#### **ORIGINAL PAPER**



# Morphology controlled synthesis of one-dimensional CoMn<sub>2</sub>O<sub>4</sub> nanorods for high-performance supercapacitor electrode application

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#### Abstract

Facile preparation of one-dimensional spinel material is highly attractive for their widespread usage in energy storage devices. Herein, we report uniform one-dimensional  $CoMn_2O_4$  nanorods were prepared by cetyl trimethyl ammonium bromide (CTAB) assisted hydrothermal technique followed by subsequent calcination process. The prepared materials were characterized to different types of physicochemical features to analyze the appropriateness of the material for the supercapacitor electrode application. The crystalline nature and bonding properties were examined by X-ray diffraction analysis and Fourier-transform infrared spectroscopic analysis. The structural and morphological features of prepared materials were analyzed using field emission scanning electron microcopy which reveals the edge curved one-dimensional nanorod structure. Furthermore, cyclic voltammetric, chronopotentiometric and electrochemical impedance spectroscopic analyses were employed to evaluate the electrochemical properties of the freshly prepared  $CoMn_2O_4$  materials. The cyclicvoltammetric studies provide the specific capacitance of 895 Fg<sup>-1</sup> at a scan rate of 5 mV s<sup>-1</sup>, whereas chronopotentiometric curves provide the highest specific capacitance of 802 Fg<sup>-1</sup> at current density of 1 Ag<sup>-1</sup>. The cyclic stability analysis shows the excellent cyclic stability which retains 87% of initial capacitance after the continuous 5000 CV cycles at a scan rate of 100 mVs<sup>-1</sup>. The outstanding electrochemical features unquestionably make  $CoMn_2O_4$  as a good candidate for supercapacitor devices.

Keywords Spinel · CTAB · Hydrothermal · CoMn<sub>2</sub>O<sub>4</sub> nanorods · Energy storage · Supercapacitors

## Introduction

The rapid economic growth in recent decades has endorsed the alarming conflict between high requirement of fossil fuels and their restricted resources. To resolve this problem, researchers have been looking for efficient relevant technologies to fabricate renewable energy storage and conversion devices whereas conserving the surroundings(Zhu et al. 2015; Wang et al. 2016; Abbasi et al. 2020; Amiri et al. 2020; Moosavifard et al. 2020). Supercapacitors or electrochemical capacitors, as a new kind of energy storage device, have fascinated more consideration since their interesting characteristics such as high-power density than batteries and high energy density than conventional capacitors (Chen et al. 2014; Xu et al. 2014a, b). With a combination, consolidation of high power density and comparatively high energy density, supercapacitors have been generally utilized in various kinds of applications including memory backup systems, wireless networks, automotives, portable consumer electronics, motor starters and other self-powered micro/ nano-electronics (Simon 2008; Zhu et al. 2008; Yesuraj et al. 2017). Supercapacitors can be categorized into two types such as electric double-layer capacitors (EDLC) and pseudocapacitors based on the energy storage mechanism (Zhang et al. 2017, 2019). In electric double-layer capacitors, the charge is stored by accumulation of charges at the electrode/electrolyte interface by achieving the formation of electric double layers (Makino et al. 2013; Wulan Septiani et al. 2020). Mostly, carbon-based materials (carbon nanotube, activated carbon, carbon aerogel and graphene oxide) exhibit the electric double layer energy storage mechanism. On the other hand, the pseudocapacitor materials such as metal oxides and conducting polymers can store charges

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through rapid and reversible surface redox reactions and it possesses much higher specific capacitance than electric double layer capacitor materials(Chen et al. 2013; Li et al. 2013; Wu et al. 2014). Therefore, developing of novel and proficient pseudocapacitor electrode materials with attractive electrochemical performances such as high electrical conductivity, electrochemical stability combined with novel structural features such as high surface area and porous structure is the hot research topic in recent years.

Transition metal oxides such as NiO (Yan et al. 2014),  $MnO_2$ (Boisset et al. 2013),  $Co_3O_4$ (Xia et al. 2011), MoO<sub>3</sub>(Zhao et al. 2013), V<sub>2</sub>O<sub>5</sub>(Yang et al. 2013), SnO<sub>2</sub>(Geng et al. 2020) and ZnO (Naeem et al. 2020) materials have been examined intensively as the advanced electrode materials for supercapacitor device application since they exhibit multiple oxidation states for fast redox reactions, low-cost and eco-friendly nature. In contrast, these aforementioned materials often experience the poor cycle life, limited rate capability and poor mechanical stability when used as supercapacitor electrode materials (An et al. 2019; Li et al. 2019; Low et al. 2019). Also, they exhibit relatively low capacitance when compared with RuO<sub>2</sub> (Hu et al. 2006) (identified as a potential supercapacitor electrode material) and these limitations have restricted their utilization in commercial supercapacitors. Consequently, it is a huge task to prepare electrode materials with superior electrochemical performances and fulfill the drawbacks of single transition metal oxide-based supercapacitor electrode materials.

Recently, mixed metal oxides such as ZnCo<sub>2</sub>O<sub>4</sub>(Mary and Bose 2018), NiCo<sub>2</sub>O<sub>4</sub>(Pu et al. 2013), MnCo<sub>2</sub>O<sub>4</sub>(Che et al. 2016),  $CuCo_2O_4$ (Vijayakumar et al. 2017) and CoMn<sub>2</sub>O<sub>4</sub> are demonstrated as efficient electrode materials for supercapacitors because of their mixed valence states that afford higher electrochemical activity and superior electronic conductivity than single metal oxides. Among them, Mn-based materials are of great interest because of their high electrical conductivity, low-cost and easily abundance and eco-friendly nature. Spinel structured CoMn<sub>2</sub>O<sub>4</sub> exhibits high electrical conductivity and attractive electrochemical features when compared with corresponding single metal oxides such as  $Co_3O_4$ and  $Mn_3O_4$  (Yunyun et al. 2015). By altering the surface morphological features, the electrochemical properties of the CoMn<sub>2</sub>O<sub>4</sub> materials could be considerably enhanced. Recently, Ji and Zhou et al. prepared cubic CoMn<sub>2</sub>O<sub>4</sub> particles which directly grown on Ni foam through hydrothermal method. The prepared CoMn<sub>2</sub>O<sub>4</sub> particles were used as binder-free electrode which provides a capacity of 140.6 mA h  $g^{-1}$  at 1 mA cm<sup>-2</sup> in three electrode configuration and an asymmetric device exhibits a specific capacitance of 77.8  $Fg^{-1}$  at 2 mA cm<sup>-2</sup> (Chen et al. 2019a, b). Potheher et al. demonstrated CoMn<sub>2</sub>O<sub>4</sub> material synthesized through hydrothermal technique. This material possessed the specific capacitance of 700  $Fg^{-1}$  at a scan rate of 5 mV s<sup>-1</sup>(Vigneshwaran et al. 2016). Furthermore, Xuetang and Fan et al. established Spinel CoMn<sub>2</sub>O<sub>4</sub> nanosheet arrays grown on Ni foam via hydrothermal route. The nanosheet arrays provide a specific capacitance of 1529 Fg<sup>-1</sup> and good rate capability. The cyclic stability studies showed that the 100% stability after 3000 cycles (Yunyun et al. 2015). Wang et al. prepared both  $MnCo_2O_4$ and CoMn<sub>2</sub>O<sub>4</sub> nanowires using thermal decomposition of organometallic compounds. The MnCo<sub>2</sub>O<sub>4</sub> and CoMn<sub>2</sub>O<sub>4</sub> affords the specific capacitance of 2108 and 1342  $Fg^{-1}$ , respectively, at a current density of 1  $Ag^{-1}$  (Paquin et al. 2015). Consequently, it is important to take essential steps for enhancing the supercapacitive properties of the CoMn<sub>2</sub>O<sub>4</sub> materials. The various synthetic routes are widely explored, including hydrothermal method, templates synthesis, co-precipitation method, thermal conversion, electrochemical deposition and many other methods. Among them, hydrothermal method has been recognized as a powerful method to provide size-controllable and well-ordered nanostructured morphology. In this endeavour, we followed the CTAB-assisted hydrothermal method to prepare  $CoMn_2O_4$  materials (Dhand et al. 2015).

Herein, we report one-dimensional  $\text{CoMn}_2\text{O}_4$  nanorods via CTAB-assisted hydrothermal technique followed by subsequent calcination process which also involved the variation of CTAB template concentration. Electrochemical measurements show that the prepared  $\text{CoMn}_2\text{O}_4$  material had better supercapacitive features with a high specific capacitance of 895 Fg<sup>-1</sup> at a scan rate of 5 mVs<sup>-1</sup>. In addition, cyclic stability studies shows that the prepared  $\text{CoMn}_2\text{O}_4$  material retained 92% of specific capacitance after 2000 cycles. The outstanding electrochemical features made as the freshly prepared  $\text{CoMn}_2\text{O}_4$  nanorod as a promising material for supercapacitor electrode applications.

# **Experimental section**

## Materials

All chemical reagents were analytical grade and utilized as received. Cobalt(II) nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), poly (vinylidene fluoride) (PVDF), carbon black and cetyl-trimethylammonium bromide (CTAB) were procured from Sigma Aldrich. N-methyl- 2-pyrrolidone (NMP), potassium hydroxide (KOH), Manganese nitrate tetrahydrate (Mn(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O) and ethanol were purchased from SRL (India). In addition, acetone and nickel foil (0.025 mm thickness) were received from Alfa aesar.

## Synthesis of CoMn<sub>2</sub>O<sub>4</sub> materials

The CTAB-assisted hydrothermal synthetic method has been followed for the preparation of spinel CoMn<sub>2</sub>O<sub>4</sub> materials. In a typical preparation of CoMn<sub>2</sub>O<sub>4</sub> materials, 1 mM of cobalt nitrate hexahydrate and 2 mM of manganese nitrate tetrahydrate were dissolved in 70 ml of DI water at room temperature using magnetic stirrer with rotating speed of 450 rpm. Then, CTAB template was added to the above suspension and stirred for half an hour. After the complete dissolution of all precursors, the suspension was transferred to 100 ml of teflon lined stainless steel autoclave and kept in hot air oven. The hot air oven was heated to 180 °C for 24 h and then it is allowed to cool room temperature normally. The resultant precipitate was collected and washed with water and ethanol to remove impurities and unreacted species. Then, it is dried in a hot oven at 80 °C for 12 h and calcined in air at 300 °C for 3 h with ramping rate of 10 °C/min. In this endeavour, the CTAB concentration was varied to get the different type of nanostructure CoMn<sub>2</sub>O<sub>4</sub> materials. The CTAB concentrations such as 0, 0.005, 0.01 and 0.02 M were used to prepare CoMn<sub>2</sub>O<sub>4</sub>-1, CoMn<sub>2</sub>O<sub>4</sub>-2, CoMn<sub>2</sub>O<sub>4</sub>-3 and CoMn<sub>2</sub>O<sub>4</sub>-4 samples, respectively. Figure 1 shows the schematic diagram of synthesis of CoMn<sub>2</sub>O<sub>4</sub>-4 material.

## Material characterization

The X-ray diffraction (XRD) patterns were acquired on a PANalytical X-pert PRO diffractometer instrument with Ni filtered Cu-K $\alpha$  radiation ( $\lambda$ =0.154060 nm) at a voltage of 40 kV and a current of 40 mA. Fourier transform infrared spectroscopy (FTIR) was recorded using Perkin-Elmer RX1' spectrophotometer instrument with 4 cm<sup>-1</sup> resolution for 20 scans and field-emission scanning electron microscope (FE-SEM, Hitachi SU6600) operated with an accelerating voltage of 15 kV for obtained morphological features.

## **Electrochemical measurements**

For electrochemical measurement, the working electrode comprising of 70 wt% of active material, 10 wt% of carbon black and 10 wt% of poly (vinylidene fluoride) (PVDF). For



Fig. 2 XRD patterns of  $CoMn_2O_4$  materials. a  $CoMn_2O_4$ -1, (b)  $CoMn_2O_4$ -2, (c)  $CoMn_2O_4$ -3 and (d)  $CoMn_2O_4$ -4

electrochemical analysis, the above-mentioned materials made slurry with N-methyl-2- pyrrolidone (NMP) solvent. The resultant slurry was coated uniformly on the surface (two side) of nickel foil and dried in hot air oven at 60 °C for 12 h. The active material's weight of the electrode is approximately 3 mg. The supercapacitor analysis was done on a biologic electrochemical workstation (Model VSP-150) in three electrode set up using 2 M KOH as an electrolyte. Standard calomel electrode and platinum foil were used as counter and reference electrodes, respectively. The supercapacitive properties of the CoMn<sub>2</sub>O<sub>4</sub> material were examined by cyclic voltammetric (CV), chronopotentiometric (CP) or galvanostatic charge/discharge (GCD) and electrochemical impedance studies (EIS). Additionally, cyclic stability test was also carried out to demonstrate cycle life of the  $CoMn_2O_4$  electrodes.

# **Results and discussion**

## X-ray diffraction analysis

The phase purity and crystallographic nature of the freshly prepared  $CoMn_2O_4$  materials were examined by

**Fig.1** Schematic diagram for synthesis of CoMn<sub>2</sub>O<sub>4</sub>-4 material



X-ray diffraction studies as shown in Fig. 2. The intensities and positions of the peaks are more consistent with the standard diffraction pattern of the tetragonal, spinel  $CoMn_2O_4$  phase with JCPDS card no.- 01-077-0471. The distinctive peaks located at 29.3, 30.8, 33.3, 36, 36.8, 44.2, 52.7, 56.5, 58.3, 65.6, and 71.2° are indexed to the (112), (200), (103), (211), (202), (220), (105), (303), (321), (116) and (305) planes, respectively. All diffraction peaks are appeared as same, however, intensities only vary.



Fig.3 FTIR spectra of  $CoMn_2O_4$  materials. a  $CoMn_2O_4\mathchar`-1,$  (b)  $CoMn_2O_4\mathchar`-2,$  (c)  $CoMn_2O_4\mathchar`-3$  and (d)  $CoMn_2O_4\mathchar`-4$ 

#### FTIR spectroscopic analysis

The internal structure and bonding properties of the synthesized materials such as  $CoMn_2O_4$ -1,  $CoMn_2O_4$ -2,  $CoMn_2O_4$ -3 and  $CoMn_2O_4$ -4 were evaluated using FTIR spectroscopic analysis as shown in Fig. 3. It is worth to note that the impurity peaks do not visible in FTIR spectrum confirms the formation of pure  $CoMn_2O_4$  materials. The FTIR spectrum provides two high-intensity peaks which are the characteristic peak of the spinel  $CoMn_2O_4$  materials. The peaks appeared at 652 and 540 cm<sup>-1</sup> are due to bending vibration of cobalt oxide at tetrahedral sites and manganese oxide at octahedral sites, respectively (Hosseini et al. 2011; Vigneshwaran et al. 2016). The basic characterization results such as XRD and FTIR have established the formation, crystalline phase and internal structure of the  $CoMn_2O_4$  in the present CTAB assisted hydrothermals synthetic method.

## Morphological analysis

The morphological features of  $CoMn_2O_4$  were evaluated using FE-SEM analysis as shown in Figs. 4, 5. Figure 4 a, b shows the lower and higher magnification FESEM images of  $CoMn_2O_4$ -1 materials which shows irregular-shaped nanoparticles, which was synthesized without CTAB template. The definite-shaped nanoparticles with the size of 90±5 nm are formed when introducing of 0.005 M of CTAB template (CoMn\_2O\_4-2) as shown in Fig. 4 c and d. When the CTAB concentration increased to 0.01 M (CoMn\_2O\_4-3), the same

Fig. 4 Lower and higher magnification FESEM images of a and  $b \operatorname{CoMn_2O_4-1}$  and c and  $d \operatorname{CoMn_2O_4-2}$  materials







morphology was obtained and the shape of the nanoparticles are getting elongated which shows in Fig. 5a, b. Figure 5c, d shows the lower and higher magnification images of  $CoMn_2O_4$ -4 material which shows the edge-curved nanorod morphology.

The size and length of the nanorods are  $30 \pm 5$  nm and  $150 \pm 5$  nm, respectively. These results signify that the CTAB template has more consequences on the morphology of the CoMn<sub>2</sub>O<sub>4</sub> materials. The nanorods morphology is more favored for electrochemical process since it provides high surface area for electrochemical redox reactions.

## **Electrochemical analysis**

The supercapacitive features of the freshly prepared  $CoMn_2O_4$  electrodes such as  $CoMn_2O_4$ -1,  $CoMn_2O_4$ -2,  $CoMn_2O_4$ -3 and  $CoMn_2O_4$ -4 were examined in a three electrode configuration using 2 M KOH electrolyte. Usually, the electrochemical properties can be demonstrated using different techniques including cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS).

A cyclic voltammetric study is utilized to evaluate the redox behavior, capacitance and reversibility nature. Figure 6a–d shows the cyclic voltammetric curves of  $CoMn_2O_4$ -1,  $CoMn_2O_4$ -2,  $CoMn_2O_4$ -3 and  $CoMn_2O_4$ -4, respectively, which were demonstrated at the scan rates from 5 to 100 mV s<sup>-1</sup> within a potential window from 0 to 0.5 V. All the CV curves exhibit the redox peaks such as the anodic peak located at approximately 0.31 V. whereas the cathodic peak positioned at approximately 0.22 V which is due to the redox process and signifying the pseudocapacitor behavior of the  $CoMn_2O_4$  materials (Cai et al. 2014; Senthilkumar and Kalai Selvan 2014).

The redox reaction may be described in the following Eqs. 1, 2 and 3. (Yunyun et al. 2015)

$$CoMn_2O_2 + H_2O^- \rightarrow CoOOH + 2MnOOH + e^-, \qquad (1)$$

$$MnOOH + OH^{-} \rightarrow MnO_{2} + H_{2}O + e^{-}$$
(2)

$$CoOOH + OH^- \to H_2O + e^-.$$
(3)

The broadness of CV curves is increasing from  $CoMn_2O_4$ -1 to  $CoMn_2O_4$ -4 confirming the superior pseudocapacitance behavior of the  $CoMn_2O_4$ -4 material. The diffusive and capacitive contributions in CV analysis (for  $CoMn_2O_4$ -4 material) were calculated by using the Eq. (4).

$$I = av^b, \tag{4}$$

where *I* is the fitting current, *v* is the scan rate. The *a* and *b* are variables. The value of *b* is determined by plotting the log (i) versus log (*v*) curves as shown in Fig. 6e. The *b* value of 0.5 demonstrates diffusion controlled progression, whereas 1.0 indicates the surface capacitive controlled process. In the present investigation, the *b* 



Fig. 6 CV curves of  $CoMn_2O_4$  materials. a  $CoMn_2O_4$ -1, b  $CoMn_2O_4$ -2, c  $CoMn_2O_4$ -3 and d  $CoMn_2O_4$ -4, e plot of rate (log i vs. log v) for the redox peaks and f Scan rate vs specific capacitance graph

values are 0.64 and 0.72 for anodic and cathodic current, respectively. This indicates that the present energy storage process is mixed behavior of diffusive and capacitive controlled process. (Chen et al. 2019a, b; Zhang et al. 2020).

The quasi symmetric feature of the redox peaks and cycles attributes the outstanding reversibility of the  $CoMn_2O_4$  electrodes. when the scan rate is raised from 5 to 100 mV s<sup>-1</sup>, the current response enhance at the same time as the shape profile of the CV curves do not altered which suggesting enhanced mass transportation and rapid conduction of electrons in the electrode material during the electrochemical process(Jadhav et al. 2016). Interestingly, the peak appeared at the anodic current was shifted towards the positive region, whereas cathodic peak drift towards the more negative region which is due to ohmic resistance and electrical polarization behavior of CoMn<sub>2</sub>O<sub>4</sub> electrodes(Cao et al. 2014). In addition, the area under the cyclic voltammetric curves is directly proportional to the specific capacitance of the corresponding electrodes. The CoMn<sub>2</sub>O<sub>4</sub>-4 provides higher area under the CV curves than other electrodes such as  $CoMn_2O_4$ -1,  $CoMn_2O_4$ -2 and CoMn<sub>2</sub>O<sub>4</sub>-3 confirming its superior pseudocapacitive behavior. The specific capacitance of the CoMn<sub>2</sub>O<sub>4</sub> electrodes were calculated from the CV curves utilizing Eq. 5.

$$Csp = \frac{\int idV}{S.\Delta V.m},\tag{5}$$

where  $\int i dV$  denotes the integral area of CV curve,  $\Delta V$  potential limit (V), *m* mass of the active material (mg), and *S* the sweep rate (mV s<sup>-1</sup>) from 5 to 100 mV s<sup>-1</sup>. The obtained specific capacitance values are 232, 511, 670 and 895 Fg<sup>-1</sup> for CoMn<sub>2</sub>O<sub>4</sub>-1, CoMn<sub>2</sub>O<sub>4</sub>-2, CoMn<sub>2</sub>O<sub>4</sub>-3 and CoMn<sub>2</sub>O<sub>4</sub>-4 electrodes, respectively, at a scan rate of 5 mV s<sup>-1</sup>. The specific capacitance of CoMn<sub>2</sub>O<sub>4</sub>-4 electrode (895 Fg<sup>-1</sup>) is approximately four-fold increases from the specific capacitance, the specific capacitance of the CoMn<sub>2</sub>O<sub>4</sub>-1 electrode (232 Fg<sup>-1</sup>). Additionally, the specific capacitance of the.

CoMn<sub>2</sub>O<sub>4</sub>-4 electrode is higher than previously published literatures based on Co<sub>3</sub>O<sub>4</sub>, (Co<sub>3</sub>O<sub>4</sub> nanoparticles (519 Fg<sup>-1</sup>)(Vijayakumar et al. 2013), hollow Co<sub>3</sub>O<sub>4</sub> nanowire (599 Fg<sup>-1</sup>) (Xia et al. 2011) and Co<sub>3</sub>O<sub>4</sub> nanowire (754 Fg<sup>-1</sup>) (Tu et al. 2012) MnO<sub>2</sub> (MnO<sub>2</sub> nanostructure (311 Fg<sup>-1</sup>) (Zhang et al. 2013), MnO<sub>2</sub> nanorods (649 Fg<sup>-1</sup>) (Kumar et al. 2016) and  $\alpha$ - MnO<sub>2</sub> nanorod (166.2 Fg<sup>-1</sup>) (Li et al. 2011) and CoMn<sub>2</sub>O<sub>4</sub> electrode materials (CoMn<sub>2</sub>O<sub>4</sub> nanofibers (121 Fg<sup>-1</sup>) (Alkhalaf et al. 2017), cubic CoMn<sub>2</sub>O<sub>4</sub> particles (77.8 Fg<sup>-1</sup>) (Chen et al. 2019a, b) and CoMn<sub>2</sub>O<sub>4</sub> (700 Fg<sup>-1</sup>) (Vigneshwaran et al. 2016). The superior

specific capacitance behavior of the  $CoMn_2O_4$ -4 electrode is explained as follows: (i) The one-dimensional nanorods exhibit high surface area which provides the more active sites for electrochemical reaction. (ii) The small dimensions of the nanorods not only enhance the transportation of electrolyte ions and also increase the absorption of ions during electrochemical analysis. (ii) It gives the short diffusion path for electron and ion transportations and remained their original structural natures.

The rate capabilities of all electrode materials were characterized through scan rate vs specific capacitance graph as shown in Fig. 6f. The specific capacitances decrease with the increasing of scan rate and this trend is explained as follows: at low scan rate, the larger time is allowed to perform electrochemical reaction actively in both inner and outer region of electrode materials and hence the specific capacitance increases. On the other hand, the outer region of electrode only participate in the electrochemical process during higher scan rate which is due to the shorter time and thus decrease the specific capacitance(Kim et al. 2016). The remaining characterizations such as electrochemical impedance spectroscopy, chronopotentiometry and cyclic stability studies



Fig. 7 Impedance spectra of CoMn<sub>2</sub>O<sub>4</sub> materials

were carried out only for  $CoMn_2O_4$ -4 electrode due to its better electrochemical properties.

The electrochemical impedance spectroscopic analyses were carried out to analyze intrinsic electrochemical properties of the  $CoMn_2O_4$ -4 electrode as shown in Fig. 7. Two main distinctive properties observed in the high- and low-frequency regions are ascribed to different resistance and capacitance phenomena during different interfacial processes in Faradaic reactions. The semicircle at highfrequency region is the characteristic of resistance at the solid oxide or electrode materials/liquid electrolyte interface owing to discontinuity in the charge transfer process. The straight line obvious at low-frequency region attributes the confirmation of diffusive charge transfer mechanism. The intercept of the real axis is due to internal resistances which are originated from the resistance produced from all the active electrode materials, the resistance of the electrolyte and the resistance created between material/current collector interfaces (contact resistance) (Bengoechea et al. 2002; Lu et al. 2016).

The more vertical line of the curve attributes the more facile electrolyte diffusion to the surface due to the small nanoparticle size and large surface area of the compared to the  $CoMn_2O_4$  -4 sample(Xu et al. 2014a, b). Figure 8a shows the chronopotentiometric curves of the  $CoMn_2O_4$ -4 electrode at a current densities of 1, 2, 3, 4, 5, 10 and 20 Ag<sup>-1</sup>. The potential limits from 0 to 0.45 V was chosen for chronopotentiometric analysis and it shown in Fig. 7. The non-linear behavior of the charge discharge curves confirms the pseudocapacitive nature which is more consistent with the CV analysis. It is interesting to note that there are two sections of CP curves, including the straight line and curved line which signifies the characteristic faradaic nature(Zhao et al. 2016). The specific capacitances were calculated by CP curves, using the Eq. 6.

$$Csp = \frac{I\Delta t}{m\Delta V},\tag{6}$$



Fig. 8 a CP curves of  $CoMn_2O_4$ -4 material and b current density vs. Specific capacitance graph



Fig.9 Cyclic stability analysis of  $CoMn_2O_4\mbox{-}4$  material at a scan rate of 100 mV  $s^{-1}$ 

where *I* denotes discharge current density (*A*),  $\Delta t$  is the discharge time (*s*),  $\Delta V$  the potential window (V) and *m* is the mass of the active material (mg). The CoMn<sub>2</sub>O<sub>4</sub>-4 electrode exhibit a specific capacitance of 802, 649, 580, 524, 466, 222 and 177Fg<sup>-1</sup> at a current densities of 1, 2, 3, 4, 5, 10 and 20 Ag<sup>-1</sup>, respectively. The specific capacitance vs. current density graph is shown in Fig. 8b. The specific capacitance values decrease with increasing of current density which is due to the time limitation process and it is more reliable with the CV curves (Yesuraj et al. 2019).

Long-time cyclic stability behavior of the materials is also great importance for high performance supercapacitor application. Cyclic stability of CoMn<sub>2</sub>O<sub>4</sub>-4 electrode is further evaluated by using continuous 5000 CV cycles at high scan rate of  $100 \text{ mVs}^{-1}$  as shown in Fig. 9. The inset of Fig. 8 shows the 1st and 5000th cycles of cyclic stability studies. Initially, the amount of specific capacitance increases at 900th of cycles which is attributed to the rising of efficient interfacial area between the electrodes and electrolyte and along with the slow activation process of the  $CoMn_2O_4$ -4 electrode(Hou et al. 2016). After that, it gradually decreases and retained 87% of initial capacitance after 5000 cycles. The superior cyclic stability property is due to the nanorods structural features of CoMn<sub>2</sub>O<sub>4</sub>-4 electrode material. The superior specific capacitance and cyclic stability features implies probable application of CoMn<sub>2</sub>O<sub>4</sub>-4 nanorod in electrode material for supercapacitors.

## Conclusion

The work established a simple CTAB assisted hydrothermal synthetic technique for the preparation of edge curved one-dimensional CoMn<sub>2</sub>O<sub>4</sub> nanorods for pseudocapacitor electrode application followed by annealing process. In this process, the CTAB template plays a key role to control the morphological features of CoMn<sub>2</sub>O<sub>4</sub> materials. The synthesized materials were characterized by XRD, FTIR and FESEM techniques to evaluate their formation, crystalline phase, bonding properties and structural features. The high concentration of CTAB provides edge curved one-dimensional nanorods structure. The electrochemical properties of the CoMn<sub>2</sub>O<sub>4</sub> materials were evaluated using cyclic voltammetric, chronopotentiometric and electrochemical impedance spectroscopic analysis. The CV curves provide the specific capacitance of 895  $Fg^{-1}$  at a scan rate of 5 mV s<sup>-1</sup>, whereas CP curves provide the specific capacitance of 802 Fg<sup>-1</sup> at a current density of 1 Ag<sup>-1</sup>. Furthermore, CoMn<sub>2</sub>O<sub>4</sub> electrode retained 87% of initial capacitance after 5000 CV cycles at a scan rate of 100 mV s<sup>-1</sup>. The outstanding electrochemical features and superior cyclic stability facilitate the obtained CoMn<sub>2</sub>O<sub>4</sub> material to be an important material for supercapacitor device applications.

## **Compliance with ethical standards**

**Conflict of interest** On behalf of all the authors, the corresponding author states that there is no conflict of interest.

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