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Enhanced supercapacitor performance by incorporating nickel in manganese oxide

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Abstract

Nickel manganese mixed oxides (Ni$_y$Mn$_{1-y}$O$_x$; 0 ≤ y ≤ 0.4) has been synthesized by in-situ inclusion of nickel during the growth of manganese oxide (MnO$_x$). Effect of nickel concentration in MnO$_x$ is investigated by Cyclic Voltammetry, Current-Voltage characteristics, Scanning Electron Microscopy and N$_2$ adsorption-desorption analysis. Variation in electronic conductivity and specific capacitance suggest that nickel concentration in MnO$_x$ matrix significantly affect the supercapacitor electrode performance. At Ni/Mn ~0.25 i.e. Ni$_{0.2}$Mn$_{0.8}$O$_x$, material crystallizes into spinel NiMn$_2$O$_4$ as prominent phase and exhibited specific surface area (118 m$^2$g$^{-1}$) with granular morphology. Furthermore Ni$_{0.2}$Mn$_{0.8}$O$_x$ exhibited low resistivity (2.07 X 10$^4$ ohm cm) and consequently high specific capacitance ~380 Fg$^{-1}$, endowing additional merits. Fabricated supercapacitor device (Ni$_{0.2}$Mn$_{0.8}$O$_x$/Ni$_{0.2}$Mn$_{0.8}$O$_x$), deliver 35 Wh Kg$^{-1}$ energy density and 3.74 kW Kg$^{-1}$ power density with remarkably high capacitive retention ~92 % after 3000 galvanostatic charge/discharge cycles. These encouraging results show great potential in developing energy storage device from manganese oxide based electrodes incorporating nickel in lattice.

Keywords

Nickel manganese mixed oxide, supercapacitor, specific capacitance, energy density

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1. INTRODUCTION

Electrochemical supercapacitors have attracted much attention as energy storage device due to their promising applications in portable electronics and hybrid electrical vehicles [1,2]. Supercapacitors store charge via (a) charge accumulation at the electrode/electrolyte interface in the form of electrical double layer (EDL) and (b) by the pseudocapacitance that arises from faradic redox transitions that go deep inside the bulk material.

Carbon materials store charge via EDL whereas transition metal oxides and conducting polymers follow redox process for charge storage [3,4]. EDL is surface dependent and therefore the resulting capacitance values are low however the charge discharge rates are high. Due to the bulk contribution, pseudocapacitors give high specific capacitance ($C_{SP}$) whereas the response time limits their application. In order to exploit high $C_{SP}$ and energy density, metal oxides have been extensively studied and the response time or charge/discharge time is modified by improving the charge collection through a support material, preferably carbon. Researchers recently focussed on mixed metal oxides as potential supercapacitor electrode materials because pristine transition metal oxides are poor conductors resulting in high equivalent series resistance with limited capacity and power density [5]. Besides good electronic conduction, mixed transition metal oxides could offer richer redox reactions beneficial for electrochemical applications [6].

Recently, many nanocomposites like $\text{Co}_3\text{O}_4@\text{MnO}_2$, $\text{Co}_3\text{O}_4$-$\text{Ni(OH)}_2$, $\text{MnO}_2$-$\text{NiO}$ are attracting great interest for supercapacitors owing to their improved traits over pristine counterparts [7-12]. Various Nickel and Cobalt composites result in high electronic conductivity consequently enhancing the electrochemical performance [11]. Liu et al.
synthesized high surface area spinel nickel manganese oxide for supercapacitor with high $C_{SP}$ 243 Fg$^{-1}$ at 5mVs$^{-1}$. Fan et al. reported MnO$_2$-NiO nanoflake-assembled tubular array on stainless steel substrate by template method where ZnO is employed as in situ sacrificial template [9]. Although high capacitance values are achieved using nano architectures, the bulk material performance and the electrode cyclability could be further improved.

In this work, we investigated the in situ inclusion of nickel in Manganese oxide ($\text{Ni}_y\text{Mn}_{1-y}\text{O}_x$; $0 \leq y \leq 0.4$) lattice and tested the composite material as supercapacitor electrodes. NiMn$_2$O$_4$ crystallizes as a prominent phase when 20 wt% NiCl$_2$ is added to 80 wt% aqueous MnCl$_2$ solution for oxidative growth of manganese oxide. Ni$_{0.2}$Mn$_{0.8}$O$_x$ exhibits highest electrical conductivity and surface area among other compositions. Proposed supercapacitor, Ni$_{0.2}$Mn$_{0.8}$O$_x$/Ni$_{0.2}$Mn$_{0.8}$O$_x$ provides high energy density 35 WhKg$^{-1}$ with ~92% retention of initial $C_{SP}$ after 3000 galvanostatic charge/discharge cycles.

2. EXPERIMENTAL

2.1 Materials. Nickel chloride (NiCl$_2$.6H$_2$O), Manganese chloride (MnCl$_2$.4H$_2$O), Sodium hydroxide (NaOH), Sodium sulphate (Na$_2$SO$_4$), isopropyl alcohol (IPA) and isoctane were purchased from Merck. Perfluorinated ion exchange resin (Nafion) was procured by Sigma Aldrich. Sodium sulphasuccinate (AOT) was used as surfactant (supplied by Alfa Aesar).

2.2 Synthesis of Nickel Manganese mixed oxide. Three aliquots of reverse microemulsions of water/AOT/isoctane [13] were prepared having 0.8 M MnCl$_2$, 0.2 M NiCl$_2$ and 2 M NaOH aqueous solutions respectively. These were thoroughly mixed in a reaction vessel and stirred for 2 hr. Excessive volume of IPA was added to break the micellar arrangement after completion of the reaction. The resulting precipitate was collected after washing several
times with IPA and deionized water. Solid product obtained after washing was dried overnight at 80°C. Different compositions of Ni_yMn_{1-y}O_x; 0.1 ≤ y ≤ 0.4 were prepared as given in Table 1(y is molar concentration of nickel in MnO_x). MnO_x and Ni(OH)_2 were also synthesized by the same method under similar conditions [14].

2.3 Preparation of electrode. 10 mg of composite material (Ni_yMn_{1-y}O_x; 0.1 ≤ y ≤ 0.4) was ultrasonically mixed with 5 wt % Nafion in IPA. The mixture after 30 min. sonication was spray deposited on 1 cm^2 area of the polished graphite sheets (2 x 1 cm) with the help of N_2 gas. After spray deposition, the film was dried at 80°C in air and weighed to estimate the loading of the composite material. Loading was found to be approximately 0.3 mg cm^-2.

2.4 Characterization. Conductivity measurements were carried out on pellet (dia. 10 mm) using Keithley 2400 source meter. Perkin Elmer model 1257 X-ray Photoelectron spectroscope (XPS) was employed to estimate the percentages of different metal oxide phases present in the specimen. Powder X-Ray Diffraction (XRD) measurements were performed with Bruker D8 Advance X-ray diffractometer. Microstructural investigations were carried out using Zeiss Ultra 55 Field emission scanning electron microscope (FESEM). Surface area of the samples were analyzed by N_2 adsorption desorption isotherms using Micromeritics ASAP-2020. High resolution transmission electron microscopy (HRTEM) and Selected Area Electron Diffraction (SAED) was conducted on Phillips Technai T-300 microscope. Electrochemical tests were performed with CHI 604D electrochemical analyzer. A piece of platinum gauze and Ag/AgCl were assembled as the counter and reference electrode respectively. Polished graphite with metal oxide/mixed metal oxide coating served as the working electrode. Cyclic voltammograms (CV) were recorded by polarizing the working electrode between 0 to 0.9V vs Ag/AgCl in 0.5 M aqueous Na_2SO_4 electrolyte. The charge/discharge characteristics of the supercapacitor cell were evaluated at different current...
density (two electrode assembly) using an Arbin instrument (model: BT2000, USA). \( C_{SP} \) was calculated from galvanostatic charge/discharge curve according to following equation [3,15]:

\[
C = \frac{I\Delta t}{m\Delta V}
\]

where \( I \) is the current, \( \Delta V/\Delta t \) is the change in potential with time and \( m \) is mass loading on the electrode.

The energy density \( (E \text{ in Wh Kg}^{-1}) \) and power density \( (P \text{ in W Kg}^{-1}) \) were expressed as

\[
E = \frac{1}{2 \times 3.6} CV^2
\]

\[
P = \frac{V^2}{4mR}
\]

where \( C \) is measured device capacitance, \( m \) is total mass loading on the electrodes, \( V \) is the operating potential range and \( R \) is the equivalent series resistance calculated from IR drop in Galvanostatic discharge curve.

3. RESULTS AND DISCUSSION

The effect of Ni incorporation in MnO\(_x\) matrix was studied using Cyclic Voltammetry (CV) and Current (I)-Voltage (V) characteristics for Ni\(_y\)Mn\(_{1-y}\)O\(_x\); 0.1 \( \leq y \leq 0.4 \). Figure 1 shows the variation of \( C_{SP} \) and electrical resistivity with different nickel percentage in MnO\(_x\). Ni\(_{0.1}\)Mn\(_{0.9}\)O\(_x\) did not show much change in \( C_{SP} \) but the resistivity is slightly increased. Ni\(_{0.2}\)Mn\(_{0.8}\)O\(_x\), compared to MnO\(_x\) shows more than twice increase in \( C_{SP} \) with drastic decrement in resistivity. Upon 20 wt% inclusion of Ni, \( C_{SP} \) of MnO\(_x\) (180 Fg\(^{-1}\)) remarkably increases to 380 Fg\(^{-1}\) with one order decrease in resistivity (1.85 X 10\(^5\) ohm cm of MnO\(_x\) to
2.07 \times 10^4 \text{ ohm cm of Ni}_{0.2}\text{Mn}_{0.8}O_x). With further increase in nickel content, Ni_{0.4}\text{Mn}_{0.6}O_x shows detrimental effect as C_{SP} decreases and resistivity increases. More importantly, drastic increment in C_{SP} of Ni_{0.2}\text{Mn}_{0.8}O_x is investigated by its structural and electrochemical analysis.

Figure 2 shows scanning electron micrographs and the surface area analysis using BET. The surface microstructure of MnO_x, Ni_{0.2}\text{Mn}_{0.8}O_x and Ni_{0.4}\text{Mn}_{0.6}O_x exhibit granular morphology. MnO_x in Figure 2a, shows aggregated spherical grains of dia. \sim 10 \text{ nm}. Ni_{0.2}\text{Mn}_{0.8}O_x exhibited an increase in grain size (dia. \sim 15 \text{ nm}) (Figure 2b). Upon increasing Ni concentration to 40 wt % (Ni_{0.4}\text{Mn}_{0.6}O_x), the composite exhibited dense microstructural features with very high aggregation (Figure 2c). It appears that the increased concentration of Ni increases the aggregation.

N_2 adsorption-desorption isotherm analysis of MnO_x show high specific surface area (80.5 m^2 g^{-1}) with Type IV isotherm with H1 type hysteresis loop (Figure 2d). Upon inclusion of 20 wt% nickel (Ni_{0.2}\text{Mn}_{0.8}O_x), surface area significantly increases to 118 m^2 g^{-1}. Nearly 50% enhancement in the specific surface area is attributed due to the complex pore network as in case of H2 hysteresis loop (Figure 2e). Increasing the Ni more than 20 wt%, the surface area shows a decrease (Figure 2f) and is attributed to the dense morphology of the composite having high Ni concentration. Pore size distribution of MnO_x (Supplimentary info S1) demonstrate the presence of mesopores (5-20 nm) whereas in Ni_{0.2}\text{Mn}_{0.8}O_x, majority of pores fall in the optimal sizes of 2-5 nm for supercapacitors [16] and thus supports the high surface area of Ni_{0.2}\text{Mn}_{0.8}O_x, consequently resulting in enhanced capacitance.

XPS analysis of MnO_x show two peaks of MnO_2 and Mn_3O_4 in Mn 2p at 641.8 eV and 642.43 eV respectively [17]. Areas covered under MnO_2 and Mn_3O_4 peak are estimated
to be 85% and 15% respectively (Figure 3a) ascertaining the simultaneous presence of MnO$_2$ and Mn$_3$O$_4$ in MnO$_x$. As shown in Figure 3b, the survey scan of Ni$_{0.2}$Mn$_{0.8}$O$_x$ confirm the presence of Mn, Ni and O in the composite. Inset shows Ni 2p XPS which is assigned to Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ peaks with two satellites (sat.). The spin energy separation of Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ is 17.5 eV which is characteristic of Ni(OH)$_2$ phase [18] Mn 2p XPS spectrum of Ni$_{0.2}$Mn$_{0.8}$O$_x$ shows a single peak at 642.4 eV (Figure 3c), analogous to that of MnO$_x$ ascertaining the absence of Mn$_3$O$_4$ in Ni$_{0.2}$Mn$_{0.8}$O$_x$.

XRD analysis of MnO$_x$ and Ni$_{0.2}$Mn$_{0.8}$O$_x$ further supported XPS results. Figure 3d shows XRD patterns of Manganese oxide (MnO$_x$) and Ni$_{0.2}$Mn$_{0.8}$O$_x$. Diffraction pattern of MnO$_x$ endorses the presence of different phases i.e. MnO$_2$ and Mn$_3$O$_4$ [19]. XRD pattern of Ni$_{0.2}$Mn$_{0.8}$O$_x$ exhibits three major diffraction peaks at 18°, 35.6° and 63.5° indexed to (111), (311) and (440) planes of spinel NiMn$_2$O$_4$ respectively [20, 21]. The diffraction pattern showed relatively amorphous character with indication of the presence of some secondary phases like MnO$_2$, Ni(OH)$_2$ and NiMnO$_3$, interestingly there is no sign of Mn$_3$O$_4$. An important observation of the work is that in situ incorporation of 20 wt% Ni in MnO$_x$ results in NiMn$_2$O$_4$ as prominent phase formation with complete suppression of manganese higher oxide (Mn$_3$O$_4$) phases. The suppression of Mn$_3$O$_4$ is attributed to its distorted spinel structure having Mn$^{2+}$ ions in tetrahedral sites and Mn$^{3+}$ ions in octahedral sites [22]. These Mn$^{3+}$ ions causes Jahn Teller distortion which is the result of departure from ideal interactions among bonding orbital and gives rise to lattice instability [23]. Ni$^{2+}$ ions can replace Mn$^{3+}$ ions from octahedral site and such a substitution might require an equivalent amount of remaining Mn$^{3+}$ ions to lose electrons and become Mn$^{4+}$ in order to maintain the charge balance consequently resulting in NiMn$_2$O$_4$. Such a cation distribution offers lesser lattice alterations during electrochemical cycling resulting in enhanced electrochemical stability of NiMn$_2$O$_4$ [8].
Annealing carried out at different temperatures helped understanding the growth of NiMn$_2$O$_4$ by intermixing of secondary phases. Figure 3e shows diffraction patterns of Ni$_{0.2}$Mn$_{0.8}$O$_x$ powder after 2hr annealing at different temperatures. XRD pattern of Ni$_{0.2}$Mn$_{0.8}$O$_x$ without any annealing treatment show three major diffraction peaks at 20 value of 18°, 35.6°, 63.5° confirming the presence of NiMn$_2$O$_4$ [24] with some other less intense peaks of MnO$_2$, Ni(OH)$_2$ and NiMnO$_3$. Annealing results in grain growth and intermixing of the secondary phases. The Ni$_{0.2}$Mn$_{0.8}$O$_x$ sample after 250°C annealing shows the presence of prominent NiMn$_2$O$_4$ with some secondary phases of MnO$_2$ and NiO and a shoulder NiMnO$_3$ at 36.7°. Here, Ni(OH)$_2$ converts to NiO which shows a peak at 61.2° corresponding to (220) plane. Further elevation in annealing temperature (450°C) shows the crystalline XRD pattern of NiMn$_2$O$_4$ with presence of NiMnO$_3$. Quantification of the above XRD pattern by Xpert High Score software via Rietveld method (supplementary information S2) suggest the percentage of prominent phase NiMn$_2$O$_4$ (81.3%) and NiMnO$_3$ (18.7%). It is assumed that the secondary phases of MnO$_2$ and NiO intermix and form NiMn$_2$O$_4$. The formation of NiMnO$_3$ could be due to dissociation of NiMn$_2$O$_4$ phase as discussed in later section. The XRD pattern of Ni$_{0.2}$Mn$_{0.8}$O$_x$ annealed at 650°C made this aspect clear and showed higher (44.5%) percentage of NiMnO$_3$ [25]. The increase in intensity of the peaks corresponds to gradual evolution to crystalline phases.

Thermo-gravimetric analysis of Ni$_{0.2}$Mn$_{0.8}$O$_x$ supports the phase transformation as observed in the X-ray diffraction. Due to loss of the adsorbed and/or structurally bonded water, TGA thermogram of Ni$_{0.2}$Mn$_{0.8}$O$_x$ (Figure 3f) shows ~18% weight loss below 120°C. Further weight loss ~ 7% between 120-250°C corresponds to the decomposition of Ni(OH)$_2$ to NiO and H$_2$O according to the following probable reaction:

$$\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O}$$
Gradual 8% weight loss between 350-450°C is attributed to the formation of NiMn$_2$O$_4$ and evolution of oxygen according to the reaction: [26]

$$2\text{MnO}_2 + \text{NiO} \rightarrow \text{NiMn}_2\text{O}_4 + \frac{1}{2}\text{O}_2$$

Major 36% weight loss between 450-700°C is attributed to the evaporation of MnO from NiMn$_2$O$_4$ according to the following reaction which is in agreement with the XRD results of Ni$_{0.2}$Mn$_{0.8}$O$_x$ oxide annealed at 650°C:

$$\text{NiMn}_2\text{O}_4 \rightarrow \text{NiMnO}_3 + \text{MnO(g)}$$

As MnO is evaporated, characteristic peaks in the XRD pattern corresponds to NiMn$_2$O$_4$ and NiMnO$_3$ which shows the simultaneous presence of both.

TEM micrographs in Figure 4a shows spherical particles with dia. ~20 nm. Continuous lattice fringes (Figure 4b) reveals d spacing 0.25 nm (311) of NiMn$_2$O$_4$. Three different planes (111), (311) and (440) of NiMn$_2$O$_4$ are observed in SAED pattern which are in agreement with XRD results (Figure 4c). SEM of Ni$_{0.2}$Mn$_{0.8}$O$_x$ (Figure 4d) shows interconnected spherical nanoparticles forming porous channels. EDX results of spherical particles show Ni/Mn ratio ~ 0.25 which is in agreement with experimental value (Figure 4e).

The electrochemical performance of Ni$_{0.2}$Mn$_{0.8}$O$_x$ is investigated by Cyclic Voltammetry (CV) and Electrochemical impedance spectroscopy (EIS). CV of Ni$_{0.2}$Mn$_{0.8}$O$_x$ show much larger area indicating higher charge storage (~380 F g$^{-1}$) than MnO$_x$ (~180 F g$^{-1}$) and Ni(OH)$_2$ (~95 F g$^{-1}$), (Figure 5a). This $C_{SP}$ is higher than previous MnO$_2$-based nanocomposites electrodes, such as the graphene/MnO$_2$-based textile (315 F g$^{-1}$) and MnO$_2$ nanosheets/graphene (263 F g$^{-1}$) [12,27,28]. Moreover, absence of any peak indicates pseudoconstant charging and discharging over whole voltammetric cycle [29]. The possible charge storage mechanism in Ni$_{0.2}$Mn$_{0.8}$O$_x$(NiMn$_2$O$_4$ prominent phase) may be explained as:

$$\text{NiMn}_2\text{O}_4 + \text{Na}^+ + \text{e}^- \rightarrow \text{NaNiMn}_2\text{O}_4$$
Complex plane plot of $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$ reveals resistive and capacitive response with change in frequency (Figure 5b). The equivalent circuit for the best fit conditions is shown in the inset. High frequency region of the Nyquist plot, represented by suppressed semicircle shows internal resistance $R_S \sim 5.3 \ \Omega$ and the high to mid frequency region represents RC circuit ($R_{CT}$, charge transfer resistance and $C_{dl}$, double layer capacitance). $R_{CT} (1\ \Omega)$, lower than earlier reported values of MnO$_2$-NiO composite indicates intimate contact formation between the current collector and electrolyte contributing to facile charge transfer [9]. A $45^\circ$ sloped line in the mid frequency range corresponds to Warburg impedance which is related to ion diffusion resistance. Inset shows Nyquist plot of MnO$_x$ and $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$ exhibiting similar behaviour in high and low frequency region. Besides, the impedance line of MnO$_x$ possess an arc in mid frequency region restricting the accessibility of ions causing low capacitance of MnO$_x$. More importantly, capacitive character of $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$ attains earlier than that of MnO$_x$ as evident from higher knee frequency below which maximum energy is easily accessible.

Effect of annealing on $C_{SP}$ of $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$ is shown by Figure 5c. Inset shows variation of $C_{SP}$ vs annealing temperature. $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$ has NiMn$_2$O$_4$ as prominent phase which shows high $C_{SP}$ 380 $\text{F g}^{-1}$. It is important to mention that the samples were dried at 80$^\circ$C for 1 hr. Extending this temperature to 250$^\circ$C for 2 hr results in $C_{SP}$ decrement to 290 $\text{F g}^{-1}$ which may be due to improved crystallinity of the material [30]. At 450$^\circ$C, single phase XRD pattern (NiMn$_2$O$_4$) shows $C_{SP}$ 220 $\text{F g}^{-1}$ which is in close proximity to the reported values [12]. Above 450$^\circ$C, crystalline evolution takes place and the crystal lattice is rigid and not easily expanded (or contracted). This consequently retards the protonation (or deprotonation) reaction of the oxide leading to drastic decrement of $C_{SP}$ at 650$^\circ$C.
Cycling life stability of MnOₓ and Ni₀.₂Mn₀.₈Oₓ is explored by relatively long time cycling at 50 mVs⁻¹ (Figure 5d). Result shows that Cₛₚ of Ni₀.₂Mn₀.₈Oₓ shows an increment in initial cycles followed by ~99% retention up to 10,000 cycles. Initial increment is probably attributed to activation process involving the increment in the number of available active sites allowing the trapped ions to gradually diffuse out [31]. Cₛₚ decay in MnOₓ decays is found to be 50% after 10,000 cycles. This remarkable difference in cycling life stability with and without nickel in MnOₓ electrode is investigated by XPS analysis before and after electrochemical cycling.

Core level Mn 2p XPS of MnOₓ after redox cycling (unlike before cycling) shows intense peak of Mn₃O₄ with relatively less intense MnO₂ peak (Figure 5e). Ni₀.₂Mn₀.₈Oₓ after electrochemical cycling shows a single peak of MnO₂ with no Mn₃O₄. This demonstrate considerable conversion of MnO₂ to less electroactive Mn₃O₄ phase during cycling (Figure 5f). This implicates that the decrement in charge storing capacity of MnOₓ was due to the gradual formation of Mn₃O₄. It is noteworthy that in-situ availability of nickel (20 wt%) in MnOₓ inhibits Mn₃O₄ formation not only during growth but also during redox cycling, thereby enhancing the electrochemical performance of Ni₀.₂Mn₀.₈Oₓ.

As a demonstration of application potential of Ni₀.₂Mn₀.₈Oₓ, a symmetric supercapacitor, Ni₀.₂Mn₀.₈Oₓ//Ni₀.₂Mn₀.₈Oₓ is fabricated and examined via GCD measurements. Figure 6a shows GCD curves of Ni₀.₂Mn₀.₈Oₓ//Ni₀.₂Mn₀.₈Oₓ at different current densities. Deviation from the linear variation of voltage with time is attributed to pseudocapacitive nature of the material. Small IR drop associated with the discharge curve ascertains low equivalent series resistance (esr) of the cell which can be calculated from the slope of linear correlation of IR drop with current density [32, 33].
Variation of $C_{SP}$ and IR drop at different current density in Figure 6b display lesser esr ~0.03 $\Omega$ favouring high power delivery in practical applications making it a potential material for supercapacitor. Moreover, $C_{SP}$ decreases with increase of current density as lesser surface area is accessible at higher current densities. It delivers energy density 35 Wh Kg$^{-1}$ with power density 3.74 kW Kg$^{-1}$ at 0.5Ag$^{-1}$ (Figure 6c). It still maintains an energy density 5.10 Wh Kg$^{-1}$ and power density 7.44 kW Kg$^{-1}$ even at high current density 12.5Ag$^{-1}$.

Long term cycling performance of $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x/\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$ was investigated by GCD cycling at 2.5 Ag$^{-1}$ (Figure 6d). Inset shows overview of charge /discharge cycles. Slight increment in $C_{SP}$ during initial 1000 cycles as observed in various reports [31], followed by 8% decrement in $C_{SP}$ in further cycles. Such a high retainability of initial $C_{SP}$ after 3000 cycles endows a long term stable material for charge storage in supercapacitor.

4. CONCLUSIONS

In situ inclusion of nickel during manganese oxide ($\text{Ni}_y\text{Mn}_{1-y}\text{O}_x$; $0 \leq y \leq 0.4$) growth and its effect on structural, electrical and electrochemical properties is investigated. Upon 20 wt % addition of nickel in MnO$_x$ ($\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$) the composite exhibited spinel NiMn$_2$O$_4$ as prominent phase with highest surface area (118 m$^2$g$^{-1}$), Consequently the superior performance in terms of highest conductivity and $C_{SP}$ ($\approx$380 Fg$^{-1}$). Galvanostatic charge discharge measurements of fabricated supercapacitor, $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x/\text{Ni}_{0.2}\text{Mn}_{0.8}\text{O}_x$ demonstrate high energy and power density (35 Wh Kg$^{-1}$, 3.74 kW Kg$^{-1}$). Furthermore, it also retains 92% initial capacitance after 3000 cycles ascribing excellent cycling stability.
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REFERENCES


List of table

Table 1. Percentage of nickel in manganese oxide.

Figure Captions

Figure 1  Effect of Ni (wt%) on resistivity and $C_{SP}$ of Ni$_x$Mn$\nu$O$_x$; 0≤ $\nu$≤ 0.4.

Figure 2  SEM micrographs (a, b and c) and $N_2$ adsorption-desorption isotherms (d, e and f) of MnO$_x$, Ni$_{0.2}$Mn$_{0.8}$O$_x$ and Ni$_{0.4}$Mn$_{0.6}$O$_x$.

Figure 3 (a) Mn 2p X-ray photoelectron spectrum (XPS) of MnO$_x$, (b) XPS survey scan with Ni 2p core level spectra in inset (c) Deconvoluted Mn 2p spectrum of Ni$_{0.2}$Mn$_{0.8}$O$_x$, (d) X-ray diffraction patterns of MnO$_x$ and Ni$_{0.2}$Mn$_{0.8}$O$_x$, (e) XRD patterns of Ni$_{0.2}$Mn$_{0.8}$O$_x$ powder annealed at 250°C, 450°C and 650°C and (f) Thermogravimetric analysis of Ni$_{0.2}$Mn$_{0.8}$O$_x$.

Figure 4 (a) TEM of Ni$_{0.2}$Mn$_{0.8}$O$_x$ and (b) HRTEM shows d spacing ~0.25 nm, (c) SAED pattern, (d) SEM and (e) EDX of Ni$_{0.2}$Mn$_{0.8}$O$_x$ with atomic percentage of Ni:Mn ~0.25.

Figure 5 (a) Cyclic Voltammograms (CV) of MnO$_x$, Ni(OH)$_2$ and Ni$_{0.2}$Mn$_{0.8}$O$_x$ at 5mVs$^{-1}$, (b) Nyquist plot of Ni$_{0.2}$Mn$_{0.8}$O$_x$ in high frequency region. Inset shows Nyquist plot of MnO$_x$ and Ni$_{0.2}$Mn$_{0.8}$O$_x$, (c) Effect of annealing temperature on CV response of Ni$_{0.2}$Mn$_{0.8}$O$_x$ electrode. Inset shows variation of specific capacitance vs annealed temperatures, (d) Cycling life test of MnO$_x$ and Ni$_{0.2}$Mn$_{0.8}$O$_x$ at 50 mVs$^{-1}$ and (e and f) Mn 2p XPS spectra of Ni$_{0.2}$Mn$_{0.8}$O$_x$ and MnO$_x$ after 10,000 CV cycles.

Figure 6 (a) Galvanostatic charge discharge (GCD) curves at different current densities, (b) Variation of IR drop and specific capacitance vs current density, (c) Ragone plot and (d) GCD cycling performance of Ni$_{0.2}$Mn$_{0.8}$O$_x$/Ni$_{0.2}$Mn$_{0.8}$O$_x$ supercapacitor cell. Inset shows overview of last cycles.
Table 1. Percentage of nickel in manganese oxide

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<td>Ni₀.₄Mn₀.₆Oₓ</td>
<td>1.90</td>
<td>2.37</td>
<td>1.60</td>
<td>65</td>
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Legend for Graphical abstract

At optimised composition (20 wt %) of nickel, composite crystallizes into spinel NiMn$_2$O$_4$ that in a supercapacitor cell gives the best performance in terms of Energy and Power density.
At optimised composition (20 wt %) of nickel, composite crystallizes into spinel NiMn2O4 that in a supercapacitor cell gives the best performance in terms of Energy and Power density.
Effect of Ni (wt%) on resistivity and CSP of Ni\textsubscript{y}Mn\textsubscript{1-y}O\textsubscript{x}; 0 \leq y \leq 0.4.
SEM micrographs (a, b and c) and N2 adsorption-desorption isotherms (d, e and f) of MnOx, Ni0.2Mn0.8Ox and Ni0.4Mn0.6Ox.

32x36mm (300 x 300 DPI)
(a) Mn 2p X-ray photoelectron spectrum (XPS) of MnOx, (b) XPS survey scan with Ni 2p core level spectra in inset (c) Deconvoluted Mn 2p spectrum of Ni0.2Mn0.8Ox, (d) X-ray diffraction patterns of MnOx and Ni0.2Mn0.8Ox, (e) XRD patterns of Ni0.2Mn0.8Ox powder annealed at 250°C, 450°C and 650°C and (f) Thermogravimetric analysis of Ni0.2Mn0.8Ox.
(a) TEM of Ni0.2Mn0.8Ox and (b) HRTEM shows d spacing ~0.25 nm, (c) SAED pattern, (d) SEM and (e) EDX of Ni0.2Mn0.8Ox with atomic percentage of Ni:Mn ~0.25.
(a) Cyclic Voltammograms (CV) of MnOx, Ni(OH)2 and Ni0.2Mn0.8Ox at 5mVs⁻¹, (b) Nyquist plot of Ni0.2Mn0.8Ox in high frequency region. Inset shows Nyquist plot of MnOx and Ni0.2Mn0.8Ox, (c) Effect of annealing temperature on CV response of Ni0.2Mn0.8Ox electrode. Inset shows variation of specific capacitance vs annealed temperatures, (d) Cycling life test of MnOx and Ni0.2Mn0.8Ox at 50 mVs⁻¹ and (e and f) Mn 2p XPS spectra of Ni0.2Mn0.8Ox and MnOx after 10,000 CV cycles.
(a) Galvanostatic charge discharge (GCD) curves at different current densities, (b) Variation of IR drop and specific capacitance vs current density, (c) Ragone plot and (d) GCD cycling performance of Ni0.2Mn0.8Ox//Ni0.2Mn0.8Ox supercapacitor cell. Inset shows overview of last cycles.

183x141mm (300 x 300 DPI)