



Studies on spray deposited Ni doped Mn_3O_4 electrodes for supercapacitor applications

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ARTICLE INFO

Article history:

Received 1 July 2018

Received in revised form

29 September 2018

Accepted 1 October 2018

Available online 2 October 2018

Keywords:

Chemical synthesis

Structural properties

FESEM

Supercapacitors

Energy storage

ABSTRACT

The doping influenced morphological alteration and its consequent impact on electrochemical properties of Mn_3O_4 electrodes has been investigated. The Ni doped Mn_3O_4 are characterized for its surface morphological, compositional, structural, optical and electrochemical properties. The polycrystalline nature of Ni doped Mn_3O_4 films with tetragonal Hausmannite crystal structure has been confirmed from x-ray diffraction. The field emission scanning electron microscope study shows that Ni doped Mn_3O_4 films have porous nanoflakes type surface morphology. The band gap energy for Ni doped Mn_3O_4 films ranges between 2.55 and 3.29 eV depending on the Ni doping. The specific capacitance of 705 Fg^{-1} from cyclic voltammetry and 740 Fg^{-1} from galvanostatic charge/discharge has been perceived. The Ni doped Mn_3O_4 electrode show good electrochemical cycling stability. The electrochemical impedance study showed charge transfer resistance of $6.8 \Omega \text{ cm}^2$ for 0.50 mol % Ni doped Mn_3O_4 electrode.

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1. Introduction

The production and storage of energy is a most imperative theme of Today's discussion in research. The rising prices and pollution are among the difficulties associated with the dependency of society on fossil fuels [1,2]. Throughout the last decade, many attempts are done to discover ecological and reproducible energy storage devices [3–6]. Among the storage technologies, supercapacitors have drawn excessive consideration due to longer cycle life than batteries, greater power density and more energy density as compared to conventional capacitors [7,8]. In certain applications requiring the low energy and high power density, supercapacitors have underway to substitute the batteries [9–12].

Supercapacitors are categorized in two sets based on their charging mechanism, namely (i) EDLCs and (ii) pseudocapacitors [13–15]. The supercapacitor performance hangs on the chemical and physical properties of the electrode. Recently, transition metal oxides, including NiO, SnO_2 , Co_3O_4 , RuO_2 , Fe_2O_3 , MnO_2 , Fe_3O_4 , ZnO and Mn_3O_4 have been considered as candidates for supercapacitor electrodes [16–21]. Amongst these, Mn_3O_4 with benefits of little cost, effective semiconducting nature and ecofriendly has been functional widely.

The doped and pure Mn_3O_4 films can be deposited by numerous techniques comprising atomic layer deposition [22], sputtering [23], co-precipitation [24], SILAR [25], chemical synthesis [26], sol-gel method [27], electrodeposition [28], hydrothermal method [29–31] and spray pyrolysis [15,21,32–35]. Amongst these, spray pyrolysis technique has little cost, straightforward and simple to use, has been recognized for number of scientific studies and technical applications.

Adjusting the morphology of the electrodes is significant in the context of Mn_3O_4 because each structure has its own merits when used in a potential application such as catalyst, sensor, rechargeable batteries, supercapacitors etc [16–18]. Recently it has been shown that catalytic, electronic and optical properties of Mn_3O_4 electrodes are highly reliant on their morphologies and crystallographic forms [31–34]. Previously, we have reported porous Mn_3O_4 thin films with tetragonal Hausmannite crystal structure. The specific capacitance of 394 Fg^{-1} was observed. Although a considerable improvement in the electrochemical performance has been noted [15], the observed specific capacitance is smaller compared with the existing literature, which can be attributed partially to the greater resistivity of the electrode that might be lowered by adding appropriate donor impurity. It is reported that appropriate doping can disturb the growth process during chemical reaction and therefore the morphology of the metal oxide can be altered by varying the doping concentration. So suitable doping can be a good

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way to change the morphology of Mn_3O_4 . Among the different doping materials, Ni can be a good dopant for Mn_3O_4 , as the ionic radii of Mn (0.80 Å) and Ni (0.72 Å) are comparable [36] and Ni had been successfully doped in manganese tetraoxide thin films previously. Nickel doping in Mn_3O_4 is a real approach to enhance the performance of Mn_3O_4 supercapacitor. The influence Ni doping on morphological, compositional, structural, optical and electrochemical properties of Mn_3O_4 thin films has been investigated.

2. Experimental

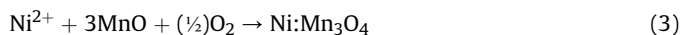
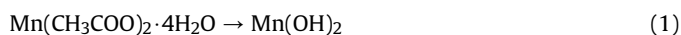
Ni doped Mn_3O_4 electrodes are deposited at various Ni concentrations. For deposition of Ni doped Mn_3O_4 electrodes manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) were used. The optimized preparative parameters used for deposition were: concentration of manganese acetate 0.8 M; deposition temperature 350 °C; spray rate 3–4 ccmin^{-1} ; carrier gas pressure 1.8 kgcm^{-2} ; substrate to nozzle distance 28 cm; Ni doping concentration 0–1 mol % and glass and FTO coated glass as substrates. For each deposition, 25 ml 0.8 M $[\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}]$ solution was mixed with 25 ml of Propan-2-ol to make the final spraying solution of 50 ml. The resulting concentration of spraying solution (50 ml) was 0.4 M. The Ni doping concentration was varied from 0 to 1 mol % by keeping all other parameters at optimized values and films were deposited by using computerized chemical spray pyrolysis technique discussed elsewhere [37].

Structural characterization of Ni doped Mn_3O_4 electrodes was performed by examining the X-ray diffraction (XRD) patterns obtained through Philips X-ray diffractometer model PW-1710 ($\lambda = 1.54060$ Å for $\text{Cu-K}\alpha$ radiation) within 2θ between 20 and 80°. Surface morphological and compositional studies were performed using JEOL JSM-6360, Mira-3, Tescan, Brno-Czech Republic, field emission scanning electron microscope (FESEM) at accelerating voltage of 20 kV. The absorption spectrum of Ni doped Mn_3O_4 was recorded through Systronic make UV–Vis Spectrophotometer (model 119). The absorption data was used to decide the type of transition and band gap.

The electrochemical performance was tested in a standard three-electrode cell on a CHI 660E, (CH Instruments, USA), with Ni doped Mn_3O_4 -working electrode, Platinum foil-counter electrode, and Ag/AgCl-reference electrode. An aqueous 1 M Na_2SO_4 electrolyte was utilised. Cyclic voltammetry (CV) investigation was performed in 0.25 to +0.45 V versus Ag/AgCl at various scan rates. The galvanostatic charging/discharging was conducted at different current densities (0.5 Ag^{-1} to 4 Ag^{-1}) inside a potential window of –0.2 to +0.4 V. The electrochemical impedance spectroscopy measurement was accomplished at AC amplitude of 5 mV in 100 kHz–1 Hz frequency range.

3. Results and discussion

The solution of manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) in aqueous/organic solvent mixture provides Mn^{2+} ions, the chemical reaction between Mn^{2+} and 2OH^- leads to formation of $\text{Mn}(\text{OH})_2$, which is then decomposed into MnO. At optimum substrate temperature, oxidation of MnO by atmospheric oxygen leads to the formation of the adherent Mn_3O_4 layer. The Nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) provides the Ni ions. The reaction can be written as [38],



The mass of Ni doped Mn_3O_4 electrodes are measured by using sensitive microbalance. It is observed that the masses for all samples were in the range of $0.54 \pm 0.03 \text{ mgcm}^{-2}$.

3.1. X-ray diffraction (XRD)

Fig. 1 displays XRD pattern of Ni doped Mn_3O_4 films deposited with various Ni concentrations. The angle 2θ is between 20 and 80°. XRD pattern represents polycrystalline Ni doped Mn_3O_4 with tetragonal Hausmannite crystal structure as accorded with standard JCPDS data card 75–1560. The prominent diffraction peaks are observed at $2\theta = 24.45^\circ$, 29.13° , 32.50° , 36.32° , 38.69° , 44.45° , 52.01° , 60.15° , and 64.90° corresponding to hkl planes (112), (202), (220), (213), (004), (400), (332), (404), and (440) respectively. The observed diffraction peak positions in Ni doped Mn_3O_4 films were matching with earlier results [33,34]. As seen from Fig. 1 and Table 1, the peak positions of the Ni incorporated Mn_3O_4 thin films with various Ni doping were closely identical to those of bulk Mn_3O_4 , manifesting the same Hausmannite lattice structure [15].

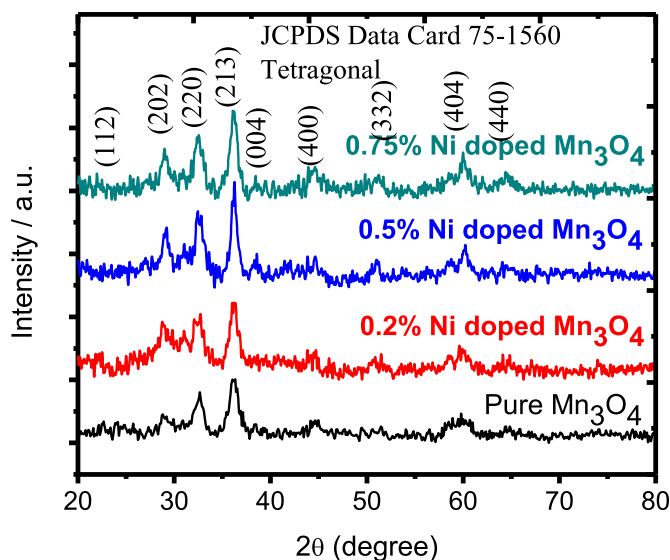


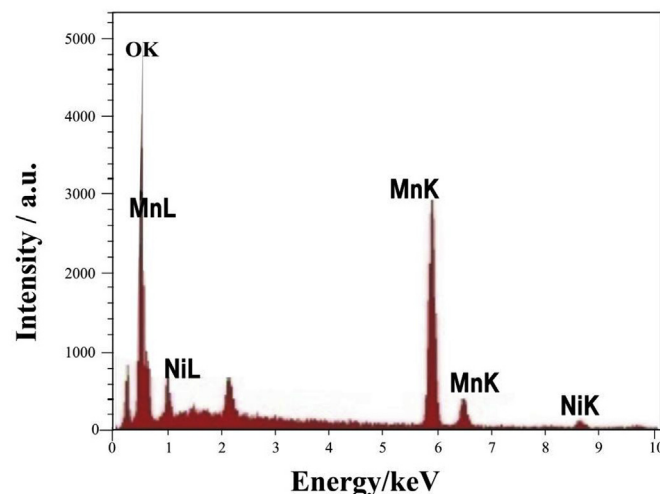
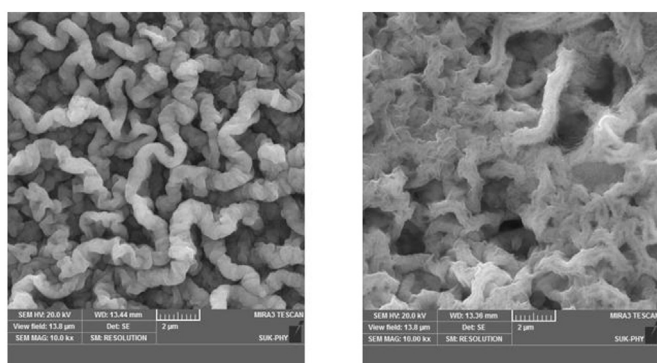
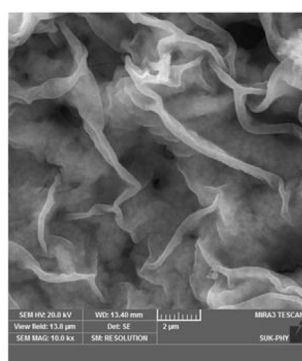
Fig. 1. XRD Patterns of spray deposited Ni doped Mn_3O_4 thin films.

Table 1
XRD data for spray deposited Ni doped Mn_3O_4 thin films.

Ni doping (mol%)	$2\theta(^{\circ})$	d (Å) calculated	d (Å) Assignment standard	Crystalline size (nm)
0	25.14	3.539	3.645 112	39
	29.20	3.056	3.079 202	
	32.67	2.738	2.878 220	
	36.34	2.470	2.377 213	
	38.12	2.359	2.355 004	
	44.35	2.041	2.035 400	
	50.98	1.790	1.777 332	
	60.10	1.538	1.540 404	
	64.85	1.436	1.439 440	
0.20	24.37	3.649	3.645 112	40
	29.07	3.069	3.079 202	
	32.76	2.731	2.878 220	
	36.39	2.467	2.377 213	
	39.58	2.275	2.355 004	
	44.74	2.024	2.035 400	
	51.54	1.772	1.777 332	
	60.21	1.536	1.540 404	
	64.86	1.436	1.439 440	

Table 1 (continued)

Ni doping (mol%)	2 θ (°)	d (Å) calculated	d (Å)	Assignment standard	Crystalline size (nm)
0.50	24.47	3.634	3.645	112	42
	29.25	3.050	3.079	202	
	32.47	2.755	2.878	220	
	36.29	2.473	2.377	213	
	38.61	2.330	2.355	004	
	44.76	2.023	2.035	400	
	52.21	1.750	1.777	332	
	60.27	1.534	1.540	404	
	64.76	1.438	1.439	440	
	23.83	3.731	3.645	112	
0.75	29.02	3.074	3.079	202	41
	32.10	2.786	2.878	220	
	36.27	2.474	2.377	213	
	38.48	2.337	2.355	004	
	43.95	2.058	2.035	400	
	53.33	1.716	1.777	332	
	60.03	1.540	1.540	404	
	65.14	1.431	1.439	440	

Fig. 3. EDS pattern of 0.5 mol% Ni doped Mn₃O₄ thin films.(a) 0.2 mol% Ni: Mn₃O₄(b) 0.5 mol% Ni: Mn₃O₄(c) 0.75 mol% Ni: Mn₃O₄Fig. 2. FESEM images of Ni doped Mn₃O₄ thin films (a) 0.2 mol%, (b) 0.5 mol%, and (c) 0.75 mol% Nickel, respectively at 10,000 $\times$ magnifications.

No other crystalline phases were detected in any of the XRD patterns. This demonstrated that Ni doping did not affect the original crystalline structure.

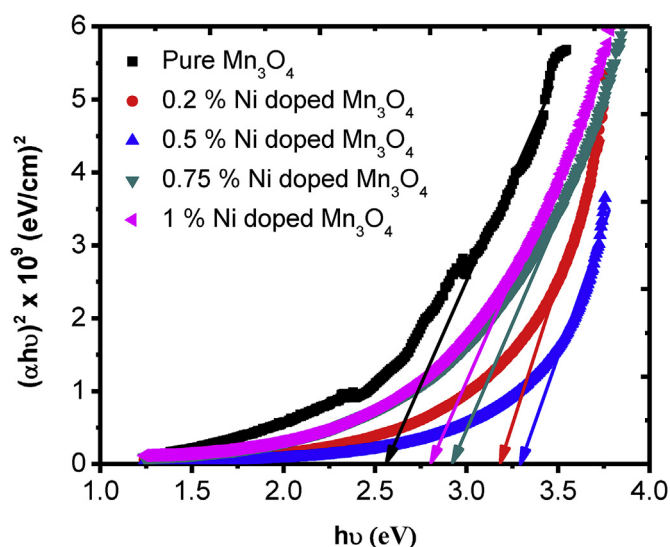
In addition, Ni doped Mn₃O₄ films are greatly oriented along (213) direction. It is witnessed that the peak (213) intensity augmented with increase Ni doping concentrations upto 0.50 mol% and decreases thereafter showing slight reorientation effect. The probable reason for such behavior is that the nickel atom alternates with manganese up to 0.5 mol% while for higher nickel doping

($\sim$ 0.5 mol%), nickel atoms go to substitutional as well as interstitial positions of Mn₃O₄ lattice [15]. The lattice parameters calculated using the standard relation [15] are found to be, $a = b = 8.135$ Å, $c = 9.28$ Å; which are closely matching with standard ($a = b = 8.14$ Å, $c = 9.42$ Å) of Mn₃O₄ thin films (JCPDS card 75–1560).

Crystalline size is calculated for the standard (213) reflection using Scherrer's formula [39]. The FWHM decrease initially with increase in nickel doping in Mn₃O₄ up to 0.50 mol% and further found to increase with further increase in nickel doping. Crystalline size is found in between 39 and 42 nm for Ni doped Mn₃O₄ with various nickel doping. Table 1 depicts 2 θ , interplanar spacing (d), assignments and crystalline size for Ni doped Mn₃O₄.

3.2. Field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS)

The modifications in surface morphology of the Ni incorporated Mn₃O₄ are presented in Fig. 2. The surface of undoped Mn₃O₄ thin film was observed as porous with densely packed and well adhered to

Fig. 4. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Ni doped Mn₃O₄ thin films.

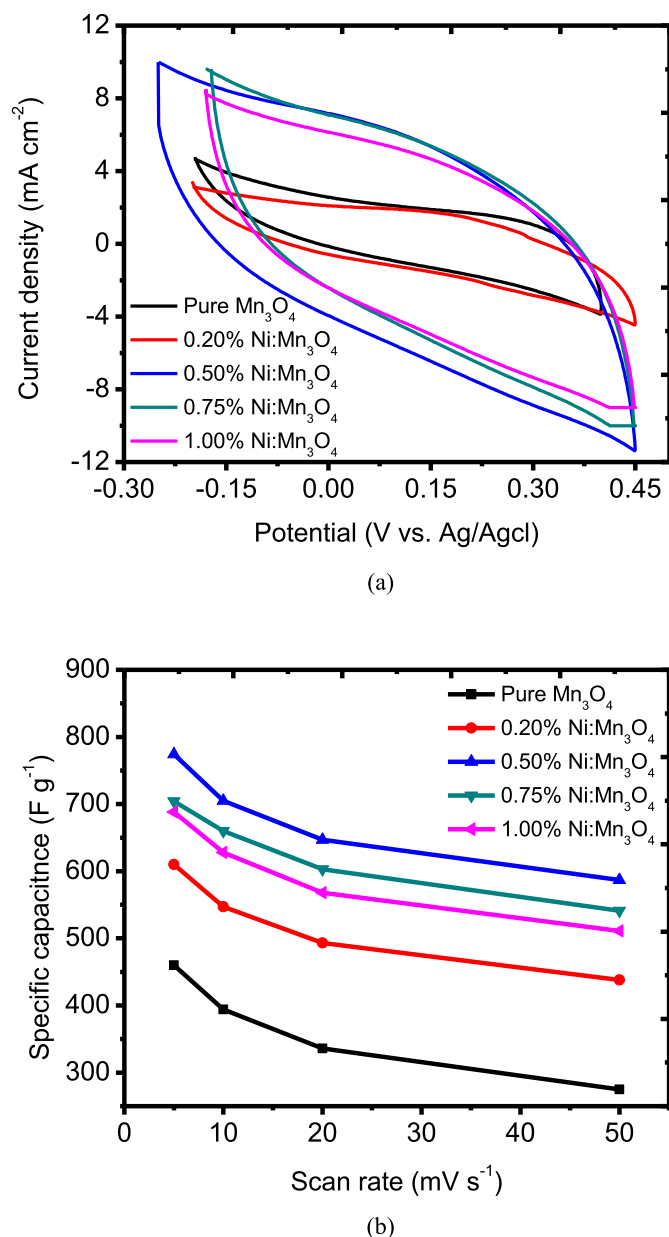


Fig. 5. (a) The CVs of Ni doped Mn_3O_4 thin film electrodes in the 1 M Na_2SO_4 electrolyte, at scan rate of 10 mVs^{-1} ; (b) Specific capacitance vs. scan rate for Ni doped Mn_3O_4 electrodes with various Ni doping.

the substrate [15]. Fig. 2 shows the FESEM images of Ni doped Mn_3O_4 deposited with 0.2 mol %, 0.5 mol % and 0.75 mol % nickel concentrations at $10,000\times$ magnifications. From figure it is seen that Ni doped Mn_3O_4 show the porous nanoflakes type surface morphology. After Nickel doping, the Mn_3O_4 thin film is transformed into highly porous nanoflakes, as seen in Fig. 2(a–c). Such porous nanoflakes afford a much larger surface area needed for supercapacitors [40,41]. The porosity is witnessed to enhance with the increase in nickel doping up to 0.50 mol%, influencing the electrochemical property. Similar transformations in morphology of the Mn_3O_4 thin film electrodes were also found in previous studies [42].

The doping of Ni in the Mn_3O_4 electrode was confirmed by energy-dispersive X-ray spectroscopy (EDS). Fig. 3 shows strong peak signals of only Mn, O, and Ni components of the 0.5 mol% Ni doped Mn_3O_4 electrode, approving incorporation of Ni in Mn_3O_4 lattice.

Table 2

Optical and electrochemical (CV) data for spray deposited Ni doped Mn_3O_4 thin films.

Ni doping (mol %)	Eg (eV)	Csp Fg^{-1}	Rs(Ω)	Rct (Ωcm^2)
0.00	2.55	394	0.50	11.70
0.20	3.15	547	0.35	10.20
0.50	3.29	705	0.25	6.80
0.75	2.87	660	0.32	8.25
1.00	2.80	628	0.33	10.00

Eg; bandgap energy, Csp; specific capacitance at scan rate of 10 mVs^{-1} , Rs; solution resistance, Rct; charge transfer resistance.

3.3. Optical

Optical characterization of Ni doped Mn_3O_4 electrodes were carried out by measuring the absorption spectra in the wavelength span of 300–1100 nm. From absorption spectra (not shown here), it is observed that the absorption edge marginally moved to shorter wavelengths with nickel doping up to 0.5 mol% showing dependence of absorbance on impurity addition [34,43]. The absorption spectra was further analysed to decide the type of transition and band gap energy by plotting a graph of $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 4. The absorption coefficient is in range of 10^4 cm^{-1} . The nature of the plots designates the direct allowed type transition. The band gap energy obtained by extrapolating the $(\alpha h\nu)^2$ versus $h\nu$ curves is found to be in between 2.55 and 3.29 eV. The bandgap upsurges with increase in Ni doping in Mn_3O_4 ion, reaches a maximum value 3.29 eV at 0.50 mol% and further decreases with Ni doping. The upsurge in bandgap of Ni incorporated Mn_3O_4 thin films can be accredited to the presence of holes formed by nickel ions substituting manganese ions in the host lattice [44]. The band gap energy of 2.55–3.29 eV obtained in present case is comparable with 2.23–2.82 eV reported for Li doped Mn_3O_4 by Amara et al. [44], 2.20–2.92 eV reported for spray deposited Zr doped Mn_3O_4 thin films by Said and coworkers [34], and 2.6–2.8 eV for thallium doped Mn_3O_4 by Sheikhshoae et al. [27].

3.4. Electrochemical

3.4.1. Cyclic voltammetry (CV)

Fig. 5 (a) shows the cyclic voltammograms of Ni doped Mn_3O_4

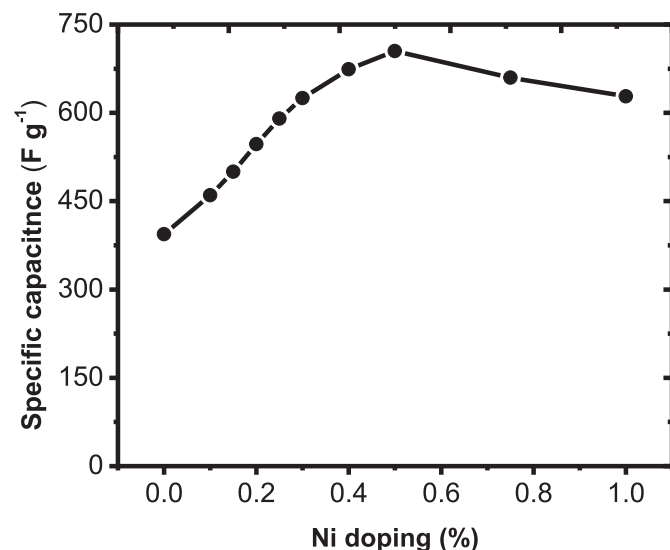
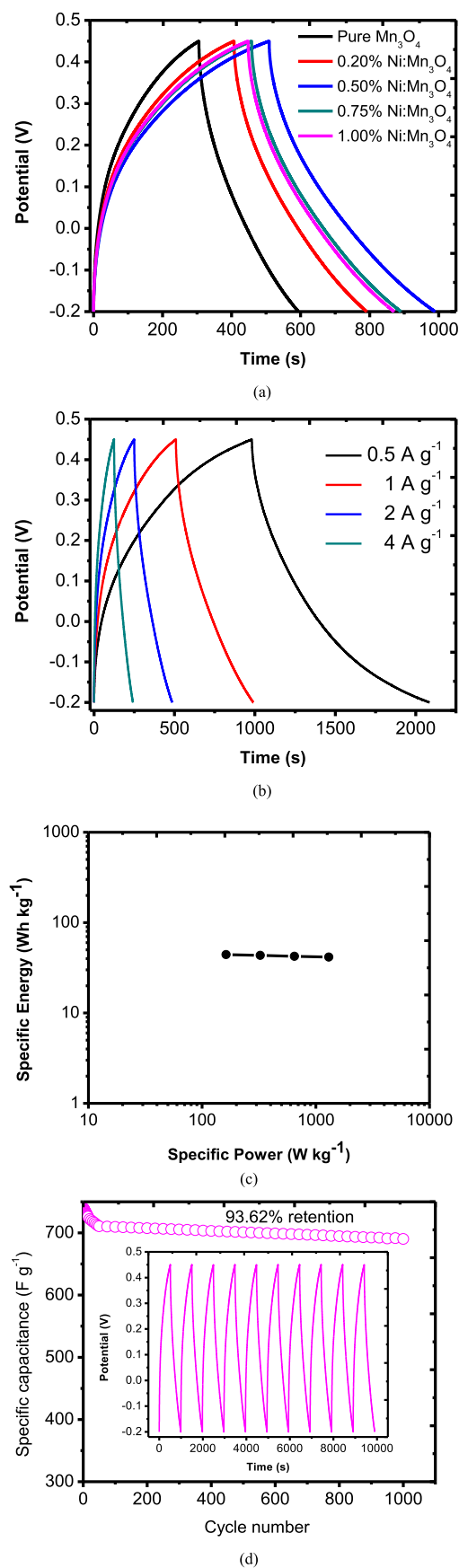


Fig. 6. Variation of the specific capacitance (at 10 mVs^{-1}) with Ni doping in Mn_3O_4 thin films.

**Table 3**

Various parameters for obtaining specific capacitance (Cs), specific energy (SE) and specific power (SP) from GCD.

CD (Ag ⁻¹)	t _{dis} (s)	Cs Fg ⁻¹	SE (Whkg ⁻¹)	SP (Wkg ⁻¹)	η (%)
0.5	981	755	44.28	162.5	95.71
1	481	740	43.42	325	94.69
2	235	723	42.43	650	93.25
4	115	708	41.53	1300	92.74

CD; current density, t_{dis}; discharge time, η; coulomb efficiency.

electrode (3 electrode assembly) at scan rate 10 mVs⁻¹ in 1 M Na₂SO₄ electrolyte within potential -0.25 to +0.45 V versus Ag/AgCl. The regular and symmetric shapes of CV curves prove the typical pseudo-capacitive performance. The specific capacitance of Ni doped Mn₃O₄ electrodes was calculated from CV curves using relation given elsewhere [15]. The specific capacitances of Ni doped Mn₃O₄ electrodes are given in Table 2.

Furthermore, Ni doped Mn₃O₄ electrodes show good rate capability (Fig. 5. (b)) with specific capacitance of 705 Fg⁻¹ (at 10 mVs⁻¹) for 0.5 mol % Ni doping, which is greater than the specific capacitance reported for Zinc Oxide/Manganese Oxide [45]. From Fig. 5 (b), the specific capacitances of all the samples decrease with growing scan rates. This is ascribed to the presence of inner active sites, which completely inhibit the redox transitions at higher scan rates of CV, probably owing to the diffusion effect of protons within the electrodes. All the electrodes showed the maximum specific capacitance at a scan rate of 5 mVs⁻¹. It is witnessed that the capacitance enhances with incorporation of Ni in Mn₃O₄ with a maximum 705 Fg⁻¹ for 0.5 mol % and diminishing thereafter for further incorporation of Ni in Mn₃O₄. This can be ascribed to porous nanoflakes type morphology of Ni doped Mn₃O₄ thin film at 0.50 mol %, which gives more surface wetting for Na₂SO₄ electrolyte with Mn₃O₄ electrode [46]. The specific capacitance of 705 Fg⁻¹ witnessed in present study is better than 263 Fg⁻¹ reported for Mn₃O₄/Ni foam prepared facile one-step hydrothermal method [47] and 430 Fg⁻¹ at 5 mVs⁻¹ for MnO₂-RuO₂@GNR electrode [48]. The large specific capacitance is accredited to the nanoflake type porous morphology of Ni doped Mn₃O₄ electrodes observed from FESEM (Fig. 2). Fig. 6 shows behavior of specific capacitance with Ni incorporation in Mn₃O₄. Even though the specific capacitance of undoped and nickel doped Mn₃O₄ are comparable to those of familiar existing carbon-based capacitors, undoped and nickel doped Mn₃O₄ are of considerable attention owing to their comparatively easy synthesis, low cost, and environment friendliness.

3.4.2. Galvanostatic charge/discharge (GCD)

To determine the voltage stability window of nickel doped Mn₃O₄, GCDs (Fig. 7a) were carried out at 1 Ag⁻¹ in a steady potential window -0.2 to +0.4 V. Fig. 7a shows that the GCD curves for nickel incorporated Mn₃O₄ electrodes. The nature of curves confirms the pseudo-capacitive behavior of nickel incorporated Mn₃O₄ electrodes. The discharge curve of the electrodes involves of two portions: an IR drop owing to internal resistance and a capacitive component (curved portion) related to the voltage change due to changes in energy within the capacitor [49]. This (IR)

Fig. 7. (a) GCD curves for Ni doped Mn₃O₄ electrodes at fixed current density of 1 Ag⁻¹, (b) GCD curves for 0.5 mol% Ni doped Mn₃O₄ electrode at different current densities, (c) Ragone plots for 0.5 mol% Ni doped Mn₃O₄ thin film electrode supercapacitor, and (d) cycling performance of the 0.5 mol% Ni doped Mn₃O₄ electrode at current density of 1Ag⁻¹. The inset shows the charge/discharge curves of the first 10 cycles.

Table 4The capacitive performance comparison of pure and doped Mn_3O_4 by this work with various manganese oxide reported in some literatures.

Order	Material	Electrolyte	Measurement Protocol	Max.capacitance	Ref.
1	Sn-doped Mn_3O_4	6 M KOH	GCD = 5 A g^{-1}	216 F g^{-1}	[52]
2	Ni-doped Mn_3O_4	0.5 M Na_2SO_4	GCD = 0.25 A g^{-1}	230 F g^{-1}	[50]
3	Ni-doped Mn_3O_4	1 M KOH	GCD = 1 A g^{-1}	707 F g^{-1}	[53]
4	Ni-doped Mn_3O_4	1 M KOH	GCD = 1 A g^{-1}	407 F g^{-1}	[54]
5	Ce-doped Mn_3O_4	1 M Na_2SO_4	GCD = 2 A g^{-1}	209 F g^{-1}	[55]
6	Cr-doped Mn_3O_4	1 M Na_2SO_4	GCD = 0.5 A g^{-1}	272 F g^{-1}	[30]
7	Co-doped Mn_3O_4	1 M Na_2SO_4	GCD = 0.5 A g^{-1}	209 F g^{-1}	[30]
8	Cu-doped Mn_3O_4	1 M Na_2SO_4	GCD = 0.5 A g^{-1}	134 F g^{-1}	[30]
9	Ni-doped Mn_3O_4	1 M Na_2SO_4	GCD = 0.5 A g^{-1}	184 F g^{-1}	[30]
10	This work	1 M Na_2SO_4	GCD = 1 A g^{-1}	740 F g^{-1}	–

drop is a common phenomenon occurring in transition metal oxides. GCDs at various current densities for 0.50 mol% Ni incorporated Mn_3O_4 are presented in Fig. 7b. Specific capacitance (C_{sp}), specific energy (SE), specific power (SP, kW kg^{-1}) and coulomb efficiency (η) are estimated by relations given elsewhere [15]. The specific capacitances obtained from GCD are specified in Table 3. Specific capacitance of 755 F g^{-1} (at 0.5 A g^{-1}) decreased to 708 F g^{-1} (at 4 A g^{-1}), which is more than 230 F g^{-1} stated for the Ni (17.3%)- Mn_3O_4 [50]. Table 4 summarizes the recent research works that were carried out in relation to the doped Mn_3O_4 electrodes including different electrolytes employed. The highest value of 740 F g^{-1} is reported for Ni doped Mn_3O_4 electrodes (Present case). This is followed by 707 F g^{-1} is for Ni doped Mn_3O_4 .

The performance characteristics of Ni doped Mn_3O_4 supercapacitors can be compared with other energy storage systems by plotting the specific energy as a function of specific power on log scale, at different current densities (Ragone plot, Fig. 7c). The

specific energy and specific power are 41.53 Wh kg^{-1} and 1300 W kg^{-1} , respectively. This type of Ni incorporated Mn_3O_4 electrode is beneficial for numerous applications needing high power density and modest energy density. The coulomb efficiency is found to be 95.71%. The results of Ragone plot are given in Table 3.

Long term cycling stability is of huge significance for performance of supercapacitor and is confirmed by GCD cycling (Fig. 7d). It is observed that specific capacitance of Ni incorporated Mn_3O_4 decreases in initial cycles and steady performance during subsequent cycles. After 1000 GCD cycles, the supercapacitor exhibits good cycling life with $\sim 6.38\%$ decrease in specific capacitance. The GCD of the first 10 cycles are revealed in inset of Fig. 7d, which designates the identical symmetric shape, suggesting that the Ni doped Mn_3O_4 electrode does not experience extensive structural changes. The holding of more than 93.62% capacitance after 1000 GCD cycling implies high reversibility of the device.

3.4.3. Electrochemical impedance spectroscopy (EIS)

Fig. 8 (a) shows Nyquist plots for Ni doped Mn_3O_4 electrodes. A semicircle was detected at high and mid frequency for all Ni doped Mn_3O_4 electrodes due to the internal resistance. The ESR of all the Ni doped Mn_3O_4 electrodes is nearly 1Ω . The EIS data can be fitted by an equivalent circuit shown in Fig. 8 (b) [31]. The elements in the equivalent circuit are solution resistance (R_s), the double-layer capacitance (C_{dl}), the charge-transfer resistance (R_{ct}), the Warburg diffusion element (W_o), and the pseudocapacitance element (C_{pseud}). It is seen that R_{ct} varies with Ni incorporation in Mn_3O_4 . The variation in R_{ct} confirms the dependency Mn_3O_4 electrode on the Ni doping which is related to the difference in crystalline structures [51]. The values of R_s obtained from the Nyquist plots are 0.50Ω ; 0.35Ω ; 0.25Ω ; 0.32Ω ; and 0.33Ω respectively for undoped, 0.20 mol %, 0.50 mol %, 0.75 mol %, and 1.00 mol %, Ni incorporated Mn_3O_4 films. The R_{ct} values obtained are $11.70 \Omega \text{ cm}^2$, $10.20 \Omega \text{ cm}^2$, $6.8 \Omega \text{ cm}^2$, $8.25 \Omega \text{ cm}^2$ and $10.00 \Omega \text{ cm}^2$ for undoped, 0.20 mol %, 0.50 mol %, 0.75 mol %, and 1.00 mol %, Ni incorporated Mn_3O_4 respectively. Among all these, the Mn_3O_4 thin film electrode deposited with 0.50 mol % Ni doping displays a maximum slope which means the most superior capacitive performance. The outstanding capacitive property along with low R_{ct} of Ni doped Mn_3O_4 electrode suggests that it is favorable for excellent electrochemical performance which is good agreement with the CV and GCD results.

4. Conclusion

In this study, doping of nickel into Mn_3O_4 films has been found to upsurge their specific capacitance and improve the surface morphology. The Ni doped Mn_3O_4 are polycrystalline with tetragonal Hausmannite crystal structure. After Nickel doping, the Mn_3O_4 thin film was transformed into highly porous nanoflakes. The optical band gap energy of the Nickel doped Mn_3O_4 electrodes is

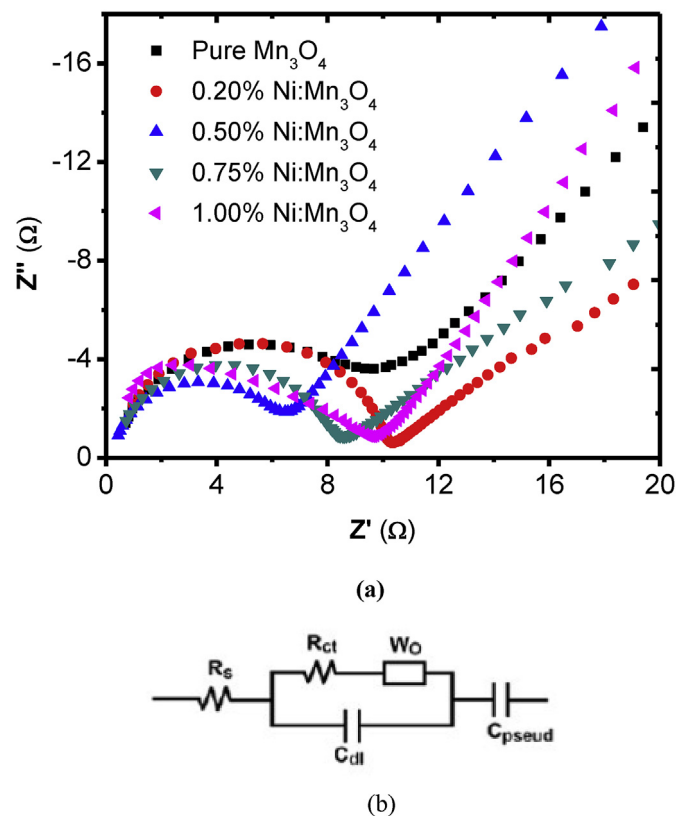


Fig. 8. (a) Nyquist plots for Ni doped Mn_3O_4 thin film electrodes in 1 M Na_2SO_4 electrolyte, and (b) equivalent circuit diagram used for analysis of the EIS data.

2.55–3.29 eV. The nickel doped Mn_3O_4 electrodes exhibit intensive specific capacitance of 705 Fg^{-1} at 10 mVs^{-1} . Specific capacitance calculated at 0.5 Ag^{-1} was 755 Fg^{-1} . The retention of 93.62% specific capacitance after 1000 cycles represents the extraordinary cycling stability of nickel doped Mn_3O_4 electrodes and is greatly analogous to other materials.

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