$ [24], $ZnCo_2O_4$ [25], $CuCo_2O_4$ [26] emerge as good alternatives for their binary spinel structure (AB_2O_4), possessing several potential oxidation states [22].

The single metal oxide Co_3O_4 is an able material with high redox behavior, exhibiting good electrochemical

properties, but it has insufficient electronic conductivity [27]. To further enhance the performance of the electrode material, a binary spinel structured metal oxide MnCo_2O_4 was chosen in this work, in which the theoretical capacitance was high. The combination of two metal oxides with two metal cations provides a scope for increased redox behavior, high cyclic stability and electrical conductivity.

Conducting polymers were also explored for supercapacitor application. Polyaniline is a cost effective conducting polymer with good assurance of electrochemical potential, which by having pi backbone [28, 29], consisting of series molecules of benzamine [30], could associate well with metal ions. With the objective of achieving an enhanced material for use as electrode in pseudocapacitor, this work presents a composite nanomaterial, MnCo_2O_4 /polyaniline in which the synergistic strength of both the binary metal oxide and a conducting polymer could be obtained. The materials in nano range structure have more potential for electro chemical behavior.

To cut the cost and make the process simple and quicker without any complexities is the prime objective of this work. Initially MnCo_2O_4 nanoparticles were prepared by solution combustion method. It was absolutely a quick and simple process and much cost effective too. The nanocomposite MnCo_2O_4 was also prepared by simple physical blending method. Following, attempts on other ratios of 0.5:0.5, 0.5:1, 0.5:2, 0.5:3, and 0.5:4, the chosen ratio of polyaniline and MnCo_2O_4 in this work was 0.5:4, as that was found to be relevant for improved efficiency. The nanocomposite MnCo_2O_4 /polyaniline was examined in comparison with pure MnCo_2O_4 , for its electro chemical capacities, through structural, morphological and electro chemical analyses. Results and evaluations of these aspects from different studies were in good accordance with each other.

The charge density study by MEM (Maximum entropy method) is a noteworthy aspect and first to be reported in this work, as the electrochemical attributes of a material could be well understood by studying the electron density and bond length that are influencing factors.

By results and observations it was confirmed that the nanocomposite MnCo_2O_4 /polyaniline revealed improved performance than the pure MnCo_2O_4 . The outcome of Maximum capacitance in the composite was 713F/g, which was higher than in the pure 875F/g.

2 Materials

The source materials chosen for material synthesis in this work were all AR grade, and utilized as they were, with no further purification. The synthesis was carried out choosing Manganese Nitrate Hexahydrate purified (Mn

$(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (extra pure AR), cobalt nitrate $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, sulfuric acid (H_2SO_4), aniline monomer, diluted HCl, distilled water, ammonium per sulfate urea and ethyl acetate.

2.1 Step 1: Solution combustion process to achieve fine powders of MnCo_2O_4 nanoparticles

The synthesis of MnCo_2O_4 nanoparticles was executed by swift and simple solution combustion method. Suitable quantities of 6 mM($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and cobalt nitrate 12 mM($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were chosen and mixed in the solvent under gradual stirring for ten minutes to form a homogenous solution. A stoichiometric proportion of the fuel material urea was added into the solution under continued stirring until it gets dissolved completely. The mixture was heated to a temperature of 80 °C for 20 min until the completion of evaporation of solvent leaving a viscous gel. Following this process, the resulting gel was placed in a hot plate of 250 °C for ten minutes. The gel gets self-ignited, followed by emanation of gases leaving dry black powder. The ignition process and formation of the resulting powder of MnCo_2O_4 was so sudden, with very short duration. The product was further subjected to calcination at 400 °C for 2 h and ground well using pestle and agate mortar to form fine powders of MnCo_2O_4 . Thus a sample of pure MnCo_2O_4 nanomaterial was obtained for further preparation of the composite. The entire process was very time saving and simple.

2.2 Step 2: Preparation of polyaniline as a component for composite

Polyaniline was synthesized through the process as reported [31].

2.3 Step 3: Physical blending to synthesis MnCo_2O_4 /polyaniline nanocomposite

For making the composite with polyaniline, initially pure MnCo_2O_4 was prepared repeating the same procedure as mentioned in step 1. The target material MnCo_2O_4 /polyaniline nanocomposite was achieved by physically blending polyaniline and MnCo_2O_4 in the ratio 0.5:4 by a pestle mortar, to obtain a homogenous mixture.

2.4 Electrochemical evaluation

The electrochemical abilities of the prepared samples were investigated through cyclic voltammetry (CV) and chronopotentiometry (CP). Electrochemical impedance spectroscopy (EIS) was also included. The examination was conducted in a three electrode arrangement in which a platinum wire, Ag/AgCl and nickel foam were set as the

Fig. 1 XRD pattern of MnCo_2O_4 and $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite

counter, reference and working electrodes respectively. The synthesized pure and composite were mixed with N-methyl-2-pyrrolidone, polyvinylidene fluoride, and carbon black homogeneously to coat the nickel foam and set as the working electrodes. Cyclic voltammetry observations were conducted in the potential range 0–0.45 V vs. Ag/AgCl and scan rates ranging from 5 to 100 mV/s. The electrolyte solution used was 6 M of KOH. The electrochemical

impedance observation was made in the frequency limit of 1 Hz to 1 MHz.

3 Result and discussion

3.1 X-ray diffraction (XRD) studies

From the XRD investigation the phase confirmation, crystalline structure and purity of the prepared materials were analysed. XRD patterns were presented in Fig. 1a. The corresponding planes of the indexed diffraction peaks were (111), (220), (311), (222), (400), (422), (511), (440). These planes implied that the structural dimension of the prepared MnCo_2O_4 nanomaterial possessed cubic spinel phase that could be ratified by the JCPDS No. 23-1237. The absence of any other peaks of impurity in the XRD graph approved the pure phase of the MnCo_2O_4 . The peaks arising at the diffraction angles 20.43° and 25.78° confirms the presence of polyaniline in the composite.

The peaks broadening is an indication of the diminished crystallite size. The average crystallite size of the pure MnCo_2O_4 and the $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ composite was 5–65 nm as calculated from the Scherrer's equation.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Table 1 Structural parameters of MnCo_2O_4 and $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite as calculated through XRD study

Materials	(hkl)	d (JCPDS) (Å)	d (cal) (Å)	a (Å)	Cell volume ($\text{\AA}^3$)	δ (10^{-5}) Line. $\text{\AA}^{-2}$	n (10^3)
MnCo_2O_4	111	4.7800	4.7775	8.2748	566.598	9.1	1.0634
	220	2.9250	2.9237	8.2694	565.4814	15.5	0.4808
	311	2.4930	2.4918	8.2643	564.4312	8.5	1.1906
	222	2.3880	2.3869	8.2688	565.3699	0.2	260.5231
	400	2.0670	2.0662	8.2640	564.3878	8.1	1.2819
	422	1.6870	1.6863	8.2597	563.4955	10	0.9142
	511	1.5911	1.5905	8.2643	564.4473	7.2	1.5231
	440	1.4613	1.4608	8.2635	564.2688	15.2	0.4947
$\text{MnCo}_2\text{O}_4/\text{PANI}$				8.2661	564.8100		
	111	4.7800	4.7787	8.2770	567.0506	4.1	3.5695
	220	2.9250	2.9240	8.2704	565.6954	2.2	9.1011
	311	2.4930	2.4923	8.2661	564.8028	3.8	4.0148
	222	2.3880	2.3871	8.2691	565.4179	0.5	77.2627
	400	2.0670	2.0664	8.2657	564.7258	0.9	34.6142
	422	1.6870	1.6863	8.2597	563.4966	3.3	4.9145
	511	1.5911	1.5906	8.2651	564.6113	12.7	0.6447
	440	1.4613	1.4608	8.2637	564.2837	0.4	133.2016
				8.2671	565.0099		

In which the value of the constant K is 0.9, as the nano-particle is spherical in shape and the wavelength of X-ray, λ is 0.154 nm. The angle of diffraction is denoted as θ and the full-width half maximum (FWHM) as β .

The lattice parameter is useful in determining the cell volume. Since the synthesized materials were found to be cubic structured confirmed by planes, the lattice constant $a=b=c$. The value of (a) could be calculated from the equation,

$$a = \left[\frac{d^2}{h^2 + k^2 + l^2} \right]^{1/2} \quad (2)$$

(d – d spacing, hkl – Miller indices or planes)

The number of dislocations per unit cell volume is given by dislocation density (δ), through which the measure of crystallographic defects could be obtained, that influences the material properties. Dislocation densities of pure and composite, calculated by the equation below, are given in Table 1. The crystallinity increased with decreased dislocation density

$$\delta = \frac{1}{D^2} \quad (3)$$

The elastic strain (E) and micro strain (ϵ) were calculated by the equations

$$E = \frac{\beta}{2 \cot \theta} \quad (4)$$

and

$$\epsilon = \frac{\beta}{4 \tan \theta} \quad (5)$$

It was observed that the strain in the composite being less than the pure indicated higher crystallite size of the composite.

The number of unit cells (n) was determined by the equation,

$$n = \frac{\pi D^3}{6V} \quad (6)$$

V -being the unit volume. The number of unit cells (n) raised with reduced dislocation density, to minimize the crystallographic defects.

The X-ray densities (dX) of the synthesized pure and composite materials were obtained by the equation

$$dX = ZM/NV \quad (7)$$

Fig. 2 **a, b** W–H plot of $MnCo_2O_4$, and $MnCo_2O_4$ /polyaniline nanocomposite

Table 2 Size-strain observation of $MnCo_2O_4$ and $MnCo_2O_4$ /polyaniline as calculated from scherrer, W–H and size-strain plot

Materials	Average crystallite size and strain (nm)						Elastic strain	X-ray density (g/cm ³)
	From scherrer's method		From W–H method		From SSP plot		(E)	(d)
	Crystallite size	strain	Crystallite size	strain	Crystallite size	Strain	(Average)	(Average)
MnCo ₂ O ₄	16.99	0.5910	18.045	0.4226	15.850	0.5637	0.1702	5.569
MnCo ₂ O ₄ /PANI	26.10	0.3406	34.8	0.21	21.802	0.3332	0.1630	5.567

Using the measure of molecules in unit cell (Z), the molecular weight (M), the Avagadro's number (N), and the unit volume (V). The values are given in the Table 1. The X-Ray density and lattice parameter are inversely related. The increased X-ray density implied reduced crystallite size.

3.2 W-HPLOT

Structural parameters vis., micro strain (ϵ) and average crystallite size (d) of the prepared pure MnCo_2O_4 and composite MnCo_2O_4 /polyaniline were further studied by WH-Plot. The corresponding equation is

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \quad (8)$$

The W-H illustrations of the pure and composite are presented in Fig. 2a, b marking $\beta \cos \theta$ against $4 \sin \theta$ for

all the peaks. Straight line appeared in both the graphs of pure and composite. Average crystallite size and micro strain were obtained from the intercept and slope respectively, and the values are given in Table 2. The results are in concurrence with that of Scherrer's.

3.3 Size-strain plot method (SSP)

The isotropic dimension of the crystal is revealed by W-H plot, indicating the influence of strain that causes uniform shift in the peaks of diffraction. Size and strain are more effectively revealed by SSP. The crystallite size could be derived from Lorentzian function and profile of strain by Gaussian function. The corresponding equation is

$$(d\beta_{hkl} \cos \theta)^2 = (k/D)^2 (d^2 \beta_{hkl} \cos \theta) + (\epsilon/2)^2 \quad (9)$$

Fig. 3 a, b Size-strain plot of MnCo_2O_4 and MnCo_2O_4 /polyaniline nanocomposite

Fig. 4 a, b Root mean square plot of MnCo_2O_4 and MnCo_2O_4 /polyaniline nanocomposite

The constant K is assigned the value $\frac{3}{4}$ due to the spherical shape of particles. Lattice spacing is denoted as d_{hkl} . D and ϵ_a are the average crystallite size and apparent strain. In the size strain plot, the x axis is plotted by $d_{hkl}^2 \beta_{hkl} \cos \theta_{hkl}$ and the y axis by $(d_{hkl}^2 \beta_{hkl} \cos \theta_{hkl})^2$. From the plot, the crystallite size is obtained from the linearly connected data and the strain from intercept y . The size strain plot is presented in Fig. 3a, b. The size-strain observations from size strain plot was in good accordance with Scherer method as evident from the Table 2.

3.4 Root mean square (RMS) strain

The relation of the RMS strain and maximum lattice strain is defined by the Wilson method, in which d is the observed and d° is the ideal interplaner spacing. The variation in d spacing and root mean square (RMS) strain were plotted against each other along X and Y axes are presented in the Fig. 4a, b. As all the points in the plot meet in a straight line making an angle of 45° to the X axis, the strain values agreed with each other.

Fig. 5 **a, b** Rietveld refinement of X-ray diffraction MnCo₂O₄ and MnCo₂O₄/polyaniline nanocomposite **c** 3D Unit cell for MnCo₂O₄

Table 3 Structural parameter of MnCo_2O_4 and $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ obtained from Rietveld refinement method

Materials	Space Group	Crystal structure	Lattice parameter (Å)	Volume (Å ³)	R _p (%)	R _{wp} (%)	X ²	R _F (%)
MnCo_2O_4	F d-3 m	Cubic	a = b = c 8.2668 $\alpha = \beta = \gamma = 90^\circ$	564.95 Å ³	0.185	0.254	1.122	0.528
$\text{MnCo}_2\text{O}_4/\text{PANI}$	F d-3 m	Cubic	a = b = c 8.2680 $\alpha = \beta = \gamma = 90^\circ$	565.19 Å ³	0.182	0.241	1.149	0.238

3.5 Rietveld refinement

Rietveld refinement, a powder profile fitting technique was employed to study the structural parameters more in detail. Background fitting, lattice constant, cell parameters, phase purity and shape aspects of the pure and composite were studied well by Rietveld refinement with XRD information. The initial parameter of space group Fm – 3 m of cubic spinel structure was given as the input. The obtained patterns are presented in Fig. 5a–c from which could be observed that Chi square values decreased. The observed and calculated values fitted with each other, the background being fitted along the polynomial curve. Pure phase of MnCo_2O_4 and $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ were confirmed by the patterns. The obtained values from Rietveld refinement method, are given in the Table 3.

3.6 Charge density analysis by MEM study

The bond length and charge distribution among the atoms are best revealed by MEM study. The charge density aspects are explored by MEM, investigating the unit cell of the material in multiple dimensions. From the data obtained from Rietveld, the charge density was determined by PRIMA, pictured and plotted by VESTA, in one, two and three dimensional perspectives [32]. The outcomes of MEM for pure and composite materials are given in Table 4. The three dimensional image of pure MnCo_2O_4 is demonstrated in Fig. 5c in which the positions of Mn, Co and O atoms are vividly seen. The (111) plane of the unit cell is shaded as shown in Fig. 6a from the 2D view of the pure and composite, narrow contour lines are observed between Mn–O, and the contour region between Co–O is little broader as seen in Fig. 6b, c. The (200) plane of unit

cell and 2D view of the pure and composite is shown in Fig. 6d, e, f. The ionic character of the materials observed through MEM images, indicated enhanced conductivity in the composite material. The electron density of Mn–O and Co–O in the composite indicated ionic nature. The electron density observation in the pure was little higher indicating less ionization. The one dimensional charge density observation plotted as a graph is placed in Fig. 7a, b revealing the Mn–O bond and Co–O bond for the pure MnCo_2O_4 and $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite. From the tabulated values of bond length and electron density of the materials, through indepth view of MEM, the composite $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ possessed higher ionic nature and better conductivity is evident.

3.7 Fourier-transform infrared spectroscopy study

The functional groups and mode of vibrations of the prepared samples were investigated by FTIR technique to further confirm the purity of the samples prepared. FTIR spectrum was generated in the wave number range of 2000–450 cm^{-1} . The corresponding graph is given in Fig. 8, plotting wave number in x axis against transmittance in Y axis. The metal–oxygen functional group with stretching vibrations was revealed by the bands appearing at 552 and 656 cm^{-1} . This confirms the phase of MnCo_2O_4 . The –C=C stretching vibrations pertaining to benzenoid and quinonoid, were reflected by the peaks forming at 1481 cm^{-1} and 1584 cm^{-1} , confirming the presence of polyaniline. The peak around 1104 cm^{-1} due to the aromatic C–H in-plane deformation. The peaks appearing at 723 cm^{-1} , 809 cm^{-1} which indicate the out-of-plane deformation of C–H in the 1,4-disubstituted benzene ring. These are confirms well with the emeraldine salt form of PANI [33].

Table 4 Bond lengths and electron density values of MnCo_2O_4 , $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite

Samples	Mn–O		Co–O	
	Bond length (Å)	Electron density at BCP ($\text{e}/\text{\AA}^3$)	Bond length (Å)	Electron density at BCP ($\text{e}/\text{\AA}^3$)
MnCo_2O_4	1.9340	1.5908	1.9447	0.9906
$\text{MnCo}_2\text{O}_4 + \text{PANI}$	1.9352	1.4314	1.9508	0.9885

Fig. 6 **a** 3D unit cell with (111) plane shaded **b** 2D contour map on (111) plane for pure MnCo_2O_4 and $\text{MnCo}_2\text{O}_4/\text{POLYANILINE}$ nanocomposite **c** 2D contour map on (111) plane for $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite. **d, e, f** The 2D view of (200) plane of the unit cell of $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite

Fig. 7 **a** one dimensional electron density profiles along Mn and O atoms in pure and composite MnCo_2O_4 . **b** One dimensional electron density profiles along Co and O atoms in pure and composite MnCo_2O_4

Fig. 8 FT-IR spectra of MnCo_2O_4 and MnCo_2O_4 /polyaniline nano-composite

3.8 High resolution scanning electron microscopy

The morphological aspects of the synthesized materials were analysed through high resolution scanning electron microscope images, as the modifications in morphology is a factor in deciding the electrochemical characteristics of nanomaterials. Images of SEM observations are displayed in Fig. 9a, b from which the particle sizes were revealed to be 5–70 nm for the pure and nanocomposite respectively. The morphology demonstrated spherical shape of MnCo_2O_4 nanoparticles, distributed uniformly with

clustered appearance. The image of the composite showed the surface of polyaniline being thrust over by spherical nanoparticles of MnCo_2O_4 .

This modification in morphology was expected to result in enriched electrochemical behaviour. The elemental mapping images of MnCo_2O_4 /polyaniline demonstrates well the uniform spread of manganese, cobalt, oxygen, carbon and nitrogen, all through the composite confirming the presence of polyaniline as seen in Fig. 9c (I, II, III, IV, V).

3.9 High resolution transmission electron microscopy

The materials synthesized were investigated for their morphology, size and hkl planes through High Resolution Transmission Electron Microscopy perspective. The images exhibited the clustered spherical shaped particles of the pure MnCo_2O_4 and they were lodged over the spread of the polyaniline in the composite MnCo_2O_4 /polyaniline that reveals 8–50 nm range of size. These values were very closely matching with the size measured through XRD. High Resolution Transmission Electron Microscopy images are given in Fig. 10a, b.

The agglomeration could be attributed to the interaction between the particles. The selected area electron diffraction patterns are presented in Fig. 10c, d. The polycrystalline character of the nanoparticles was well indicated by the concentric circles and distinct diffraction rings.

3.10 Cyclic voltammetry analysis

The electro chemical aspects of the materials for performance as electrode in supercapacitor were examined

Fig. 9 **a, b** HR-SEM images of MnCo₂O₄ and MnCo₂O₄/polyaniline nanocomposite **c** (I), (II), (III), (I V), (V) mapping image of MnCo₂O₄/polyaniline

Fig. 10 **a, b** HR-TEM image of MnCo_2O_4 and MnCo_2O_4 /polyaniline nanocomposite **c, d** SAED image of MnCo_2O_4 and MnCo_2O_4 /POLYANILINE

through cyclic voltammetry. The analysis was performed in 6Mof KOH electrolyte solution for which the potential ambit was 0 to 0.45 V at scan rates varying from 5 to 100 mV/s. The cyclic voltammetry curves are presented in Fig. 11 a, b. At 5 mV/s, the low scan rate, a pair of redox peaks was observed, as shown in the graph. The specific capacitance of the pure and composites were obtained from the equation below using integration of the cyclic voltammetry curve area [34]

$$SC = \frac{1}{V \times m \times (V_a - V_c)} \int_{V_a}^{V_c} IV \times dV \quad (10)$$

where $V_a - V_c$ is the potential window. Clear redox peaks were seen for both the materials MnCo_2O_4 and MnCo_2O_4 /polyaniline. The higher specific capacitance was confirmed for the composite in comparison to the pure as the calculated maximum specific capacitance was 713 F/g and 875 F/g for MnCo_2O_4 and MnCo_2O_4 /polyaniline respectively at the scan rate of 5 mV/s. Lower the scan rate, higher was the specific capacitance obtained and vice versa. At lower scan rate the electrolyte ions could reach and access the

active sites of the interior deepness of the electrode material, for having sufficient time to diffuse into it. Unlike that, as the electrolyte ions could interact only with the exterior surface locations at higher scan rates, the value of specific capacitance falls low.

3.11 Galvanostatic charge/discharge analysis

Following the cyclic voltammetry study, chronopotentiometry analysis was also carried out to study the electro chemical abilities and determine the specific capacitance of the materials. The CP study was performed in 6 M KOH electrolyte solution, in the potential ambit of 0–0.4 V at varying current densities 0.5–4 A/g and charge/discharge process of both the pure and composite were examined. It was observed that the discharge time exhibited by MnCo_2O_4 /polyaniline electrode was longer compared to the pure MnCo_2O_4 electrode, implying increased electro chemical performance in the composite as could be seen from the CP curves given in Fig. 12a, b.

The specific capacitance (C_s) obtained for both pure and composite materials with corresponding current

Fig. 11 **a, b** CV curves of MnCo₂O₄ and MnCo₂O₄/polyaniline nanocomposites at different Scan rates

densities 0.5 A/g were 555 F/g, 665 F/g respectively, as calculated by the equation.

$$CS = \frac{I \cdot \Delta t}{m \cdot \Delta v} \quad (11)$$

where I —Applied current (A), Δt —Time taken for the discharge, m —The mass of active electrode, Δv —The discharge potential.

The increased efficiency with higher specific capacity outcome in the composite as calculated from cyclic voltammetry study is well confirmed by CP curves also. The achieved maximum specific capacitance of 665 F/g in MnCo₂O₄/polyaniline was higher than in the MnCo₂O₄ with 555 F/g by CP observations. The improved efficiency could be attributed to the enhanced charge transfer process between the electrolyte and the composite electrode. The spread of polyaniline in the composite provides ample surface area, restricting the accumulation

of MnCo₂O₄ nanoparticles, thereby persuading effective charge transfer.

3.12 Electro chemical impedance spectroscopic study

The materials were investigated for their electrochemical performance in electrode–electrolyte system through electro chemical impedance spectrum. Marking Z' along the X and Z'' along the y axes, The Electrochemical impedance Spectroscopy observation was plotted in the frequency region of 1 Hz to 1 MHz for pure and composite electrodes as seen from the graph in Fig. 12c. This is an indication that, the composite electrode possessed lower resistance. When the frequency was low, straight line was observed for both the materials. The Warburg impedance is a reflection of diffusion of ions into the material acting as electrode and diffusion resistance in the KOH electrolyte.

Fig. 12 **a, b** Charge discharge curve of MnCo_2O_4 and $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ composite materials **c** EIS spectrum of MnCo_2O_4 , $\text{MnCo}_2\text{O}_4/\text{polyaniline}$

Fig. 13 **a** CV curves of $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite in two-electrode system **b** CP curves of $\text{MnCo}_2\text{O}_4/\text{polyaniline}$ nanocomposite in two-electrode system

Table 5 Specific capacitance value of MnCo₂O₄ and MnCo₂O₄/polyaniline nanocomposite calculated from CV

Materials	Specific capacitance				
	5 mV/s	25 mV/s	50 mV/s	75 mV/s	100 mV/s
MnCo ₂ O ₄	713	596	480	428	399
MnCo ₂ O ₄ /PANI	875	650	633	570	473

The solution resistance (Rs) which is a measure of ionic conductivity through the electrolyte, observed for the pure electrode was 4.07 Ω and for the composite electrode were 2.75 Ω. The lower (Rs) value of the composite implied higher conductivity [35] of MnCo₂O₄/polyaniline by increased active sites facilitating the entry of ions

3.13 Electrochemical characterization of symmetric two electrode assembly

The efficiency of the MnCo₂O₄/polyaniline as electrode material was examined in a symmetric two electrode setting with potential window of 0.0–0.6 V in different scan rates. This observation could demonstrate well the electrochemical performance of the material as in a real time capacitor system. The cyclic voltammetry curve is presented in Fig. 13a revealing the electrochemical characteristics of the tested electrode material. The absence of redox peak in the Fig. 13a is an indication of the non-faradic charge–discharge process. The cyclic voltammetry curves displayed the Electric Double Layer Capacitor nature of the capacitance. Higher capacitance

of MnCo₂O₄/polyaniline was evident from the stability of the curves with no fluctuations (Table 5).

The CP curve is presented in Fig. 13b as obtained from running MnCo₂O₄/polyaniline in the two electrode assemblage in a range of varying current densities. The specific capacitance was calculated applying the equation

$$C_s = \frac{4 \cdot C}{m} \quad (12)$$

where, m is the sum of the masses of the two electrodes. The specific capacitance values obtained for varying current densities of (0.25 A/g), 0.5 (A/g), (0.75 A/g) and (1A/g) are 113 F/g, 108 F/g, 105 F/g and 103 F/g respectively. The comparison is given in the Table 6 below.

4 Conclusion

To sum up, a simpler, economical and less time consuming solution combustion- physical blending method based nanocomposite MnCo₂O₄/polyaniline was synthesized and analysed for supercapacitive enhancement. The pure MnCo₂O₄ and composite MnCo₂O₄/polyaniline were thoroughly examined for their characteristics by relevant studies. From the results and discussion higher performance of the nanocomposite as a supercapacitive electrode material was evident. The results from various studies were well matching. The maximum specific capacitance achieved for MnCo₂O₄/polyaniline was 875 F/g and for the pure MnCo₂O₄ was 713 F/g at 5 mV/s scan rate. The nanocomposite showed higher capacitance and lower

Table 6 Findings of this work and other previous works

S. no	Sample	Preparation Methods	Specific capacitance	Electrolyte,	Refs.
1	MnCo ₂ O ₄ nanosheet	Electro deposition	290 F/gat 1 mV/s	2 M KOH	[36]
2	MnCo ₂ O ₄ nanowire array	Hydrothermal method	349.8 F/g1 at 1 A/g	1MKOH	[37]
3	MnCo ₂ O ₄	Combustion method	497 F/g at 0.5 A/g	1MKOH	[38]
4.	MnCo ₂ O ₄₋₅ spindle-like microstructures	Solvothermal synthesis	343 F/g at 0.5A/g	2 M KOH	[39]
5.	MnCo ₂ O ₄₋₅ nanoparticles	Chemical transformation method	158 F/g at 5 mV/s	1 M Na ₂ SO ₄	[40]
6.	manganese spinel graphene hybrid nanoplates	Mixed solvothermal method	571 F/g at 1 A/g	1 M KOH	[41]
7	MnCo ₂ O ₄₋₅	Hydrothermal route	151.2 F/g at 5 mV/s	1 M KOH	[42]
8	MnCo ₂ O ₄ Nanosheet	D-glucose-assisted solvothermal process	346 at 1 A/g	6 M KOH	[43]
9	Cracked ellipsoidal-like MnCo ₂ O ₄₋₅ /graphene	Chemical transformation Hydrothermal	252.3 F/g at 0.5 A/g	2 M KOH	[44]
10	MnCo ₂ O ₄ /3DG	Solid phase synthesize method	503.75 F/g 1 A/g	3 M KOH	[45]
11.	MnCo ₂ O ₄	Solution combustion method	555 F/g 0.5 A/g	6 M KOH	Present work
12	MnCo ₂ O ₄ nanosheets	One-step electro deposition	290 F/g at 1 mV/s	2 M KOH	[36]
13.	MnCo ₂ O ₄ nanomaterial	Low temperature solution combustion method	10 Mv/s was 270 F/g	1 M sodium nitrate	[46]

resistance proving to be a relevant electrode material for use in supercapacitor.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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