Nanostructured spinel manganese cobalt ferrite for high-performance supercapacitors

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We report on the synthesis of manganese cobalt ferrite (MnCoFeO₄) nanoparticles via a simple one-pot co-precipitation method and their characterization through energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Fourier transform infrared (FT-IR) spectroscopy and N₂ adsorption/desorption techniques. The MnCoFeO₄ supercapacitor showed the maximum specific capacitance of 675 F g⁻¹ at a scan rate of 1 mV s⁻¹. Its energy and power densities were 18.85 W h kg⁻¹ and 337.50 W kg⁻¹, respectively, at a current density of 1.5 A g⁻¹. The cyclic stability was scrutinized via galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS). The degradation of the supercapacitive performance was only 7.14% after 1000 GCD cycles, indicating an excellent long-term stability. The equivalent series resistance (ESR) remained nearly constant even after 1000 GCD cycles.

1. Introduction

Nowadays, the worldwide community suffers from serious environmental problems arising from an excessive combustion of fossil fuels. Consequently, many researchers have paid great attention to manipulate the clean and sustainable energy sources as well as efficient energy conversion and storage technologies. Batteries and supercapacitors are the typical devices used for the storage of electrical energy. Both of these store electricity through electrochemical processes. Compared to the batteries, the supercapacitors are characterized by higher power density, rapid charge/discharge, and long-life service. Despite the advantages of high power density and high cycle life of supercapacitors, their intrinsically low energy density (i.e. the amount of energy stored per unit weight) has limited them from widespread commercial applications in comparison to batteries. To this end, increasing their energy density requires an extensive research and development, including the merge of batteries and supercapacitors.

According to their active materials, supercapacitors (SCs) are classified into two main types: electrochemical double layer capacitors (DCs) and electrochemical pseudocapacitors (PCs). The active material in the DCs is composed of carbonaceous (carbon-based) materials, such as activated carbon, graphite, and graphene. Energy is stored physically within a DC via charge accumulation across the electrode/electrolyte interface. As for PCs, the active material is primarily composed of a transition metal (TM) oxide, a TM nitride or a conducting polymer. Energy is stored electrochemically within a PC via the reversible interfacial redox reactions in TMs or via ion intercalation throughout the electrode in conducting polymers. Due to the intrinsic low specific capacitance (Cₛₚ) and low energy density stored in the current SCs, it is vital to explore new materials that simultaneously exhibit high Cₛₚ as well as high conductivity. TMs are characterized by being cost-effective and displaying multiple oxidation states in addition to their fast and reversible faradaic redox reactions. Therefore, TMs are engrossed as the electrode materials for supercapacitor applications because of their outstanding electrochemical performance. In addition, TM oxides can provide a higher theoretical Cₛₚ than that of the conventional carbon-based materials and a better electrochemical stability than that of the polymeric materials. Among them, RuO₂ has been widely investigated as a promising candidate because of its better conductivity and high Cₛₚ; however, it is limited by its high cost, rarity, and toxicity. Alternative inorganic electrode materials such as MnO₂, Co₃O₄, NiO, V₂O₅/VO₄, WO₃ and Fe₂O₃ have been intensively investigated in SC applications owing to their wide availability, chemical stability, mechanical strength, safety, and eco-friendliness. Recently, ferrites as SC materials have been explored by researchers due to their various redox states, electrochemical stability as well as remarkable magnetic, catalytic, optical, and electrical properties. Ferrite-based materials have been synthesized in diverse nanostructured forms, including nanoparticles, nanotubes, nanofibers, nanowires, nanorods, nanolakes, nanomesh arrays, nanosheets, and hollow structures. Ferrites can be synthesized via various synthesis techniques.
Co, and Fe are majorly (+II), (+III), and (+III), respectively. In
cocreate the octahedral sites. Besides, the valence states of Mn,
Co, in the form of Co2+, could occupy both octahedral and
oxidation state (+III) and occupied the octahedral sites, while
Al
NiCuFe2O4, 44.0 4.62 1001.99 12
NiCoFe2O4, 50.0 4.79 1426.23 12
Mn atoms in MnCoFeO4 prefer
to occupy the tetrahedral positions, while Co atoms prefer to
occupy the octahedral sites. Besides, the valence states of Mn,
Co, and Fe are majorly (+II), (+III), and (+III), respectively. In
contrast, Martens28 has studied the magnetoptical properties of
MnCoFe2−yO4 (where x = 0, 0.5, and 1.0) prepared using a
conventional ceramic technology with a final sinter treatment
in oxygen for 24 h at 1300 °C and found that Mn has the
oxidation state (+III) and occupied the octahedral sites, while
Co in the form of Co2+, could occupy both octahedral and
tetrahedral positions with the latter being more favorable.
These observations were confirmed by two later studies based on
submicron MnCoFe2−yO4 spinel ferrites by Chassaing et al.28 and Laarj and Kacim.34 In both studies, MnCoFe2−yO4
spinel ferrites were prepared from the oxalic precursors and subjected
to annealing treatment between 600 °C and 700 °C.
Numerous binary TM ferrites have been investigated for
supercapacitor applications such as ZnFe2O4,37 CoFe2O4,14
MnFe2O4,37 CuFe2O4,26 and SnFe2O4.10 However, few research
studies were carried out on ternary TM ferrites as the electrodes
for supercapacitor applications as listed in Table 1.
Herein, MnCoFeO4 was synthesized in the form of nano-
particles via the co-precipitation method and characterized by
EDS, XRD, TEM, FT-IR analyses, and N2 adsorption/desorption.
Its supercapacitive performance in 6 M KOH was investigated
via cyclic voltammetry (CV) and galvanostatic charging/
discharging (GCD). The cyclic stability was studied via GCD
and electrochemical impedance spectroscopy (EIS). The
materials showed an exceptional Csp as compared to the Csp of
those reported in the literature.
2. Experimental methods
2.1. Preparation of MnCoFeO4
To obtain MnCoFeO4, 0.005 mole of MnCl2·4H2O was dissolved
in 50 ml deionized water, 0.005 mole of CoCl2·6H2O was dissolved
in 50 ml deionized water, and 0.01 mole of anhydrous
FeCl3 was dissolved in 250 ml deionized water. The three
solutions were mixed together with continuous stirring and kept at 65 °C until thermal equilibrium was achieved. Then,
100 ml of 0.8 M NaOH solution was added dropwise to the
mixed solution with continuous stirring and a black precipitate
was formed. The formed precipitate was separated from the
liquid phase and washed several times with deionized water via
centrifugation until neutrality. The neutrality of the decanted
aliquot was checked using phenolphthalein indicator. Finally,
the washed precipitate was dried at 100 °C.
2.2. Characterization of MnCoFeO4
Elemental composition was identified by means of energy-
dispersive spectroscopy (EDS) using an Oxford EDS detector.
The structural characteristics of the prepared material were
investigated via X-ray diffraction (XRD) using a PANalytical
X’pert PRO diffractometer with a Cu Kα radiation. The particle
morphology of the prepared material was studied via high-
resolution transmission electron microscopy (HR-TEM) using
a JEOL JEM-2100 (Japan) electron microscope, operating at an
accelerated voltage of 200 keV. Prior to the analysis, the sample
was dispersed in ethanol using a probe sonicator and then a drop of the much-diluted sample solution was deposited on a
carbon-coated copper grid and allowed to be evaporated at
room temperature. Fourier transform infrared (FT-IR) spec-
troscopy was performed in the range of 400–4000 cm−1 to
determine the metal oxide peaks using a PerkinElmer Spectrum
One spectrophotometer. The adsorption capability of the
prepared material and its specific surface area were investigated
by N2 gas adsorption/desorption (at 77 K) and Brunauer–
Emmett–Teller (BET) analysis, respectively, using a Quantach-
rome NOVA Station A (version 11.03).
2.3. Electrochemical measurements
A working electrode was prepared using a homogenous slurry of
MnCoFeO4 with carbon black acting as a conductive additive

Table 1  Supercapacitive performance of MnCoFeO4 compared with some other ferrite-based materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Csp (F g⁻¹)</th>
<th>ED (W h kg⁻¹)</th>
<th>PD (W kg⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCoFe2O4</td>
<td>76.9</td>
<td>7.90</td>
<td>1711.95</td>
<td>12</td>
</tr>
<tr>
<td>NiCoFe2O4</td>
<td>50.0</td>
<td>4.79</td>
<td>1426.23</td>
<td>12</td>
</tr>
<tr>
<td>NiCuCo2O4</td>
<td>44.0</td>
<td>4.62</td>
<td>1001.99</td>
<td>12</td>
</tr>
<tr>
<td>CuCo2O4</td>
<td>397.0</td>
<td>3.53</td>
<td>198.50</td>
<td>49</td>
</tr>
<tr>
<td>AlCO2CuFe2O4 (x + y + z = 1)</td>
<td>256.0–540.0</td>
<td>0.58–8.42</td>
<td>128.00–270.00</td>
<td>49</td>
</tr>
<tr>
<td>MnCoFeO4</td>
<td>670.0</td>
<td>3.15</td>
<td>2250.00</td>
<td>This work</td>
</tr>
</tbody>
</table>
and poly(vinylidene difluoride) acting as a binder in a DMF solvent with a weight ratio of 70 : 20 : 10. The prepared slurry was stirred for about 48 h at room temperature, then coated onto a part of a 1 cm × 2 cm chip of nickel foam (as a supporter and current collector) and dried at 60 °C. The supercapacitive performance of the prepared MnCoFeO₄ electrode was investigated using a three-electrode cell containing the working electrode (the prepared electrode under study), a counter electrode (a Pt coil) and a reference electrode (a saturated calomel electrode, SCE) in a 6 M KOH solution at room temperature. The electrochemical measurements involved cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and electrochemical impedance spectroscopy (EIS) using the electrochemical workstation (CHI 760D, CH Instruments, U.S.A.). CV measurements were performed within the potential window of 0–0.45 V at different scan rates (from 1 to 100 mV s⁻¹). GCD measurements were carried out at different current densities (1.5–10 A g⁻¹) within the same potential window. The EIS measurements were performed in the frequency range of 100 kHz to 0.1 Hz at the steady-state open circuit potential (0.261 V vs. SCE) with a sinusoidal perturbation amplitude of 10 mV. EIS parameters were derived using EC-Lab V10.40 software.

The specific capacitance \( C_{sp} \) \( \text{F g}^{-1} \) was then calculated from data obtained from CV and GCD measurements according to eqn (1)²⁹,²² and (2)¹⁴,¹⁷,³⁸ respectively.

\[
C_{sp} = \frac{\int I(dV)}{m\Delta V}
\]

(1)

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

(2)

where \( I \) is the response current (A), \( m \) is the mass of active material (g), \( v \) is the scan rate (mV s⁻¹), \( \Delta V \) is the potential window (V), and \( \Delta t \) is the discharge time (s). The coulombic efficiency \( (\eta) \) was calculated from GCD measurements as follows:³⁹,⁴⁰

\[
\eta = \frac{t_d}{t_c} \times 100
\]

(3)

where \( t_c \) and \( t_d \) are the times of charging and discharging with the same current density, respectively. The energy density and the power density of the MnCoFeO₄ supercapacitor can be calculated from eqn (5) and (6)¹⁴,⁴⁰–⁴²

\[
E = \frac{1}{2}C_{sp}\Delta V^2
\]

(4)

eqn (4) can be reformed as follows:

\[
E = \frac{1}{2} \frac{\Delta V I t}{m}
\]

(5)

\[
P = \frac{E}{I}
\]

(6)

where \( I \) is the response current (A), \( m \) is the mass of active material (kg), \( \Delta V \) is the potential window (V), and \( t \) is the discharge time (h).

3. Results and discussion

3.1. Material characterization

Fig. 1a demonstrates the EDS spectrum of the prepared MnCoFeO₄, showing the peaks of Mn, Co, Fe, and O elements. The presence of these elements in the formed precipitate confirmed that Mn, Co, and Fe have co-precipitated simultaneously in the oxide form. The elemental composition obtained from EDS analysis reveals that the atomic percentages of Mn, Co, Fe, and O are 10.14%, 9.81%, 18.75%, and 61.30%, respectively. As a result, their atomic ratio is approximately 1 : 1 : 2 : 6. Fig. 1b shows the XRD pattern of the prepared material. All diffraction peaks are coincident to the Miller

Fig. 1 (a) EDS spectrum, (b) XRD pattern, and (c) FT-IR spectrum for the as-prepared MnCoFeO₄.
indices (111), (220), (222), (400), (422), (511), (440) and (622) of the standard data for MnCoFeO₄ (cubic, space group: Fd3m, ICDD card number: 04-010-1895), which confirms the formation of MnCoFeO₄ with the spinel structure. Fig. 1c displays the FT-IR spectrum of MnCoFeO₄ recorded in the frequency range 4000–400 cm⁻¹. The lower-frequency band (493 cm⁻¹) is assigned to the octahedral groups ([Fe³⁺–O²⁻] and [Mn³⁺–O²⁻]), while the higher-frequency band (610 cm⁻¹) is assigned to the stretching of the tetrahedral groups ([Co²⁺–O²⁻]) present in the spinel ferrite.²⁴ The FT-IR absorption bands appearing at 3383 cm⁻¹ and 1625 cm⁻¹ are referred to adsorbed water molecules.⁴¹

Fig. 2 shows the HR-TEM images of the as-fabricated MnCoFeO₄, indicating the formation of nanoparticles with sizes ranging ca. 30–40 nm. Fig. 3a shows the N₂ adsorption/desorption isotherm for the as-synthesized MnCoFeO₄. According to the IUPAC classification of gas adsorption/desorption isotherms,⁴³ the obtained N₂ adsorption/desorption isotherm is of type IV, which is characteristic to the mesoporous materials. The characteristic feature of this isotherm is its hysteresis loop, which arises when the adsorption and desorption curves do not coincide and is associated with the capillary condensation taking place in the mesopores. Moreover, the initial part, where adsorption/desorption curves are coincident, is attributed to the monolayer-multilayer adsorption. These features confirm the mesoporous structure of the prepared MnCoFeO₄. It is worth mentioning that porous materials are generally classified according to their pore size (d) into three categories: macroporous (d > 50 nm), mesoporous (d = 2–50 nm), and microporous materials (d < 2 nm).⁵⁻³ Fig. 3b shows the pore diameter distribution curve obtained by the Barrett-Joyner–Halenda (BJH) method using the desorption branch of the nitrogen isotherm.¹⁷ It reveals an average pore diameter of 10.036 nm. The BET method likely yields a value of actual surface area if the isotherm is either of type II or type IV.⁴¹ Hence, the surface area obtained from multipoint BET is noted to be 104.963 m² g⁻¹.

### 3.2. Electrochemical characterization

#### 3.2.1. Specific capacitance

The electrochemical capacitive performance of the as-fabricated MnCoFeO₄ was examined via CV and GCD measurements. The CV curves of MnCoFeO₄ were recorded at different scan rates in the potential range of 0–0.45 V SCE in 6 M KOH (Fig. 4a). The CV curves show faradic-type capacitive features, where two peaks appear at ~0.38 V and ~0.19 V for the oxidation and reduction processes, respectively. The specific capacitance \( C_{sp} \) obtained from CV measurements is dependent on the scan rate, where the peak current density \( I_p \) of MnCoFeO₄ clearly increases as a function of scan rate. The maximum \( C_{sp} \) (675 F g⁻¹) is obtained at the lowest scan rate (1 mV s⁻¹), while \( C_{sp} \) calculated at 100 mV s⁻¹ is 238.81 F g⁻¹ (the inset of Fig. 4a). This could be attributed to the existence of a large Ohmic resistance at large scan rates.⁷ In addition, the electrolyte ions do not have a sufficient time, at high rates of potential scanning, to entirely diffuse through the electrode nanopores wherever the faradaic reactions occur.⁸ Also, this behavior suggests that there are parts of the electrode surface inaccessible at high rates of charging/discharging.⁴⁴ Therefore, electrical energy is electrochemically stored in an efficient manner in the MnCoFeO₄ supercapacitor at a slower scan rate.

Moreover, Fig. 4a demonstrates the pairs of distinct and broad redox peaks corresponding to the redox transitions of Co³⁺/Co²⁺ and Mn³⁺/Mn²⁺. The redox peaks of Co³⁺/Co²⁺ and Mn³⁺/Mn²⁺ seem to be merging together because their standard electrode potentials are comparable (1.92 and 1.50 V NHE, respectively). The probable processes associated with the capacitive behavior of MnCoFeO₄ can be related to the presence of two redox systems. The redox reactions related to both systems could proceed according to eqn (7)⁶ and (8)⁴², respectively.

\[
\text{Co}^{2+}/\text{Co}^{3+} \text{ system: } \text{CoFe}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow \\
2\text{FeOOH} + \text{CoOOH} + \text{e} \quad \text{(7)}
\]

![HR-TEM images of the as-prepared MnCoFeO₄](image_url)
Mn\textsuperscript{2+}/Mn\textsuperscript{3+} system: \[\text{MnFe}_2\text{O}_4 + \text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{FeOOH} + \text{MnOOH} + e^- \quad (8)\]

The CV profiles (at different scan rates) demonstrate the same behavior, revealing the reversibility of the redox reactions. In addition, with the increase in the scan rate, both oxidation and reduction peaks shift towards more anodic and cathodic directions, respectively. For example, upon increasing the scan rate from 1 to 100 mV s\textsuperscript{-1}, the anodic peak potential (\(E_{p,a}\)) increased from 0.358 to 0.378 V\textsubscript{SCE}, while the anodic peak current (\(I_{p,a}\)) increased from 2.063 to 52.494 (A g\textsuperscript{-1}). This effect results from the unavoidable overpotential due to the increase in the internal diffusion resistance and \(I_p\) increases with \(v\) due to the fast interfacial kinetics.\textsuperscript{14}

Galvanostatic charge/discharge (GCD) measurement is an accurate technique for determining the electrochemical performance of supercapacitors particularly for those based on pseudo-capacitance.\textsuperscript{46} Fig. 4b displays the GCD curves recorded for MnCoFeO\textsubscript{4} in 6 M KOH. Unlike the GCD curves of carbon-based materials exhibiting a semi-triangular shape, where their capacitances are mainly attributed to a pure electric double layer capacitance, the GCD curves of MnCoFeO\textsubscript{4} show...
deviations from linearity due to its pseudocapacitive nature. Clearly, the MnCoFeO₄ electrode demonstrates higher charging and discharging times as the current density decreases, resulting in higher values of specific capacitance (Fig. 4c). For example, on decreasing the current density from 10 A g⁻¹ to 1.5 A g⁻¹, Cₛₚ increases from 112 to 670 F g⁻¹. Furthermore, the columbic efficiency (η%) increases with the current density up to 89% at 4 A g⁻¹, after which it becomes constant (~81%).

Power density (PD) and energy density (ED) are two important parameters for the evaluation of the electrochemical performance of supercapacitors and electrode materials. Fig. 5a displays the Ragone plot of MnCoFeO₄ obtained from GCD measurements with the current densities ranging from 1.5 to 10 A g⁻¹. Fig. 5a demonstrates that the ED stored in MnCoFeO₄ and its corresponding PD (at a current density of 1.5 A g⁻¹) are 18.85 W h kg⁻¹ and 337.50 W kg⁻¹, respectively. On the other hand, at a current density of 10 A g⁻¹, ED and PD values are 3.15 W h kg⁻¹ and 2250.00 W kg⁻¹, respectively. Table 1 depicts the supercapacitive performance parameters, including Cₛₚ, PD, and ED for MnCoFeO₄ and some ternary and quaternary TM ferrites. It should be noted that MnCoFeO₄ has an excellent Cₛₚ and PD in comparison to those of the previously investigated materials.

3.2.2. Cycling stability. Cycling stability is another important factor that determines the efficiency and durability of supercapacitors, which can be expressed in terms of capacitance retention (%) and coulombic efficiency (η%). Fig. 5b illustrates the capacitance retention (%) and η% of the prepared supercapacitor recorded during 1000 continuous GCD cycles at a high current density (10 A g⁻¹). The capacitance retention (%) increases up to 200 cycles and reaches 111.43%. Following this, it starts to decrease and reaches ~92.86% after 1000 GCD cycles, indicating an excellent long-term stability. In addition, the coulombic efficiency increases with time and reaches 114% after 1000 GCD cycles. The excellent stability of MnCoFeO₄ could be attributed to the synergistic effects of the three transition metals.

EIS is a powerful tool used to investigate the features of an electrode/electrolyte interface as supercapacitors by evaluating the frequency behavior and equivalent series resistance (ESR). EIS offers information about the internal resistance of the electrode material and the resistance between the electrode and the electrolyte. EIS spectra (Fig. 5c) display a depressed semicircle in the high-frequency region linked to an inclined straight line in the low-frequency region. The slope of the inclined line is decreased after 1000 GCD cycles. The equivalent circuit used to analyze EIS spectra is depicted in the inset of Fig. 5c.

The time constant (QR₀W) represents the depressed semicircle in the high-frequency region, where R₀ is the charge-transfer resistance caused by the faradaic process and Q is a constant phase element representing the non-ideal double-
layer capacitance. Table 2 reveals that $R_s$, representing the ESR, remains nearly constant even after 1000 GCD cycles. The ESR includes electrolyte resistance, internal resistance of the electrode and contact resistance between the electrode and the current collector. $R_s$ suffers a slight increase from 53.37 $\Omega$ to 78.74 $\Omega$, indicating that the amount of charge stored in this material is slightly decreased. The linear part of the curve is inclined by $\sim 45^\circ$, indicating Warburg impedance ($W$) that is related to the frequency-dependent diffusion resistance of electrolyte ions.\textsuperscript{15,37,67} The value of $W$ increases from 59.67 $\Omega$ s$^{-0.5}$ to 101.90 $\Omega$ s$^{-0.5}$, indicating a slowdown in the diffusion rate due to a somewhat difficult penetration of electrolyte ions through the electrode mesopores with long-term use.

4. Conclusions

Mesoporous MnCoFeO$_4$ nanoparticles, with diameters in the range 30–40 nm, were successfully synthesized via a one-pot simple co-precipitation method without annealing as confirmed by the TEM analysis. The XRD results confirmed the spinel structure of the fabricated MnCoFeO$_4$ nanoparticles. The BJH average pore diameter was found to be 10.036 nm and the BET surface area was 104.963 m$^2$ g$^{-1}$.

The equivalent series resistance (ESR) remained nearly the same even after 1000 GCD cycles. The energy and power densities of the MnCoFeO$_4$ supercapacitor were 18.85 Wh kg$^{-1}$ and 92.86% after 1000 GCD cycles, respectively, indicating an excellent long-term stability. The cyclic stability was scrutinized via GCD and EIS. The capacitance retention (%) was 111.43% and 92.86% after 200 and 1000 GCD cycles, respectively, indicating an excellent long-term stability. The equivalent series resistance (ESR) remained nearly the same even after 1000 GCD cycles.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

27 V. V. Jadhav, M. K. Zate, S. Liu, M. Naushad, R. S. Mane, K. N. Hui and S.-H. Han, \textit{Appl. Nanosci.}, 2016, 6, 511–519.