Chapter

Effect of Different Metals Doped in Nickel Oxide Nanomaterials on Electrochemical Capacitive Performance

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Abstract

Recently, the various porous nano metal oxides used for the electrochemical energy storage supercapacitor applications. Some researchers focus on the binary as well as ternary metal oxides and more metal oxide complex composite materials used for the supercapacitors. In the review article focused on the effect of different metals doped in a nickel oxide nano material on the electrochemical capacitive performance, discussion on methodologies, charge storage mechanism, latest research articles and prepared nanostructures. Nowadays nickel oxide is developing electrode material for storage of charge due to its higher thermal stability, excellent chemical stability, cost effective materials, higher theoretical values of specific capacitance, naturally rich and environment friendliness material. The various metals doped in NiO and their composite oxides have shown good structural stability, reversible capacity, long cycling stability and have been also studied nano structured electrode materials for electrochemical supercapacitor applications.

Keywords: Metal oxide, Nickel Oxide, electrochemical supercapacitor, Nanomaterial

1. Introduction

Nowadays, in this research on the rapid growth of electronic portable energy storage devices and hybrids electrical vehicles, the call for high power density and energy density resources has been increased manifold. Supercapacitor also called ultracapacitor or electrochemical capacitors, exhibits higher power density than the normal capacitor and higher energy density than the batteries. The electrochemical capacitor shows faster charge–discharge mechanism behavior and also exhibits long cycle stability. Therefore, supercapacitor or electrochemical capacitor indicates bridge between the normal capacitor and fuel cell, batteries. The electrochemical supercapacitor has two main types based on the charge storage mechanism (i) Electrochemical double layer capacitor (EDLc) is based on electrostatically charge storage mechanism and (ii) pseudocapacitor is electrochemical charge storage mechanism. The carbon-based materials (Activated carbon materials, graphene oxide) used for the preparation of EDLc supercapacitor, transition metal oxide also used for the preparation of active electrode materials for pseudocapacitor and hybrid supercapacitor exhibits

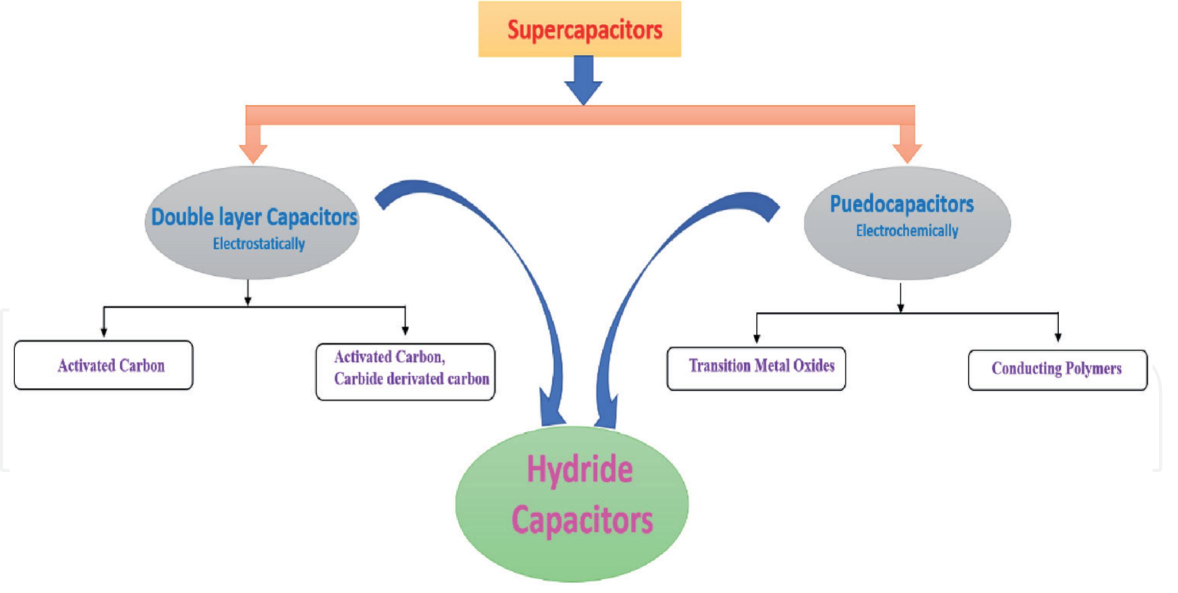

Figure 1.
Classifications of the electrochemical supercapacitor.

intermediate properties between the EDLc and pseudocapacitor behaviors schematic diagram shown **Figure 1**.

The effect of different morphologies on the charge storage at the active electrode materials for the supercapacitor application. The 1D, 2D, and 3D morphology increase the active materials surface area due to an increase in the power density and specific capacitance. It is an important role in electrochemical capacitors. The active electrode materials should be higher specific capacitance, structural stability, and good mechanical to provides long cycling lifetimes. The nano porous active electrode materials prepared by using carbon materials, metal oxides, and conducting polymers such as graphene oxide [1, 2], activated carbon [3] and derivatives of carbide materials [4–10], CuO, NiO, RuO2, Cu2O, Fe2O4, CoO, MnO [11–17] and polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) [18–22], The transition metal oxide electrode shows excellent properties of electrochemical performance (Specific capacitance, power density, and cycling stability) than the other types of the electrodes.

Generally, research has been carried out on the various transition metal oxide materials like cobalt oxide [23], iridium oxide [24], nickel oxide (NiO) [25], manganese oxide [26], iron Oxide [15], ruthenium oxide [13], and zinc oxide [27]. Currently, research on nickel oxide with other composite electrode materials just like a NiO//graphene oxide, Carbon nanotubes (CNT)//NiO, Ru doped nickel oxide, Cu doped nickel oxide, Cerium doped nickel oxide, and so on [28]. In the fabrications of high-performance supercapacitor at the laboratory, some interruptions occur due to nanostructured morphological structures with the large surface area of the electrode materials. Therefore, the nanostructures of the SEM images are an important parameter for supercapacitor applications. The electrochemical specific capacitance, power density, and cycling stability depend on the morphological structures due to so many researchers work on the synthesis of various types of nanostructured morphologies. But the Nickel oxide electrochemical specific capacitance does not get at maximum (In case of practical its value is 1000F/g) and the theoretical value is 2584F/g. Thus, gets maximum capacitance value, the growth of the nanostructured morphological materials with increased conductivity, lower interfacial resistance, and large surface area of the promising electrode materials is a promising solution.

There are several reports available on the synthesis of nanomaterials and electrochemical characterizing with more conductivity. NiO nanomaterials show excellent physical as well as chemical properties such as mesoporous and hierarchical porous nature, large surface area, and more electronic conductivity. The nanoporous electrode provides a large surface area that can enhance the electrochemical performance because increases the interactions between electrolytes with active electrode materials occurs faradic reaction at the interfacing sites. Further, an available large quantity of porosity nature can be more diffusion of the electrolytic electrons or ions in the electrodes and improve the volume alteration during the charge–discharge cyclic process due to enhances the cycling life of the active electrode materials. The oxide materials can be prepared by the various method can occur different type morphologies such as nanorod, nanoparticles, nanowire, nanoflower, nanotube, nanosheet, nanoneedles by Hydrothermal, Successive ionic adsorption and reaction (SILLAR), chemical precipitation, chemical bath deposition (CBD), sol–gel, solvothermal and electrodeposition methods.

Nickel oxide (NiO) exhibits multiple oxidations states these properties more suitable for the redox reaction or faradic reactions which gets maximum specific capacitance. One of the disadvances is the less electronic conductivity of the electrode. Therefore, large efforts have been dedicated to the manufacture of nanomaterials electrodes the exceptional advantages of some metal oxide doped NiO nanomaterials enhance the higher conductivity. Recently, the literature survey found that the Cu doped NiO nanomaterials, Co-doped nickel oxide, Mn-doped nickel oxide, Cerium doped nickel oxide were found to be very promising for the supercapacitor applications. In this review article, metal oxide doped nickel oxides materials for electrochemical supercapacitor applications have also been discussed briefly. However, to our best knowledge, there is no review found on the development of metal oxides doped NiO nanomaterials electrodes for supercapacitors applications. The energy storage mechanism in metal oxide doped nickel oxide electrode materials also discussed in this review article.

2. Principle of energy storage mechanism in electrochemical supercapacitor

In recent year, the energy storage and energy conversion are a big challenge and concern to the researchers. The excellent electrochemical performance depends on the properties of electrode materials. The electrochemical supercapacitor consists of a three importance parts one is electrode materials and another is an electrolyte, separator. The electrode materials are a most important part in an electrochemical capacitor. In the literature survey, the electrochemical electrical double layer capacitor made by carbon materials as a graphene oxide, activated carbon, carbon nanotubes and derivatives of a carbon materials, pseudocapacitor made by using a metal oxide or conducting polymers and hybrid supercapacitor is a made by using combination of the carbon-based materials and metal oxide. The charge storage mechanism of Electrical double layer capacitor (EDLc) is based on the electrostatically. The electrolytes and electrode materials interfaces on the surface layer in EDLc. The charge storage mechanism of the pseudocapacitor based on the electrochemically i.e. faradic reactions occur in the electrode and electrolytes interface and in the advance hybrid's supercapacitor consist of a both electrostatics and electrochemical charge storage mechanism.

The ideal electrical double layer capacitor electrode materials show rectangular in shape of cyclic charging -discharging cures but if the electrode shows pseudocapacitor behaviors then the curves show the nonlinear rectangular shapes, these nonlinear curves consist of oxidation- reduction peak. This peaks clearly indicates that the electrode materials and electrolytes interfaces occur faradic reactions during the cyclic voltammetry process **Figure 2**.

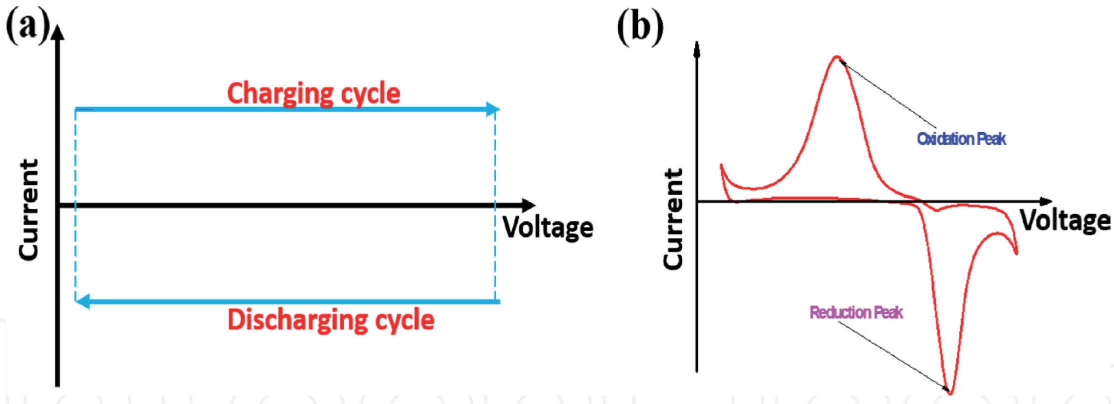

Figure 2.
The charging -discharging cyclic voltammetry curve of electrochemical supercapacitor (a) EDLC curve and (b) pseudocapacitor curve.

2.1 Charge storage mechanism within NiO nano materials

Generally, the metal oxide electrodes show higher power density than the carbon materials and higher electrochemical stability than the conducting polymer material electrodes. The charge store on the surface of the carbon based EDLCs supercapacitors and in puedocapacitor the charge store in porous nano materials, it occurs faradic reactions between the electrode materials and electrolytes. The NiO materials more suitable for supercapacitors applications because they exhibit several required properties.

- NiO exhibit good electrically conductive materials.
- Its shows multi-oxidation states.
- Its shows large surface area of the active materials.
- NiO nano materials shows higher theoretical values of Cs.
- Its exhibit large cycling stability.
- Its shows higher specific capacitance values than the other materials.

NiO have been promising materials for supercapacitor applications due to the exhibits higher theoretical specific capacitance, but in practical case these NiO materials does not get or shows highest specific capacitance values. Sometimes, achieve higher specific capacitance of NiO materials because the NiO shows higher charge storage at the highly porous nanostructure materials, low resistance between electrode and electrolytes, highly conductive substrate. In the practical case NiO based supercapacitors observed in the literature survey, the specific capacitance values 50 to ~1000F/g. The NiO nano materials shows pseudocapacitive nature, during the cyclic voltammetry process these nano-materials exhibits redox reaction mechanism and it's converted to NiOOH and reversible state. Sometimes, during the redox cycles, the cathodic current peaks and anodic current peaks shifted more towards the positive and negative axes as the scan rate was increased. The shifting of peaks currents which is maybe due to the highly accessible surface area of the porous NiO nanostructures and the fast ionic/electronic diffusion rate during redox reaction.

NiO and its binary as well as ternary composite materials prepared as various techniques by using some additives and binder free method. Therefore, the prepared NiO based binary as well as ternary composite or metal doped NiO materials shows lower conductivity and higher interfacing resistance. Due to metal oxides directly synthesized on conductive electrode substrate have the advantage as it can not only result in higher capacitance but also minimize the contact resistance. Various conductive substrates like stainless steel (SS), ITO glass, FTO glass, carbon cloth, carbon mesh, Ni foam, and copper strip electrodes have been used to preparations of the nanostructured metal oxides. It should be mentioned that the electrode metal oxide/hydroxides material deposited directly on to the current collector electrodes is the best choice to minimize the resistance and enhances the electrochemical performance of the electrode materials.

3. Synthesis techniques

Different techniques are used for the synthesis of the nanomaterials. The synthesized nano materials have been formed various nanostructures and proper required porous materials. It is well known that the nano structure morphology of the synthesized electrodes plays an important role in electrochemical redox reactions. The nanostructured electrodes increase the interactions between the electrode and electrolytes due to enhances the performance of the electrochemical performance.

In the chapter, we place advancing a comprehensive summary of the synthesis techniques, pure NiO and metal doped NiO based nanostructures with electrochemical analysis. Following methods briefly discussed one by one.

3.1 Hydrothermal method

Hydrothermal synthesis method is one of the most common used for one-pot synthesis techniques to prepare a wide range of metal oxides [29, 30]. Hydrothermal synthesis process is solution based. We know that these hydrothermal methods provide good crystallinity structures and highly nano porous morphological shape selectivity to oxides-based materials [31]. Generally, the precursors of metal oxides are formed by mixture of reaction ingredients being heated at sealed Teflon-lined stainless-steel autoclave. Solvents under the room temperature to high temperature range and various pressure ranges are used to formations of the nanostructure materials. Generally, the temperature is used higher than 1000C and a pressure will be established mechanically in a closed autoclave system. In hydrothermal techniques to the reaction temperature other parameter like volume of solvent, reaction time also have importance impact on the final synthesis morphology of the materials. By controlling the various parameters such as reaction time, pH value of percussor solutions, reaction temperature and concentration of the precursor solution, it can produce various dimensional (0D, 1D, 2D and 3D) morphologies with large surface area based porous nanostructures. A lot of researcher groups have made optimize the reaction conditions and prepares superior morphologies to enhance the electrochemical performance of the nano materials, which will be discussed in details later section.

3.2 SILAR method

These SILAR methods is a solution-based techniques, it is widely used for the synthesis of the various type of metal oxide/hydroxide thin films, these techniques more commonly used to preparations of the different type nanostructured materials. SILLAR is a simple, cost effective, binder free method and it is appropriate method for synthesis of large-scale of nanostructure materials [32].

3.3 Chemical bath deposition method

The chemical bath deposition (CBD) techniques were first discovered by Nagayama in 1988 [33]. This technique mostly used in prepare of the metal oxide thin films for various applications. The principle of CBD method deals with the immersion of a substrate in a precursor solution [34, 35]. Then the grown-on metal oxide/hydroxide precipitates on the substrate surface to produces a thin well adherent and binder less film. These techniques beneficial due to its low cost, low temperature, binder less, and various adjustment parameter for preparations of different nanostructured materials and also more suitable for large-scale deposition particularly for the preparation of uniform oxide thin films on samples. This method usually needs a strong chemical oxidant or reducing agent to drive reactions to take place. Recently, this technique is very popular in today's for preparations of different types metal oxides as well as hydroxides like NiO thin film nanostructures.

3.4 Electrodeposition method

The electrodeposition is a one of the most widely used method to formations of different metal oxides as well as hydroxides nano materials [36]. This electrodeposition method is based on electrochemical oxidation- reduction (redox) reaction and the metal oxides/hydroxides are deposited on to the conducting substrate electrode. In these techniques, the optimal of the anion and adjustment of appropriate pH of the solution during the deposition is very crucial parameter. Although, this is a simple method to preparations of metal oxides/hydroxides with uniform grown morphology on electrode.

3.5 Spray pyrolysis method

Among the chemical techniques mentioned above, spray pyrolysis is most popular today for the large area thin film formation. Spray solution results directly into oxide formation. It has number of advantages. (1) Doping is easy as required amount of dopant can be added by mixing proper amount of solution of the dopant. (2) Like vapor deposition technique, spray pyrolysis does not require high quality target or vacuum at any stage hence this is one of the great advantages of this technique in the industrial applications. (3) Deposition rate and the thickness of the film can be easily controlled by controlling spray parameters. (4) Deposition in the moderate temperature range 150°C - 500°C is possible. (5) There is no restriction on the size and surface morphology of the substrate. (6) It is possible to prepare multilayer or multi compositional films. Due to these advantages, numbers of conducting and semiconducting materials were prepared by spray pyrolysis technique [37, 38]. In the present work, spray pyrolysis set up (Labotronics make) was used to prepare thin films of cobalt oxide, manganese oxide, manganese doped cobalt oxide, ruthenium oxide, ruthenium doped cobalt oxide and ruthenium doped manganese: cobalt oxide (ternary oxide) thin films by both aqueous as well as non-aqueous routes.

3.6 Microwave-assisted method

Although, the hydrothermal method and solvothermal synthesis method are the most useful methods to preparations of the different types nanostructures materials with controllable structure, size and morphology [39, 40], In hydrothermal method synthesis nanomaterials required more time for the reactions. Therefore, the microwave-assisted method is being used widely for the synthesis of different types nanostructure materials in few minutes. Microwave synthesis has become a popular method. Which substantially reduces the reaction time. The microwave-assisted method can suppress side reactions and provide rapid kinetics of crystallization growth. Using the microwave- solvothermal coupled method; one can not only effectively reduce the reaction time but can also control the morphology. It can produce narrow particle size distribution with high purity and large surface area of the active electrode materials. Therefore, microwave-solvothermal technique is an effective technique to fabricate the different types metal oxide and hydroxides with desired morphology.

4. Pure NiO electrode for supercapacitor applications

The different method used to preparation of the different type's nanostructure nickel oxides/hydroxides. There have been many reports on NiO nanostructures including porous nano/microspheres [41, 42], nanosheets [43], nanoflowers [44] and nanofibers [45]. In general, the proper porous nanostructure plays an important role in electrochemical charge storage mechanism due excellent electrical conductivity and the large surface area [46–48]. The overview of pure NiO prepared by using different synthesis methods and their electrochemical performance is tabulated in **Table 1** [49–63]. The following section briefly discusses on various synthetic routes for the fabrication of pure NiO nanostructures and their supercapacitor properties.

4.1 Hydrothermal method

In the hydrothermal synthesis route provides by the 3D nanostructures of materials with large surface area, these properties more suitable for the supercapacitor applications. Generally, 3D nanostructured electrodes are prepared on the conducting substrate foams like nickel foam. Ni foams exhibits highly porous structures and conductive substrate for synthesis of NiO. In the hydrothermal method's various adjustable parameters like reaction temperature, reaction time, concentration of percussor solutions, pH and so on are used to preparation of the different type's nanostructures. This is due to the increases in the conductivity of the electrodes of the pure NiO. The nanosheets and flower-like morphology of NiO composed of flabbergasted lotus-root- like nanosheets were also fabricated by hydrothermal method [44]. The concentrations of reaction reagent in the reaction medium also have the key role to control the morphology of metal hydroxides and metal oxides.

4.2 SILLAR and chemical bath deposition

This method compared to hydrothermal method, relatively a smaller number of researchers work on preparations of the pure NiO. The specific capacitance SC of NiO were observed in aqueous NaOH and KOH electrolytes observed 129.5 F/g and 69.8 F/g respectively [34]. Xia et al. [57] successfully prepared the NiO monolayer hollow-sphere composed of porous net-like NiO nanoflakes film (SSA 325 m_2/g) by chemical bath deposition using polystyrene sphere template. The SC value for this porous NiO films was found to be 311 F/g with an excellent capacitance retention which is due to the porous structure that could alleviate the structure distortion caused by volume expansion during the cycling process [56].

Nano materials Synthesis techniques	**Morphological view**	**Electrolytes**	**Specific capacitance**	**Specific surface area (m^2/g)**	**Cycling stability**	**Reference**
Hydrothermal	Nanoparticles	6 M KOH	609 F/g at 5 A/g	58.5	500	[41]
Hydrothermal	Nanowires	1 M LiPF4	348 F/g at 10 mV/s	85.18	100	[49]
Hydrothermal	Nanoflakes	2 M KOH	137.7 F/g at 0.2 A/g	107.5	1000	[50]
Hydrothermal	Double-shelled hollow nanospheres	—	612.5 F/g at 0.5 A/g	92.99	1000	[51]
Hydrothermal	Nanocolumns	1 mol/L KOH	390 F/g at 5 A/g	102.4	1000	[52]
Hydrothermal	Nanosheets-assembles	2 M KOH	989 F/g at 3 mV/s	—	1000	[53]
Hydrothermal	Pine-cones	2 M KOH	337 F/g at 2 mV/s	265	100	[54]
Hydrothermal	Nanoflakes	2 M KOH	411 F/g at 0.2 A/g	227	100	[55]
Chemical bath deposition	Monolayer porous hollow-sphere arrays	—	311 at 1 A/g	325	—	[56]
Chemical bath deposition	Flackes	1MNaOH	129.5F/g	—	—	[34]
SILLAR	nanoflakes	2 M KOH	674F/g	122.36	2000	[25]
SILLAR	nanosheets	a 1-(2,3 -dihydroxypropyl)-3-methylimidazolium hydroxide	205.5	36.3	5000	[57]
Electrodeposition	Core/shell	—	1635 F/g at 2 mV/s	—	—	[58]
Electrodeposition	Nanoporous film	—	1776 F/g at 1 mV/s	264	—	[59]
Electrodeposition	nanoflakes	1MKOH	222F/g			[60]
Electrodeposition	Porous NiO	1MKOH	351F/g	—	—	[61]
Microwave	Flower-like hollow nanospheres	2 M KOH	585 F/g at 5 A/g	176	1000	[39]
Microwave	Nanoplatelets	2MNaOH	1200 F/g at 1 A/g	e	1000	[40]

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Nano materials Synthesis techniques	Morphological view	Electrolytes	Specific capacitance	Specific surface area (m^2/g)	Cycling stability	Reference
Microwave	Hierarchical porous ball-like surface	Hydroxide Ions	420 F/g at 0.5 A/g	125	1600	[55]
Spray method	larger grains	1MKOH	23 mF/cm2			[62]
Spray method	heaps	2MKOH	405F/g	—	1000	[64]
Spray method	Small pores	2MKOH	564 F/g	—	1000	[63]

Table 1.
Pure NiO prepared using various methods and their electrochemical supercapacitor performances.

4.3 Electrodeposition method

In 1997 year, the porous NiO nanostructure materials were reported by Srinivasan et al. [65], where shows a very little capacitance value is 59 F/g. However, in 2004 year, the capacitance value observed 138 F/g has been reported for 3D NiO on stainless steel conducting substrate [66]. 1D mesoporous core shell structure shows the hexagonal lyotropic $Ni(OH)_2$ synthesized by electrodeposition [67]. The main drawback of NiO is a lower electrical conductivity, and the achieving higher conductivity has a great, the NiO/ITO showed increased conductivity and thus improved the SC (1025 F/g) compared to NiO/Ti (416 F/g) [68].

4.4 Spray pyrolysis method

Among numerous chemical techniques mentioned in schematic (**Figure 3**) SPM is the most popular today because of its applicability to produce variety of doped and undoped metal oxide films [69]. The basic principle involved in SPM is the pyrolytic decomposition of salts of a desired compound onto the preheated substrates. The atomization of the spray solution into a spray of fine droplets also depends on the geometry of the spraying nozzle and pressure of a carrier gas. Every sprayed droplet reaching the surface of the hot substrate undergoes pyrolytic (endothermic) decomposition and forms a single crystallite or clusters of crystallites as a product. The remaining volatile byproducts and solvents escape out in the form of vapor phase. The substrates provide thermal energy for the decomposition and subsequent recombination of the constituent species, followed by sintering and crystallization of the clusters of crystallites and thus coherent films are formed. The required thermal energy is different for the different materials and the solvents used.

Nickel oxide (NiO) films can be prepared using various chemical methods. Among these, spray method is a mechanically simple, cost-effective, and large

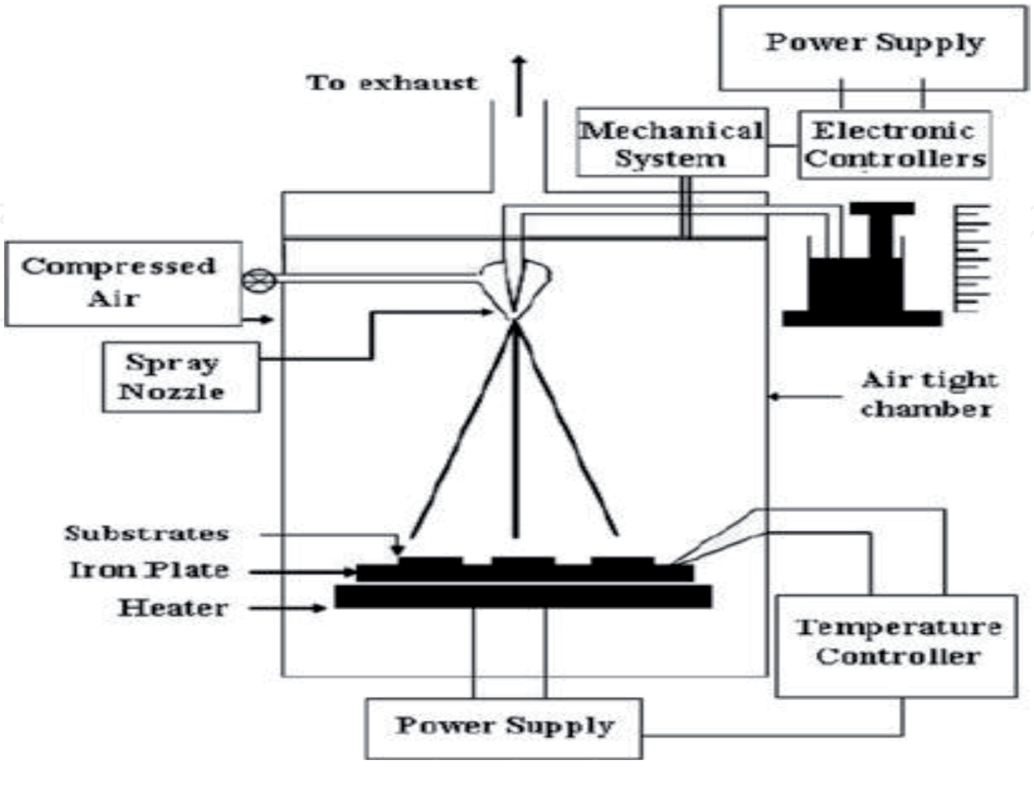

Figure 3.
Schematic spray pyrolysis deposition method. (Adapted with permission from Ref. [69]. Copyright 2021, Elsevier.)

surface deposition method. The various precursors are used for preparation of NiO thin films electrodes using different in gradient sources like nickel nitrate, nickel acetate and nickel chloride [70]. Yadav et.al reported specific capacitance of the pure NiO is 564F/g at 1A/g in 2 M KOH electrolytes with 1000 cyclic stability [70]. Kate et.al reported that the NiO thin films were successfully deposited using spray method, the observed specific capacitance values is 1000F/g at 5 mV/s scan rate [71].

5. Metals doped in NiO nanomaterials for supercapacitor applications

A great development has been achieved in developing low cost, higher conductivity, porous materials and more simple methods for the synthesis of various metal doped oxide electrodes for electrochemical supercapacitor applications. In the previous point discussed, pure NiO has drawn rigorous research interests due to its promising properties and some drawback of the electrochemical analysis. However, pure NiO exhibits lower specific capacitance values (SC) and it is providing lower electrochemical stability. There are several reasons for the low stability and low capacitance of pure NiO. Such as conductivity of NiO materials is very poor, does not proper electrolytes interactions of the nanomaterials and so on. But if we want to increase the electrochemical stability with capacitance then we have to dope the proper metals, so that the conductivity of the nanomaterials will increases and also the capacitance will be increased. In the following **Table 2** [28, 72–80] shows metal oxide doped in NiO and its effect on electrochemical performance. Various method is used to formations of the metal doped NiO nanostructures like hydrothermal, spray, sol–gel, chemical bath, facile chemical synthesis and so on.

In the hydrothermal method various adjustable parameters used for the for the synthesis of different types nanostructured morphologies. Such as temperature controlled, concentration of the percussor, reaction time and different types

Different Metal Doped NiO	Nano materials Synthesis techniques	Morphological view	Electrolytes	Specific capacitance	Cycling stability	Reference
Mn-NiO	Facile chemical synthesis route	Nanoparticle	6MKOH	369.6F/g		[72]
Mn-NiO	Hydrothermal	Nanostructured arrey	6MKOH	1166f/g	5000	[73]
Cu-NiO	citrate-gel	Particle size		559F/g	50	[74]
Al-NiO	Hydrothermal	Nanosheet	1MKOH	2253F/g	5000	[75]
Co-NiO	Spray method	Grannular	2MKOH	835F/g	1000	[76]
Co-NiO	Laser deposition	Flowerlike	1MKOH	720F/g	1000	[77]
Ce-NiO	Chemical method	Porous layer	1 M LiOH, NaOH and KOH	1500F/g	2000	[78]
Ce-NiO	Sol–gel	Nanoflaske	1MKOH	2424F/g	2000	[28]
Ce-NiO	Sol–gel	Spongy like		110F/g	1000	[79]
Cu-Co-Ce-Ni	Hydrothermal	Nanoflaske based nanoflower	1MKOH	2696F/g	3000	[80]

Table 2.
Different Metal doped in NiO prepared using various methods and their structural, electrochemical supercapacitor performances.

substrate foams are used for the preparations of the large surface area of the nano-structured morphologies. In schematic **Figure 4** shows effect of all above parameters on the nanomaterials and formations of the different nano structures [81]. The 1D or 2D structures like NiO nanorod, $Ni(OH)_2$ nano-wall and Co_3O_4 nanowire/nanosheet arrays can be attained by using simple hydrothermal of directly putting the substrates into precursor solutions (contain metal salts and alkali), maintaining for a certain time at appropriate temperature and following annealing treatment (**Figure 4**). The morphological structures and their size strongly depend only on the reaction conditions, such as reaction temperature, reaction time, and concentration of the precursor solutions and its ratios proportionality of the reactants. The observed structures of the NiO are the small nano array and Nickel hydroxides small nano wire like morphological structures.

In sol gel synthesis is a one of the widely used method for the formation of the large number nano materials. Saraynya et.al shows that the cerium doped nickel oxide more active and suitable materials for the supercapacitor applications [28]. They are observed highest specific capacitance value is 2444 F/g at 5 mV/s at a 1%

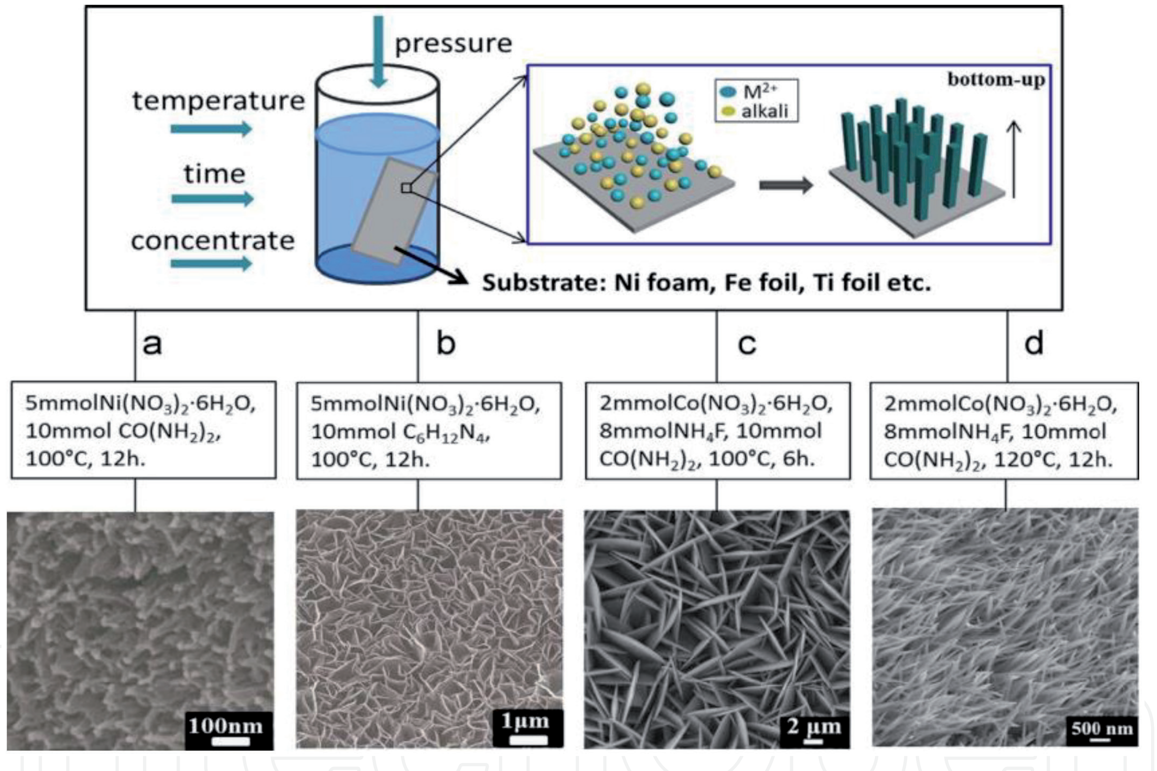

Figure 4.
Schematic hydrothermal deposition with using various parameter. (Adapted with permission from Ref. [81]. copyright 2021, Elsevier).

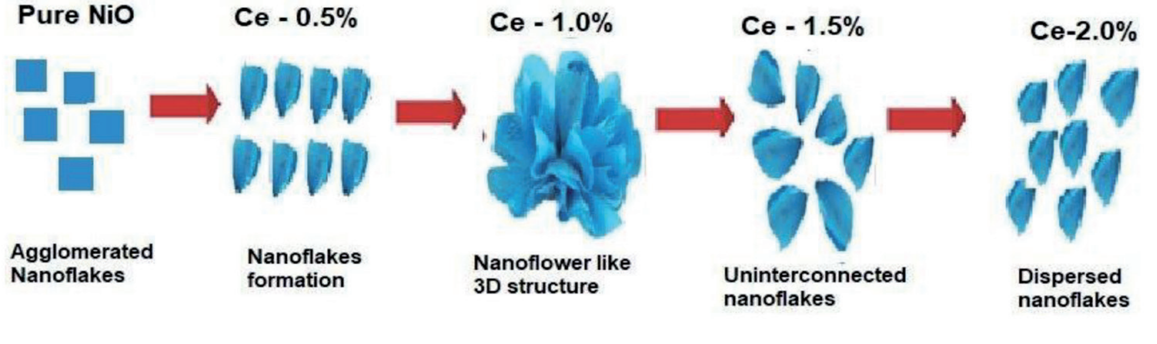

Figure 5.
The effect on nanostructure by using various doping percentage in NiO. (Adapted with permission from Ref. [28]. Copyright 2021, Elsevier).

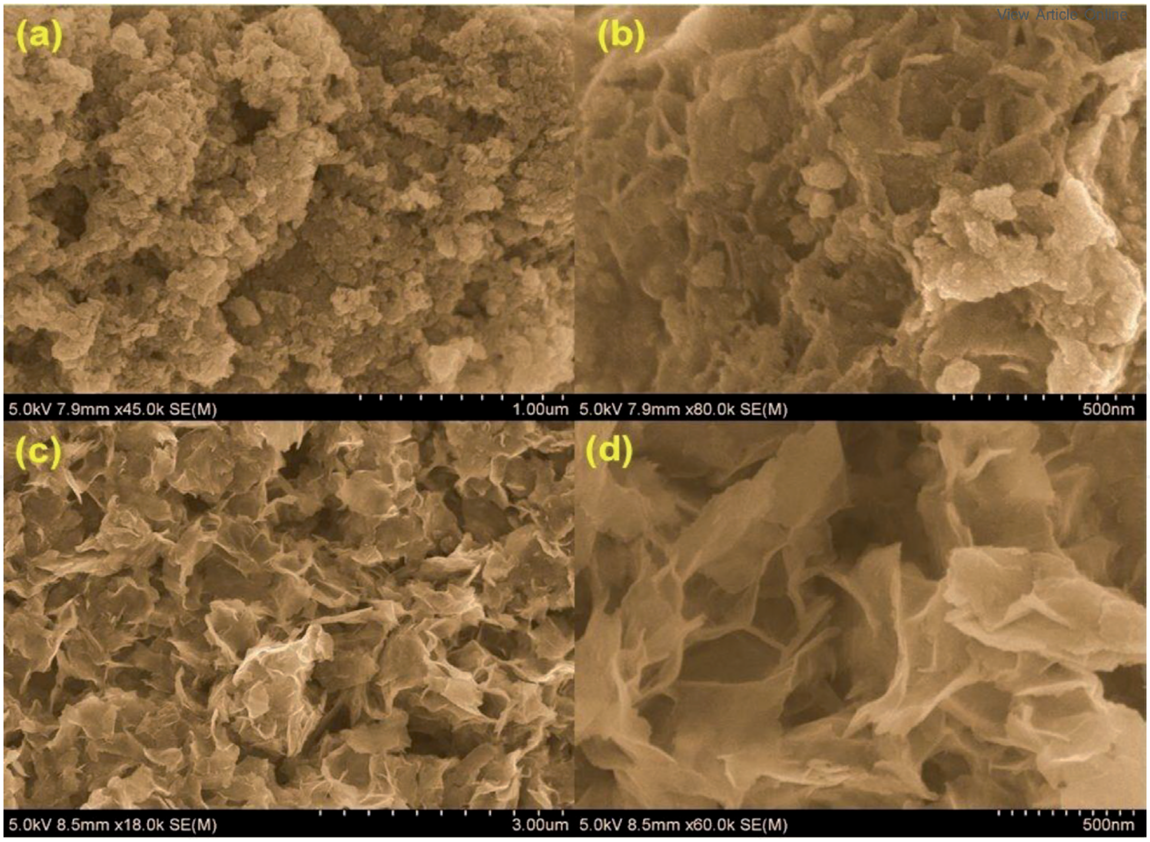

Figure 6.
(a and b) The SEM images of pure NiO and (c and d) The SEM images of 1% Ce doped NiO. (Adapted with permission from Ref. [28]. Copyright 2021, Elsevier).

cerium doped nickel oxide. In a **Figure 5** shows the pure NiO is lower value of specific capacitance because these NiO clearly indicates agglomerated nanostructured morphologies, but in the cerium doped NiO exhibits highest specific capacitance due to the morphologies flake like and large active electrode surface area for the access of the electrons. Here in **Figure 6** shows percentage of the metal dopant increases the structure of the nanomaterials change, it clearly indicates mostly important parameter for the proper formations of the nanostructured morphology for charge storage supercapacitor applications. The 1% Cerium doped NiO formatted 3D nanoflower like structure with accessible large surface [28].

6. Materials selection and challenges of the supercapacitor

The effect of transition metal oxide doped NiO by spray method shows more electrochemical performance than the pure NiO. Kate et.al show that the cobalt doped nickel oxide highest specific capacitance value is 835F/g at 5 mV/s in a 2MKOH electrolytes. Sharanya et.al shows that the the cerium doped nickel oxide is exhibits pseudocapacitive nature and good candidate materials for the supercapacitor applications, his shows that the highest specific capacitance of the Ce doped NiO is 2444F/g [28].

6.1 Selection of electrode materials for supercapacitor applications

Electrochemical energy storage devices play an important role in developing green energy for future to the society. After evaluating the published literature survey, we noticed that a great research has been carried out on electrochemical supercapacitor applications. A great challenge on the to investigate the electrochemical highly performed electrode materials. The various researches focused on the preparation of the large surface of the material morphologies and enhancing conductivity, and electrolytes to obtain high energy and power densities with long cycle life. Therefore, it is necessary to the selection of electrode materials for the electrochemical supercapacitor. Therefore, herein we proposed some designing high-performance electrode materials for supercapacitors, such as specific surface area, proper selecting electrolytes, conductivity of the electrode's materials and design more porous different types nanostructures.

7. Challenges in the supercapacitor applications

Various challenges in the electrochemical supercapacitor such as enhances specific surface area of the electrode materials, enhances the conductivity of the electrode materials, maintain proper thickness of the electrodes, proper electrolytes used in charge storage mechanism, fabrications of the device, suitable separator used between the electrodes, leakage problem in devices and maintain the equivalent series resistance of the electrode materials. All of the above challenges most important in the supercapacitor application.

8. Conclusions

In the chapter, we have scientifically drawn the recent progress on a transition metal doped nickel oxide (NiO) as the energy storage materials for supercapacitor applications. The effect of the metal doped nickel oxide on the supercapacitor and developing nanostructures of pure NiO and metal oxide doped NiO based pseudocapacitor electrodes have been discussed. If you want to get maximum capacitance, you need to have a specific surface area, it is crucial parameter to obtain suitable morphologies of electrode materials. Clearly indicates that the various nanostructures of the electrodes such as flower, flake, nanobelt, nanowire, nanorod, hollow, core-shell, granular particles thin films are needed to improve the electrochemical performances further. The specific surface area and conductivity of the electrodes are two most important critical parameters that determine the supercapacitor performance which has to be optimized.

Nickel oxide is a semiconductor material, it shows lower electric conductivity so it has the same effect on the electron motion and hence the effect on the specific capacitance of the supercapacitor. To improve electric conductivity, NiO is often combined with nanostructured conductive transition metal oxides such as cerium, copper, aluminum, and magnesium to produces Metal doped NiO based electrodes. In this way, good electrical conductivity and rich electroactive sites for the electrolyte ions are obtained. The metal dope nickel oxide is shows pseudocapacitive nature. The doping of other metal oxides can also introduce impurity band effects and can enhance the electrochemical performance.

It is critical for researchers to improve both synthesis conditions and material qualities in order to fully leverage the potential of NiO-based electrode materials. High specific capacitance and long-term cycle stability are also concerning that must be addressed. This is the focus of the authors' on-going work. Other hand the synthesis methodologies, there are many issues pertaining to the measurement techniques and electrode preparation process that require attention. Furthermore, engineering factors like fabrication of electrodes, choice of electrolytes, membrane separators and packaging are not well established and thus need extensive investigation.

Conflict of interest

The authors declare no conflict of interest.

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