Chapter

Application of Ferrites as Electrodes for Supercapacitor

Ankur Soam

Abstract

Apart from the magnetic properties, ferrites have been considered as efficient electrodes for next generation energy storage devices. This chapter will include applications of spinel ferrites such as $MnFe_2O_4$, $CoFe_2O_4$, $ZnFe_2O_4$ and $NiFe_2O_4$ in supercapacitor. In ferrites, the charge storage arises from the fast-reversible surface redox reactions at the electrode/electrolyte interface. In particular, the electrode material with high specific capacitance, wide range of operating potential, low synthesis cost and its availability on the earth are highly desirable to fabricate a supercapacitor. Ferrites with mixed oxidation states have proved as promising electrodes in supercapacitors. In this chapter, we summarize the different synthesis methods of ferrites based nanocomposites and their electrochemical properties for supercapacitor application.

Keywords: ferrites, nanocomposites, electrochemical properties, electrodes, supercapacitor

1. Introduction

The continuous depletion and consequently the increased cost of the fossil fuel has now become an economic problem for a nation. Moreover, the production of CO_2 from massive use of fossil fuel in transportation and industrial operations increases the greenhouse gases which are responsible for significance change in climate (global warming). In future, the demand of fossil fuel is expected to be increased rapidly. Therefore, some alternative energy storage systems need to be developed in order to meet the demand of energy consumption. Battery is being widely utilized in electric vehicles and electronic devices because of its large energy density [1–4]. However, the maintenance at regular interval and low power density are some drawbacks with battery.

Among various energy storage devices, supercapacitor technology has attracted tremendous attention to be used in high power application because of their higher power density and longer cycling life [5–9]. **Figure 1** depicts the power density and energy density of capacitor, battery and supercapacitor. The capacitor with largest power density occupies the top position, however, the energy density is much lower. Battery can exhibit larger energy density but with lower power density. The supercapacitors occupy the important space between capacitor and battery with larger power density than batteries and greater energy density than capacitors. Supercapacitors are considered suitable candidates as energy storage in portable consumer electronic devices, memory back-up systems, microelectro-mechanical systems, hybrid electric vehicles and medical devices [10–17]. Further

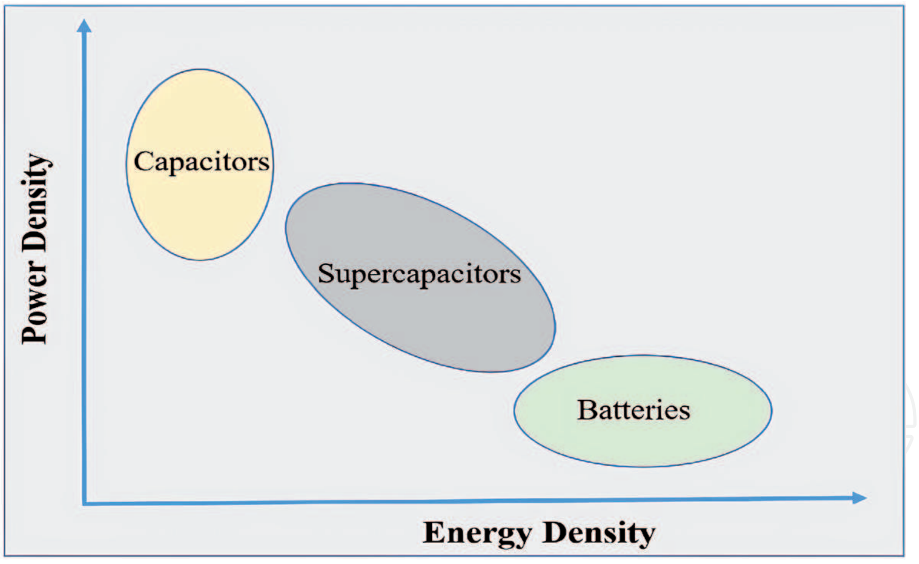

Figure 1.
Ragone plot for various charge storage devices. Supercapacitors occupy the space between capacitors and batteries with larger energy density than capacitors and larger power density than batteries.

improvements are being made in order to extend the applications of supercapacitor in different purpose [18–20]. Due to a simple structure (similar electrodes), supercapacitor technology can be integrated on a Si chip with energy harvesters [21–23].

Supercapacitor can store an excess energy from the harvester and return back when required. The supercapacitor performance is governed by the electrodes, current collectors, separator and electrolyte. The surface morphology and electrical properties of electrodes are the major factors which mainly control the energy storage in supercapacitor. In this connection, a lot of efforts are being made towards developing new materials for electrodes and improving their electrochemical properties [24–29]. Many materials and their composites have been explored as electrodes for supercapacitor [30, 31].

Supercapacitor electrodes can be categorized in two types, 1) Metal oxides, which involve faradaic process to store the charge (Pseudocapacitor) [32–34], 2) carbon and silicon based materials, these materials store the charge in electric double layer (EDL) [27, 35–37]. EDLCs exhibit high rate capability and longer cycle life, but low energy storage capacity is a major issue for them [38–40]. On the other hand, metal oxide based supercapacitor exhibits larger capacitance and energy density than EDLC but the poor rate capability and limited charging/discharging cycle numbers are some of their drawbacks [7, 15, 41]. To design a supercapacitor with larger energy density without compromising the rate capability is a major challenge. In this context, several electrode materials and their combinations have been evaluated for high performance supercapacitor [5, 42–44]. The ferrite materials are also being considered as potential electrodes in supercapacitor because of their different oxidation states, low price, environmental benignity, and their large abundance [26, 45–49]. Moreover, their synthesis process is simple and suitable for production at industrial scale. MFe_2O_4 (M = Mn, Co, Ni, Zn, or Mg) ferrites have been extensively used in supercapacitor. These binary oxides can offer large capacitance due to involvement of two ions in redox reactions [13, 47, 50]. Subsequently, several studies were performed on ferrite materials such as nickel ferrite, bismuth ferrite, cobalt ferrite, manganese ferrite, as electrodes in supercapacitor [46, 51–53]. Ferrites of the form MFe_2O_4 (M = Ni, Co, Zn, etc.) have been considered as potential electrodes in energy storage devices because of their good chemically stability and electronic properties. Moreover, their nanocomposite can be synthesized using water based solution without any organic solvent (**Figure 2**). In this chapter, research progress

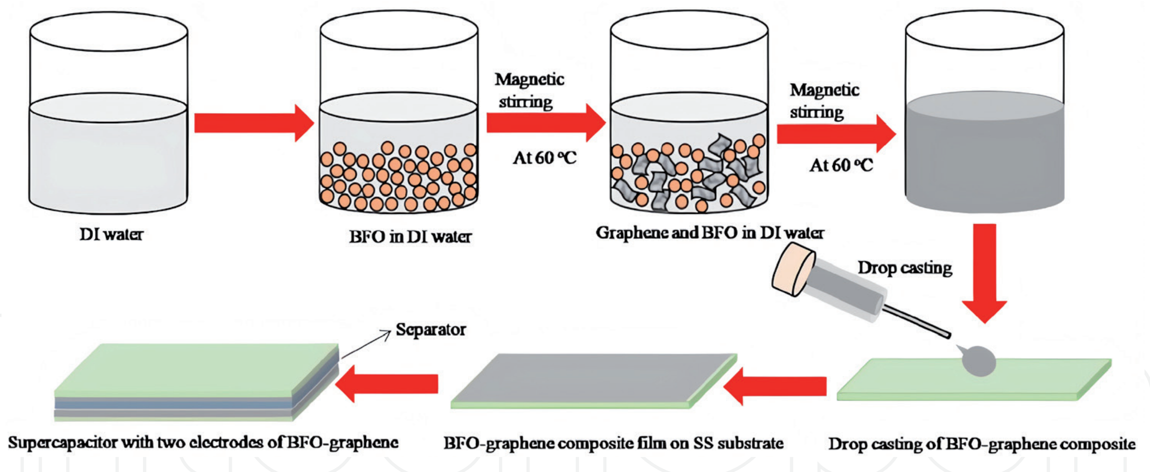

Figure 2.
Synthesis of ferrite (bismuth ferrite)–graphene nanocomposite as electrodes for supercapacitor using water based solution [34]. Bismuth ferrite and graphene were mixed in DI water and then deposited on a conducting substrate by drop casting process to fabricate the electrodes for supercapacitor.

on ferrite based electrodes (MFe_2O_4 types) for supercapacitor have been summarized. The supercapacitor performance of ferrite depends on their morphology, synthesis process, used precursors, and composition.

2. Cobalt ferrite ($CoFe_2O_4$)

$CoFe_2O_4$ with high magnetic properties has good mechanical hardness and chemical stability, which make it suitable candidate in magnetic device applications [54]. Apart from above properties, $CoFe_2O_4$ has also shown good electrochemical performance in supercapacitor [52, 55–59]. $CoFe_2O_4$ nano-flakes synthesized by chemical bath deposition process have been utilized in supercapacitor [52]. The nano flakes were deposited on a stainless steel substrate with thickness of 5.3–7.0 μm. The electrochemical properties were investigated in three electrode system with 1 M NaOH electrolyte. The nano-flakes showed a specific capacitance of 366 F g^{-1} (interfacial capacitance of 0.110 F cm^{-2}) at scan rate of 5 mVs^{-1}. The nano-flakes electrode could preserve 190 Fg^{-1} capacitance at scan rate of 100 mV/s^{-1}. At such larger scan rates, the inner active sites of the electrodes might not participate in redox process, resulting in decrease in the capacitance. The $CoFe_2O_4$ nano-flakes retained 90.6% capacitance after 1000 cycles.

Pawar et al. [60], have synthesized $CoFe_2O_4$ nanoparticles (average size 23 nm) by sol–gel method for supercapacitor application. $CoFe_2O_4$ nanoparticles exhibited pseudocapacitive behavior in 1 M KOH electrolyte with a three-electrode system as observed from the CV curves. The specific capacitance determined from galvanostatic charge discharge process were found to be 15 Fg^{-1} at current density of 0.6 Ag^{-1}. This lower value of the capacitance may be due to the poor electrical conductivity of $CoFe_2O_4$ nanoparticles. An improved electrochemical performance was achieved with $CoFe_2O_4$/FeOOH nanocomposite synthesized by one-step hydrothermal approach [61]. A mixture of $CoFe_2O_4$/FeOOH nanocomposites, carbon black and polyvinylidenefluoride (PVDF) in ratio of 80:10:10 wt% was used as electrode. The electrode of $CoFe_2O_4$ with FeOOH exhibited good value of capacitance at larger currents which is essential for a supercapacitor. The electrode showed specific capacitance of 332.4, 319.4, 257.2, 239, 193.1, and 180 F g^{-1} at the current densities of 0.5, 1, 2, 5, 8, and 10 A g^{-1}, respectively. About 8.7% loss in capacitance was observed after 1000 cycles.

Mesoporous $CoFe_2O_4$ thin film also demonstrated good value of specific capacitance of 369 Fg^{-1} at 2 mV/s^{-1} in 1 M KOH electrolyte with wide potential window of −1.2 to +0.5 V [62]. The capacitance degraded to 167 Fg^{-1} upon increasing the scan rate to 100 mV/s^{-1} . The mesoporous $CoFe_2O_4$ film was prepared by a chemical spray pyrolysis technique from the aqueous medium at 475°C substrate temperature. The film was observed to be uniform on the substrate and free from any crack with mesoporous type surface morphology. $CoFe_2O_4$ thin film consists of grain with size in the range of nm. The electrode of mesoporous $CoFe_2O_4$ film showed power density of 28.74 $kWkg^{-1}$ with maintaining energy density of 27.14 $Whkg^{-1}$.

A large specific capacitance of 429 Fg^{-1} was obtained by $CoFe_2O_4$ nanoparticles in 6 M KOH electrolyte at 0.5 Ag^{-1} [63]. These nanoparticles were prepared by hydrothermal and coprecipitation methods using nitrates, chlorides and acetates precursors with average size from 11 to 26 nm and surface area of ~34 $m^2\ g^{-1}$. The nanoparticles has shown an excellent capacitance retention of 98.8% after 6000 cycles at high current density of 10 Ag^{-1}. The above results indicate that $CoFe_2O_4$ nanoparticles with the above morphology may be a promising electrode material for supercapacitor. A composite of reduced graphene oxide and $CoFe_2O_4$ (RGO–$CoFe_2O_4$) was examined for supercapacitor application [64]. The electrode of RGO–$CoFe_2O_4$ showed a specific capacitance of 123.2 F g^{-1} which is larger than that of individual constituents RGO (89.9 F g^{-1}) and $CoFe_2O_4$ (18.7 F g^{-1}) at current density of 5 mA cm^{-2}. However, about 22% loss in capacitance was observed for the electrode RGO–$CoFe_2O_4$ after 1000 cycles.

Xiong et al. have developed ternary nanocomposite of cobalt ferrite/graphene/polyaniline as electrode for high-performance supercapacitor [65]. Hydrothermal method was used to make $CoFe_2O_4$ nanoparticles and graphene nanosheets and then polyaniline (PANI) coating was performed on $CoFe_2O_4$ by in situ polymerization process. A large specific capacitance of 1133.3 F g^{-1} at a scan rate of 1 mVs^{-1} was observed by the hybrid ternary nanocomposite electrode in 1 M KOH electrolyte. 716.4 F g^{-1} specific capacitance was determined in two electrode system in the same electrolyte and at the same scan rate of 1 mVs^{-1}. The electrode demonstrated long cycle stability about 96% retention of initial capacitance after 5000 cycles. The synergistic effects of three components in the ternary composite improved the electrochemical performance of the electrode. The graphene nanosheets greatly enhance the electron transfer in the electrode and surface area of the electrode, leading to increase in the overall capacitance [8]. In addition, PANI also contributes to the pseudocapacitance of $CoFe_2O_4$ nanoparticles.

Cobalt ferrite nanoparticles were also used as negative electrode in an asymmetric supercapacitor with positive electrode of $Co(OH)_2$ and $Co_2Fe(CN)_6$ particles [55]. The negative electrode of $CoFe_2O_4$ showed a specific capacitance of 758.86 F g^{-1} at 2 mV s^{-1} in 1 M KOH electrolyte. Overall, the asymmetric supercapacitor with electrode combination of $CoFe_2O_4$‖AC, $CoFe_2O_4$‖$Co(OH)_2$ and $CoFe_2O_4$‖$Co_2Fe(CN)_6$ provided the specific capacitance of 339, 127 and 125 F g^{-1} at 1 mVs^{-1} scan rate.

3. Manganese ferrite ($MnFe_2O_4$)

$MnFe_2O_4$ based electrodes exhibited good capacitive properties in aqueous electrolyte [53, 66–70]. It is observed that $MnFe_2O_4$ stores the charge by pseudo mechanism in aqueous electrolyte [71]. Shin-Liang Kuo et al. [71] have shown that charge storage in $MnFe_2O_4$ involves insertion/extraction of proton into/from the lattice at both the Mn- and Fe-ion sites. In that study, $MnFe_2O_4$ was synthesized by coprecipitation method for supercapacitor application. For electrochemical characterization, the

$MnFe_2O_4$ powder was mixed carbon black and PVDF, and then coated on current collector. Electrochemical performance was determined with a three-electrode cell in 1 M KCl aqueous solution. The overall specific capacitance of 63.4 Fg^{-1} was determined for the electrode and specific capacitance of 115 Fg^{-1} for $MnFe_2O_4$ electrode. Baoyan Wang et al. [53] have studied the effect of surfactants on the electrochemical performances of $MnFe_2O_4$ synthesized by solvothermal method. The capacitive performances of $MnFe_2O_4$ colloidal nanocrystal cluster was observed to be larger than $MnFe_2O_4$ hollow sphere in aqueous $LiNO_3$ electrolyte. In that work, an almost rectangular CV curves were obtained for $MnFe_2O_4$ in a potential range of −0.4-1.5 V. Addition of surfactants leads to increase in the capacitance of $MnFe_2O_4$ in $LiNO_3$ electrolyte. It may be due to the reduction of interfacial tension between electrode and electrolyte in presence of surfactants with promoting the diffusion of lithium ions. After addition of different surfactants, SDS (Anionic surfactant sodium dodecyl sulphate), Triton-X-100 (non-ionic surfactant p-toctylophenol) and P123 (poly(ethylene glycol)-block-poly(propylene glycol)-blockPoly(ethylene glycol)), the capacitance increased about 36.8%, 22.8% and 12.8%, respectively.

V. Vignesh et al. [69] have reported electrochemical properties of $MnFe_2O_4$ spherical nanoparticles (20–50 nm) synthesized by simple and facile coprecipitation method. The capacitor performance was evaluated in different electrolytes, 1 M $LiNO_3$, 1 M Li_3PO_4 and KOH. The $MnFe_2O_4$ nanoparticles showed specific capacitance of 173, 31 and 430 F g^{-1} in electrolytes of 3.5 M KOH, 1 M $LiNO_3$ and 1 M Li_3PO_4, respectively. However, excellent rate performance was observed in 3.5 M KOH electrolyte with good retention of capacitance at higher current densities. Supercapacitor with two electrodes of $MnFe_2O_4$ nanoparticles exhibited specific capacitance of 245 F g^{-1}, and energy density and power density of 12.6 Wh kg^{-1} and 1207 W kg^{-1}, respectively in 3.5 M KOH electrolyte.

Further, the electrochemical performances of $MnFe_2O_4$ colloidal nanocrystal clusters (CNCs) was investigated in symmetric supercapacitors with different aqueous electrolytes [72]. The specific capacitances of $MnFe_2O_4$ electrode was found to be 97.1, 93.9, 74.2 and 47.4 F g^{-1} in electrolytes 2 M KOH, 2 M NaOH, 2 M LiOH and 2 M Na_2SO_4, respectively. It was found that $MnFe_2O_4$ CNCs exhibited better performance in 6 M KOH electrolyte with the specific capacitance of 152.5 F g^{-1} and retention of capacitance of about 76% after 2000 cycles. $MnFe_2O_4$ colloidal nanocrystal assemblies (CNAs) with size of 420 nm, composed of 16 nm nanoparticles showed specific capacitance of 88.4 Fg^{-1} calculated at the current density of 0.01 Ag^{-1} [70]. When the current increased from 0.01 to 2 Ag^{-1} $MnFe_2O_4$ CNAs retained 59.4% capacitance, and 69.2% capacitance after 2000 cycles. The electrochemical performance of $MnFe_2O_4$ CNAs was related to the size of primary nanoparticles in the CNAs.

Further improvement in $MnFe_2O_4$ based supercapacitor was made by making nanocomposite of $MnFe_2O_4$ with grapheme [66, 68, 73–75]. Isara Kotutha et al. [73] have used one-pot hydrothermal approach to prepare rGO/$MnFe_2O_4$ nanocomposite. A maximum specific capacitance of 276.9 Fg^{-1} was determined for the rGO/$MnFe_2O_4$ nanocomposite at scan rate of 10 mVs^{-1} in 6.0 M KOH electrolyte. A flexible supercapacitor of $MnFe_2O_4$/graphene using current collectors of flexible graphite sheets has been fabricated [66]. The flexible supercapacitor exhibited specific capacitance of 120 F g^{-1} at 0.1 A g^{-1} with retaining 105% capacitance after 5000 cycles.

Larissa H. Nonaka et al. [68] have achieved 195 Fg^{-1} capacitance for $MnFe_2O_4$ nanoparticles on a crumpled graphene sheet at scan rate of 0.5 Ag^{-1} in 0.05 M KCL electrolyte. A pseudocapacitive behavior was observed in the CV curves which indicates that there is major contribution from $MnFe_2O_4$ to the overall capacitance of the hybrid electrode. A larger specific capacitance of 454.8 F g^{-1} at 0.2 A g^{-1} was obtained by a ternary $MnFe_2O_4$/graphene/polyaniline nanocomposite fabricated by a facile two-step approach. The ternary nanocomposite also exhibited outstanding rate capability about 75.8% capacitance retention at 5 A g^{-1} and excellent cycling stability, 76.4% retention in capacitance after 5000 cycles. Specific capacitance of 307.2 F g^{-1} at 0.1 A g^{-1} has been achieved with symmetric supercapacitor. The device exhibited a maximum energy density of 13.5 W h kg^{-1}.

4. Zinc ferrite ($ZnFe_2O_4$)

Zn ferrite is widely used electrode material in supercapacitor because of its non-toxic nature, strong redox process, good chemical stability and high storage capacity of 2600 F g^{-1} [76–81]. Furthermore, the morphology of $ZnFe_2O_4$ can also be tuned such as nanoparticles [78, 82], nanorods [83] and nano-flakes [78, 80], offering large surface area for charge storage. M. M. Vadiyar et al. [84] have reported an empirical relationship between surface wettability and charge storing capacity for $ZnFe_2O_4$ nano-flake thin films. Different electrolytes, 1 M KOH, NaOH, LiOH and their combinations were chosen for this study. All the CV curves for $ZnFe_2O_4$ nano-flake recorded in the above electrolytes exhibited pseudocapacitive behavior in the scan range of 0.0 to −1.3 V. $ZnFe_2O_4$ nano-flakes exhibited larger area under the CV curves in 1 M KOH due to small hydrated K^+ and its fast intercalation and deintercalation on the electrode surface. This is found with good agreement with the smaller contact angle value of 12° and larger surface energy of 71 mJ m^{-2}.

$ZnFe_2O_4$ thin film synthesized by successive ionic layer adsorption and reaction (SILAR) method has shown good value of capacitance specific of 471 Fg^{-1} in aqueous electrolyte of 1 M NaOH at a scan rate of 5 mVs^{-1} [85]. The synthesized thin film of $ZnFe_2O_4$ was also used in solid-state symmetric supercapacitor which exhibited specific capacitance of 32 Fg^{-1} in voltage window of 1.0 V. A power density of 277 Wkg^{-1} with energy density of 4.47 $Whkg^{-1}$ was achieved with $ZnFe_2O_4$ thin film based supercapacitor. A specific capacitance of 615 F g^{-1} has been achieved for binder free $ZnFe_2O_4$ thin films at current density of 3 mA cm^{-2} [79]. The porous $ZnFe_2O_4$ thin film was tested in asymmetric supercapacitor as a negative electrode with positive electrode of Mn_3O_4. The device showed a specific capacitance of 81 F g^{-1} with energy and power density of 28 Wh kg^{-1} and 7.97 kW kg^{-1}, respectively. 74% retention was observed in capacitance after 3000 cycles.

$ZnFe_2O_4$ nanoparticles (size 20–30 nm) synthesized by combustion method was used for supercapacitor application [86]. The electrode showed a large maximum specific capacitance of 1235 F g^{-1} calculated at 1 mA cm^{-2}. The electrochemical performance of $ZnFe_2O_4$ material was also demonstrated in an asymmetric supercapacitor as negative electrode and nickel hydroxide as positive electrode. The device exhibited voltage window of 1.7 V with specific capacitance of 179 Fg^{-1} calculated at 2 mVs^{-1}. 3-D aligned $ZnFe_2O_4$ nano-flakes on flexible stainless steel mesh substrate have shown promising results as electrode in asymmetric supercapacitor with $Ni(OH)_2$ [87]. The asymmetric device exhibited large value of specific capacitance of 1625 F g^{-1} at 1 mA cm^{-2} with 97% retention in capacitance after 8000 cycles.

$ZnFe_2O_4$ microspheres synthesized by solvothermal approach demonstrated a specific capacitance of 131 Fg^{-1} [81]. The electrode of $ZnFe_2O_4$ microspheres could retain 92% capacitance after 1000 cycles. $ZnFe_2O_4$ anchored on multiwalled carbon nanotubes (CNT) yielded a high specific capacity of 217 mAh g^{-1} at 5 mV s^{-1} [88]. A solid-state symmetric supercapacitor with $ZnFe_2O_4$-CNT exhibited a highest specific energy of 12.80 Wh kg^{-1} and a specific power of 377.86 W kg^{-1}.

M. M. Vadiya et al. [78] have developed self-assembled $ZnFe_2O_4$ nanoflakes@ $ZnFe_2O_4$/C nanoparticles heterostructure electrode for high performance supercapacitor application. The hybrid electrode showed very high value of specific capacitance of 1884 Fg^{-1} determined at a current density of 5 mA cm^{-2}. A flexible asymmetric supercapacitor was also designed using $ZnFe_2O_4$ nano-flakes@ $ZnFe_2O_4$/C nanoparticles heterostructure as a negative electrode and reduced graphene oxide as a positive electrode. A specific capacitance of 347 F g^{-1} was achieved from the supercapacitor. The asymmetric supercapacitor exhibited an energy density of 81 Wh $kg^{-1}$and power density of 3.9 kW kg^{-1}. Only 2% loss in the capacitance was observed after 35000 cycles.

$ZnFe_2O_4$ nanoparticles were dispersed on nitrogen-doped reduced graphene for supercapacitor application [82]. The reduction of graphitic oxide, the doping of nitrogen to graphene and dispersion of $ZnFe_2O_4$ nanoparticles were achieved in a single process. The structure of $ZnFe_2O_4$/NRG exhibited a specific capacitance of 244 Fg^{-1} calculated at 0.5 Ag^{-1}. The electrode has also demonstrated good rate capability with retention of 131.5 Fg^{-1} capacitance at 10 Ag^{-1}. $ZnFe_2O_4$/NRG retained 83.8% capacitance after 5000 cycles. In this type of electrode, the graphene sheets provide high exposure of active sites for redox process and high dispersion of nanoparticles resulting good capacitive performance of the electrode [89, 90].

$ZnFe_2O_4$ nanorodes with rGO showed a specific capacitance of 1419 Fg^{-1} at scan rate of 10 mVs^{-1} in 2 M KOH solution. The electrode demonstrated good retention of capacitance about 93% after 5000 cycles. The improved electrochemical performance is due to the large surface area offered by rGO and good electrical conductivity [83]. The porous nano-flakes-$ZnFe_2O_4$ thin films demonstrated a larger capacitance of 768 Fg^{-1} at current density 5 mA cm^{-2} with energy density of 106 Wh kg^{-1} and power density of 18 kW kg^{-1} [76]. The electrode had good cycle stability about 88% retention of capacitance after 5000 cycles.

5. Nickel ferrite ($NiFe_2O_4$)

Among various metal ferrites, $NiFe_2O_4$ is one of the promising ferrite material for supercapacitor application. Several studies are available on $NiFe_2O_4$ and their nanocomposite as electrode in supercapacitor [46, 91–94]. $NiFe_2O_4$ particles with submicron-sized synthesized by the molten salt process demonstrated a specific capacitance of 18.5 F g^{-1} at a scan rate of 10 mV/s [95]. $NiFe_2O_4$ nanospheres showed a specific capacitance of 122 F g^{-1} at current density of 8.0 Ag^{-1} [26]. The results showed that the capacitance is increased with increasing the KOH concentration. $NiFe_2O_4$ nanospheres could store specific energy of 16.9 Wh kg^{-1} at a high current density of 8.0 Ag^{-1}.

Nagesh Kumar et al. [96] have synthesized mesoporous $NiFe_2O_4$ nanoparticles (size 10–15 nm) by one step hydrothermal method. The mesopores were distributed homogeneously on the surface of $NiFe_2O_4$ particle. A surface area of 148 m^2g^{-1} was calculated for the mesoporous $NiFe_2O_4$ nanoparticles. It exhibited high value of specific capacitance of 1040 Fg^{-1} at 1 Ag^{-1} in a three-electrode configuration with 2 M KOH electrolyte. However, 30% loss in capacitance was observed for $NiFe_2O_4$ nanoparticles after 500 cycles. $NiFe_2O_4$ synthesized by combustion route showed a specific capacitance of 454 Fg^{-1} with good cycle stability for 1000 charging-discharging cycles [46].

To improve the capacitive properties, graphene based materials have been mixed with $NiFe_2O_4$ [97–99]. Soam et al. [98] obtained a specific capacitance of 207 Fg^{-1} from ferrite/graphene nanocomposite in 1 M Na_2SO_4 electrolyte (**Figure 3**). This value of capacitance was observed about 4 times greater than $NiFe_2O_4$ electrode. $NiFe_2O_4$ with graphene nanosheets exhibited a stable capacitance about 95% over 1000 cycles. Numerous pores in the electrode might be responsible for improved

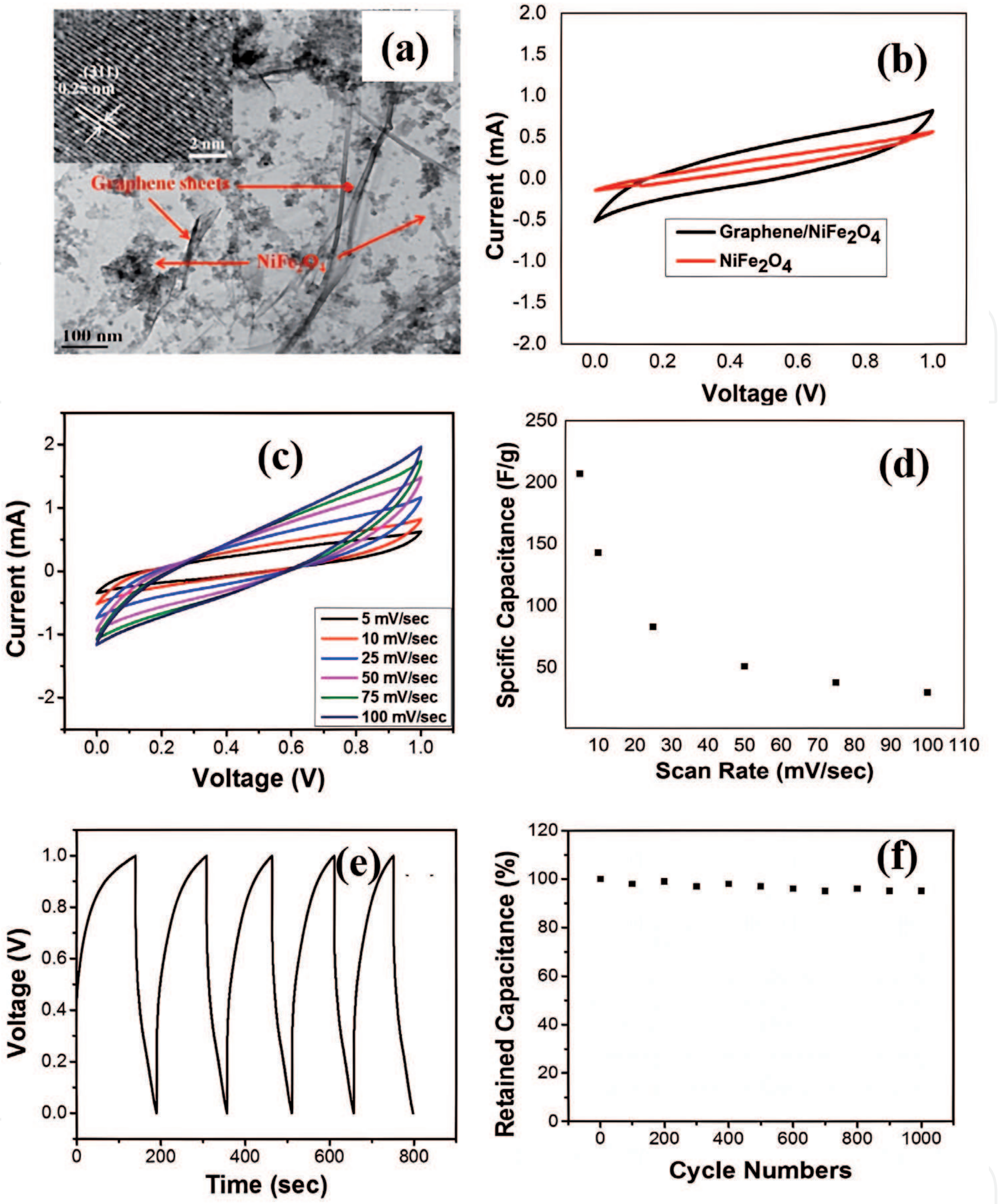

Figure 3.
(a) TEM images of graphene/$NiFe_2O_4$ nanocomposite. $NiFe_2O_4$ nanoparticles have good contact with graphene, providing fast charge transportation within the electrode (b) CV curves of graphene and $NiFe_2O_4$ recorded at 5 mVs^{-1}. The nanocomposite of graphene/$NiFe_2O_4$ exhibited larger area under CV curve, indicating better charge storage capacity than $NiFe_2O_4$. (c) CV curves at different scan rates for graphene/$NiFe_2O_4$ nanocomposite. (d) Capacitance versus scan rate for the graphene/$NiFe_2O_4$ nanocomposite, the electrode exhibited specific capacitance in the range of 207-30 Fg^{-1} at scan rates of 5-100 mVs^{-1} and (e) charging/discharging curves with constant current of 0.5 mA. (f) Cycle stability test performed over 1000 cycles [98].

electrochemical performance of $NiFe_2O_4$. Zhuo Wang et al. [100] have studied the reduce graphene oxide–$NiFe_2O_4$ nanocomposites for supercapacitor application. rGO-$NiFe_2O_4$ nanocomposites were prepared by hydrothermal process with varying the pH value of solution (8, 10, 12 and 14). rGO-$NiFe_2O_4$ synthesized with pH value of 10 exhibited the largest surface area of 459.6 $m^2\ g^{-1}$. A specific capacitance of 218.47 Fg^{-1} was achieved for the rGO-$NiFe_2O_4$ (pH -10) at 5 mV/s^{-1}, which is the largest among all the samples.

Addition of conducting network of PANI to $NiFe_2O_4$ improved the electrochemical performance of PANI-$NiFe_2O_4$ nanocomposite electrode [101]. A specific capacitance of 448 Fg^{-1} was achieved with PANI-$NiFe_2O_4$. The electrode showed 80% retention in the capacitance after 1000 cycles at the rate of 10 $mAcm^{-2}$. A composite of mesoporous $NiFe_2O_4$ with multiwall carbon nanotubes (MWCNTs) prepared via hexamethylene tetramine (HMT) assisted one pot hydrothermal process exhibited large value of specific capacitance, 1291 F g^{-1} determined at 1 A g^{-1} [92]. The electrode showed capacitance retention of 81% over 500 charge–discharge cycles in 2 M KOH electrolyte. The asymmetric device with $NiFe_2O_4$/CNT nanocomposite as cathode and N-doped graphene as anode demonstrated a specific capacitance of 66 F g^{-1} with energy density of 23 W h kg^{-1} and power density of 872 W kg^{-1}.

$NiFe_2O_4$ nanoparticles grown on a flexible carbon cloth substrate via hydrothermal method demonstrated a high capacitance 1135.5 F g^{-1} in 1 M H_2SO_4 electrolyte and 922.6 F g^{-1} in 6 M KOH electrolyte with current density of 2 $mAcm^{-2}$ [93]. The large capacitance can be attributed to the conductive 3D network of carbon cloth and large surface area for $NiFe_2O_4$ nanoparticles. The binder free electrode of $NiFe_2O_4$ nanocone forest on carbon textile (NFO-CT) exhibited specific capacitance of 697 F g^{-1} calculated by CV at scan rate of 5 mV s^{-1} [94]. Further, a solid state supercapacitor of NFO-CT also demonstrated good value of capacitance of 584 F g^{-1} at 5 mV s^{-1}. Moreover, the device showed good cycle stability with 93.57% capacitance retention over 10,000 cycles. These results indicate that NFO-CT may be a promising candidate for high performance supercapacitor. The capacitance of $NiFe_2O_4$ was also observed to be dependent on the synthesis process [91]. The $NiFe_2O_4$ synthesized by combustion, polyol-mediated and sol–gel methods have different morphology and consequently different value of capacitance. A high specific capacitance value of 97.5 Fg^{-1} was obtained from sol–gel synthesized method. The size of grains and pores are smaller for sol–gel synthesized $NiFe_2O_4$ which could be the reason for better value of capacitance.

1D $NiFe_2O_4$/graphene composites prepared via hydrothermal process exhibited specific capacitance of 481.3 F g^{-1} at a current density of 0.1 A g^{-1} [97]. The 1D $NiFe_2O_4$/graphene electrode maintained 298.2 F g^{-1} capacitance upon increasing the current density to 10 A g^{-1}. The electrode demonstrated outstanding cycle stability over 10000 cycles (about 1% degradation in capacitance). On the other hand, 40% loss of capacitance was observed for $NiFe_2O_4$ electrode (125 to 75 F g^{-1}). The excellent electrochemical performance of $NiFe_2O_4$/graphene composites electrode is due to the conducting network of graphene and large number of redox active site from $NiFe_2O_4$. Ternary nitrogen-doped graphene/nickel ferrite/polyaniline (NGNP) nanocomposite showed specific capacitance of 645.0 F g^{-1} at 1 mV s^{-1} [99]. In a two-electrode symmetric system, the energy density and power density were determined to be 92.7 W h kg^{-1} and 110.8 W kg^{-1}, respectively. About 90% retention in capacitance was seen after 10,000 cycles. The electrochemical behavior of NGNP is improved due to combined effects of EDLC and pseudocapacitor.

6. Conclusions

In this chapter, electrochemical performance of selected ferrites ($CoFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$, and $NiFe_2O_4$) and their nanocomposites with conducting carbon network for supercapacitor has been reviewed. Their synthesis process was also highlighted. The surface morphology of these materials plays an important role in supercapacitor. These materials store the charge by redox process. However, poor electrical conductivity is the main limitation to be used them in fast charging/

discharging supercapacitor. In this regard, their nanocomposites with graphene enhanced the electrochemical performance. Nano-flakes type structure with graphene exhibited great electrochemical performance in supercapacitor.

Conflict of interest

The authors declare no conflict of interest.

Author details

Ankur Soam
Institute of Technical Education and Research, Siksha 'O' Anusandhan (Deemed to be University), Bhubaneswar, India

*Address all correspondence to: ankursoam007@gmail.com

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