

Project Report on

Hydrothermally synthesized Nanoflower-like structured NiO electrode for Supercapacitor Applications

Submitted by

Ponnam Rahul

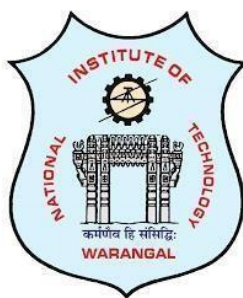
Roll No : 21PHE0011

Third Year, Second Semester

Integrated M.Sc. in Physics

Under the supervision of

Prof. K. Thangaraju

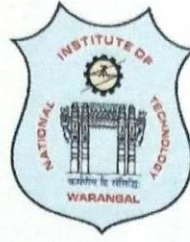


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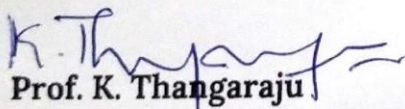
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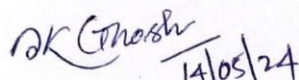
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CERTIFICATE

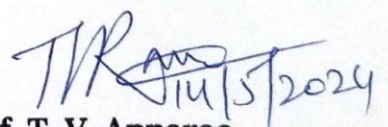
This is to certify that **Mr. Ponnamm Rahul**, bearing Roll No: 21PHE0011, third-year, second-semester student of Integrated M.Sc. Physics has carried out the project work on “Hydrothermally synthesized Nanoflower-like structured NiO electrode for Supercapacitor Applications” as a part of his Integrated M.Sc. Physics coursework.


Prof. K. Thangaraju

Seminar Guide


14/05/24
Prof. Surya K. Ghosh

Seminar Coordinator


14/05/2024
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Abstract:

The Nickel oxide has been synthesized using hydrothermal method. The structure and morphology of the NiO was characterized by X-ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM), revealing nanoflower-like morphology. NiO calcinated at 300° C to form the uniform distribution. Electrochemical studies using Cyclic Voltammetry at different scanning rates from 5 to 100 mV/s exhibit that the NiO sample (calcinated at 300° C) showed improved Specific capacitance of 1111 F/g at the scan rate of 5 mV/s. This nanoflower-like structure enhances ion diffusions paths in the electrochemical reactions. The NiO nanoflowers could be a promising electrode material for supercapacitor application.

Introduction:

With the increase in energy demand and Owing to the limited crude oil storage and global warming situation, there is a necessity for breakthrough in rechargeable batteries and supercapacitor science and technology to satisfy the future development of a low-carbon and sustainable economy. Rechargeable batteries are being considered as promising power devices for electric vehicles (EVs) and efficient energy storage devices for sustainable energy, such as wind or solar energy. However, the charge storage of current rechargeable batteries mainly depends on the intercalation/ de-intercalation of cations (H^+ or Li^+) within the crystalline structure of electrode materials, and thus is controlled by the diffusion of cations within the crystalline framework, which significantly limits the charge/discharge rate of batteries.

The supercapacitors has emerged with the potential to enable major advances in energy storage devices. Supercapacitors are governed by the same fundamental equations as conventional capacitors, but utilize higher surface area electrodes and thinner dielectrics to achieve greater capacitances. This allows for energy densities greater than those of conventional capacitors and power densities greater

than those of batteries. The energy storage capacities of supercapacitors are several orders of magnitude higher than those of conventional dielectric capacitors, but are much lower than those of secondary batteries. They typically have high power density, long cyclic stability and high safety, and thus can be considered as an alternative or complement to rechargeable batteries in applications that require high power delivery or fast energy harvesting.

Supercapacitors fill the gap between batteries and traditional devices. In terms of specific energy and specific power. Batteries and low temperature fuel cells are typical low power devices whereas conventional capacitors may have a power density of $>10^6$ watts per dm^3 at very low energy density. The supercapacitor should have a longer cycle life than batteries because there is little or no chemical change. The Ragone plot (Figure 1) clearly describes the energy density and power density of capacitors, supercapacitors, batteries and fuel cells.

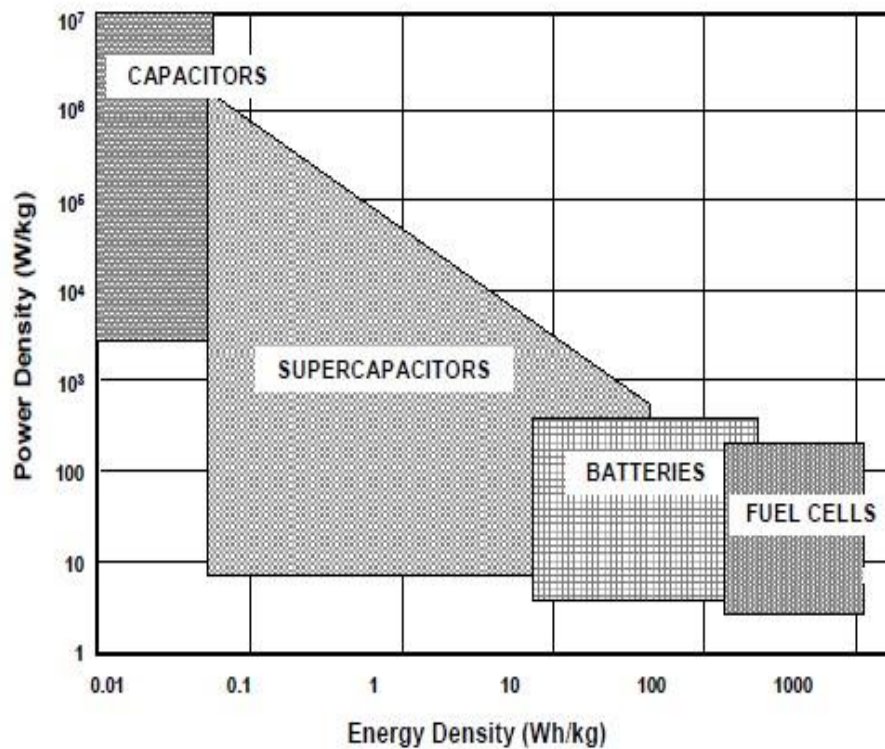


Figure 1: Ragone Plot (Power density Vs Energy Density)

Classification of Supercapacitors:

Supercapacitors have been divided into three general categories: electrochemical/electric double-layer capacitors, pseudocapacitors, and hybrid capacitors. (See Figure 2) Each category has been characterized by its own unique mechanism for storing charge. They are as follows non-Faradaic, Faradaic, and a combination of the two. Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between electrode and electrolyte. A non-Faradaic mechanism, by contrast, does not use a chemical mechanism. Rather, charges are distributed on surfaces by physical processes that do not involve the making or breaking of chemical bonds.

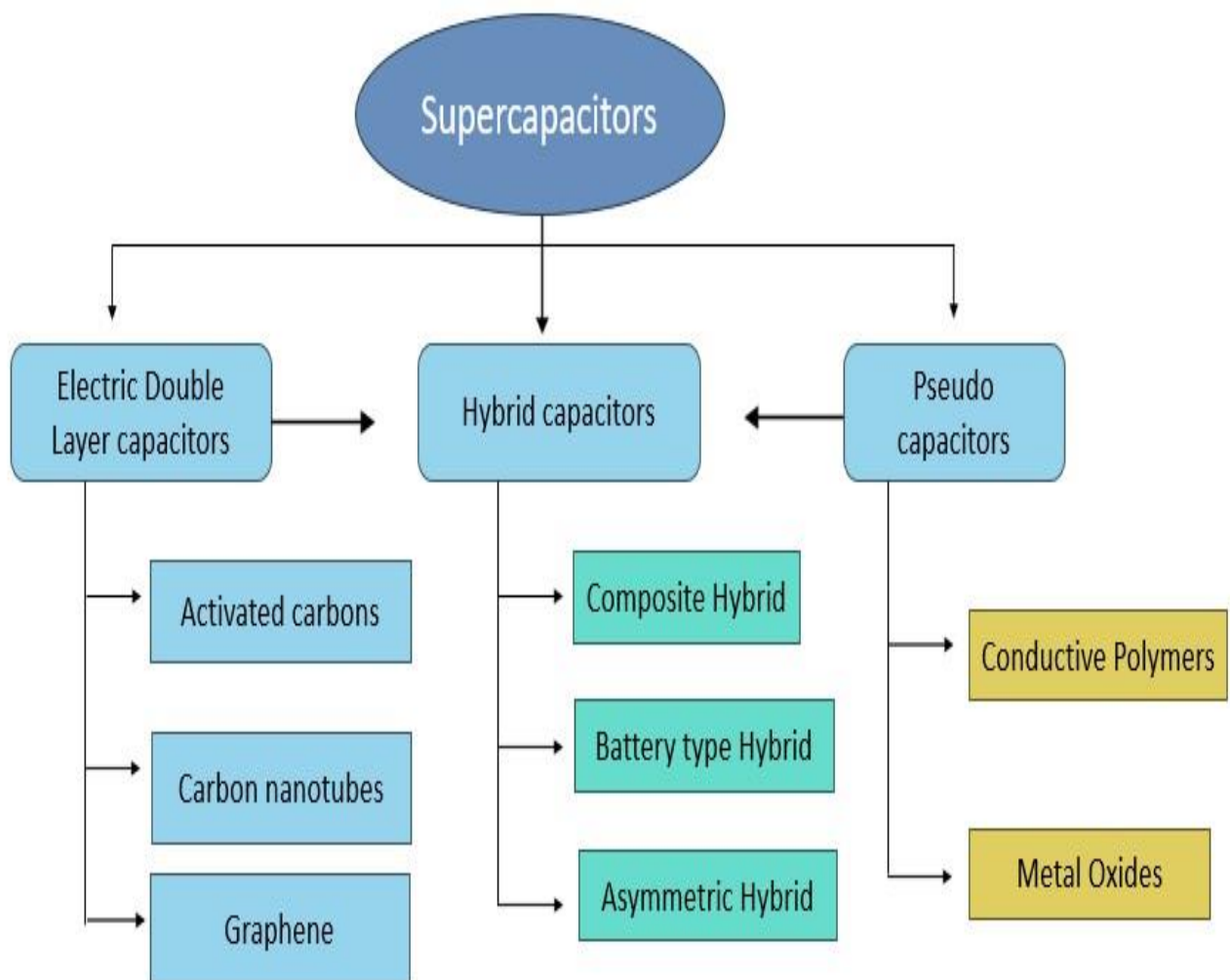


Figure 2: classification of Supercapacitors

Electric Double Layer Capacitors:

Electrochemical double-layer capacitors (EDLCs) are constructed from two carbon-based electrodes, an electrolyte, and a separator. Figure 3 provides a schematic of a typical EDLC. Like conventional capacitors, EDLCs store charge electrostatically, or non-Faradically, and there is no transfer of charge between electrode and electrolyte. EDLCs utilize an electrochemical double-layer of charge to store energy. As voltage is applied, charge accumulates on the electrode surfaces. Following the natural attraction of unlike charges, ions in the electrolyte solution diffuse across the separator into the pores of the electrode of opposite charge. However, the electrodes are engineered to prevent the recombination of the ions. Hence, a double-layer of charge is produced at each electrode. These double-layers, coupled with an increase in surface area and a decrease in the distance between electrodes, allow EDLCs to achieve higher energy densities than conventional capacitors. As there is no transfer of charge between electrolyte and electrode, there are no chemical or composition changes associated with non-Faradaic processes. For this reason, charge storage in EDLCs is highly reversible, which allows them to achieve very high cycling stabilities.

Electrochemical batteries are generally limited to only about 10^3 cycles. Because of their cycling stability, EDLCs are well suited for applications that involve non-user serviceable locations, such as deep sea or mountain environments. The performance characteristics of an EDLC can be adjusted by changing the nature of its electrolyte. An EDLC can utilize either an aqueous or organic electrolyte. Aqueous electrolytes, such as H_2SO_4 and KOH , generally have lower minimum pore size requirements compared to organic electrolytes, such as acetonitrile. However, aqueous electrolytes also have lower breakdown voltages. While the nature of the electrolyte is of great importance in supercapacitor design, the subclasses of EDLCs are distinguished primarily by the form of carbon they use as an electrode material. Carbon electrode materials generally have higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and

metal oxides. Different forms of carbon materials that can be used to store charge in EDLC electrodes are activated carbons, carbon aerogels, and carbon nanotubes.

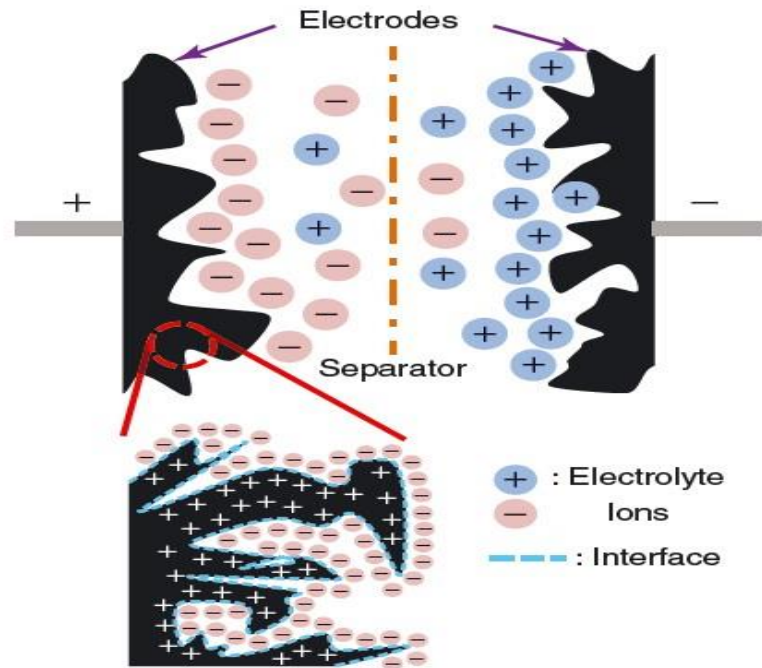


Figure 3: Electric Double Layer Capacitor

$$C = \frac{A * \epsilon}{d}$$

C = capacitance, A = Area, d= distance between electrodes, ϵ = permittivity.

Activated Carbons:

Activated Carbons is less expensive and possesses a higher surface area than other carbon-based materials, activated carbon is the most commonly used electrode material in EDLCs. Activated carbons utilize a complex porous structure composed of differently sized micropores (< 20 Å wide), mesopores (20 - 500 Å), and macropores (> 500 Å) to achieve their high surface areas. Although capacitance is directly proportional to surface area, empirical evidence suggests that, for activated carbons, not all of the high surface area contributes to the capacitance of the device. This discrepancy is believed to be caused by

electrolyte ions that are too large to diffuse into smaller micropores, thus preventing some pores from contributing to charge storage. Larger pore sizes correlate with higher power densities and smaller pore sizes correlate with higher energy densities.

Carbon Nanotubes:

Unlike other carbon-based electrodes, the mesopores in carbon nanotube electrodes are interconnected, allowing a continuous charge distribution that uses almost all of the available surface area. Thus, the surface area is utilized more efficiently to achieve capacitances comparable to those in activated carbon-based supercapacitors, even though carbon nanotube electrodes have a modest surface area compared to activated carbon electrodes. The efficiency of the structure allows energy densities comparable to other carbon-based materials.

Graphene:

Graphene possessing high thermal/electrical conductivity, mechanical strength, chemical stability, and large surface area, graphene distinguishes itself from other competitive carbon materials. It became the rising advanced material for supercapacitor applications. Graphene is a flat 2D honeycomb-shaped monolayer sheet of carbon atoms that is the basic building blocks of other carbon materials as illustrated in Figure 4.

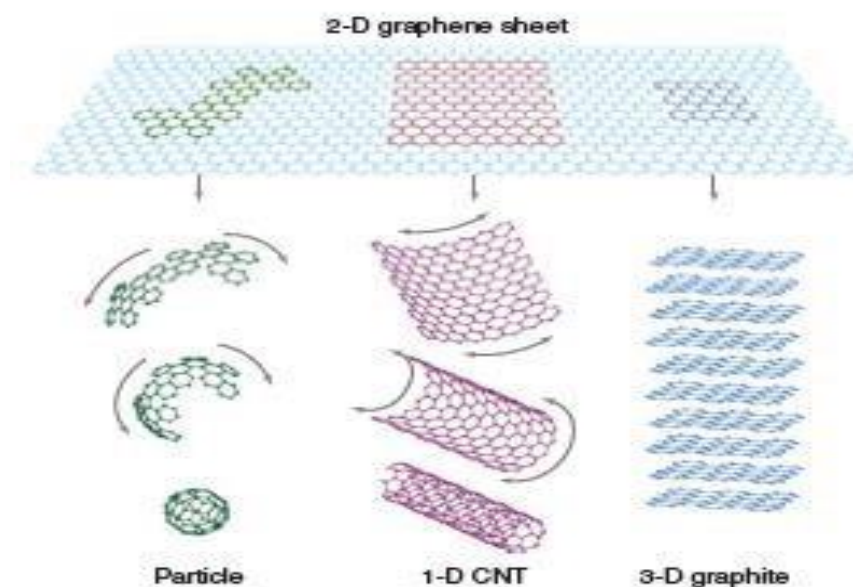


Figure 4: 2D Graphene

Pseudocapacitor:

The storage mechanism in Pseudo capacitor is electrochemical in nature. Faradaic processes allow pseudocapacitors to achieve greater (10 -100 times) capacitances and energy densities than EDLCs. Pseudocapacitors store charge faradiacally through the transfer of charge between electrode and electrolyte. This is accomplished through electrosorption, reduction-oxidation reactions, and intercalation processes.

Pseudocapacitors involve redox-active electrode surfaces. The energy is stored in the pseudocapacitor in the form of a redox chemical reaction. The application of external potential facilitates the activation of the redox couple on the electrode surface during charge. During the discharge, this process is reversed, and the redox-active surface groups redirect to the original state.

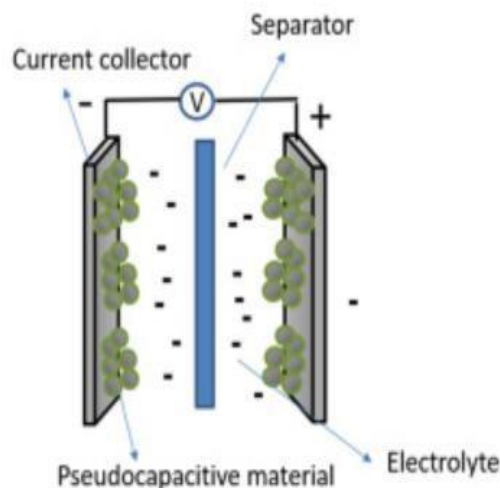


Figure 5: Pseudocapacitor

The electrolyte provides the internal ionic circuit for the redox reaction to occur. The energy stored in pseudocapacitors is attributed to the redox chemical reaction taking place at the electrode surface. Thus pseudocapacitors have a higher energy density compared to the EDLCs. The pseudocapacitive reaction can follow three mechanisms:

1. **Underpotential deposition:** This phenomenon occurs when ions deposit on the two dimensional (2D) metal electrolyte interface at potentials lower than their reversible reduction potential. The capacitance observed through this phenomenon is high ($\sim 2200 \mu\text{F cm}^{-2}$), but the potential window is tiny (0.3–0.6 V), and hence energy density is limited.
2. **Redox Pseudocapacitance:** This is the most common process observed in pseudocapacitors where faradaic reactions occur on the surface of the active material across which potential is being applied (e.g., metal oxides like RuO_2 , conductive polymers). This process can be described as reversible electrochemical adsorption. A capacitance of $\sim 5000 \text{ F cm}^{-3}$ can be achieved depending on the surface redox-active couple.

3. **Intercalation pseudo capacitance:** This occurs through the redox-active intercalation chemistry of electrode materials which has a faster time scale compared to the conventional battery-type intercalation chemistry (e.g., Nb_2O_5 , nanosized LTO, V_2O_5).

The intercalation chemistry is fundamentally similar to that of lithium-ion batteries. In this process, the contribution from surface redox pseudo capacitance and electrostatic pseudo capacitance is also observed in addition to the intercalation phenomenon. This involves a wider potential window, and hence higher energy density is achieved compared to EDLCs. The newly developed charge storage mechanism for intercalative pseudocapacitive behaviour.

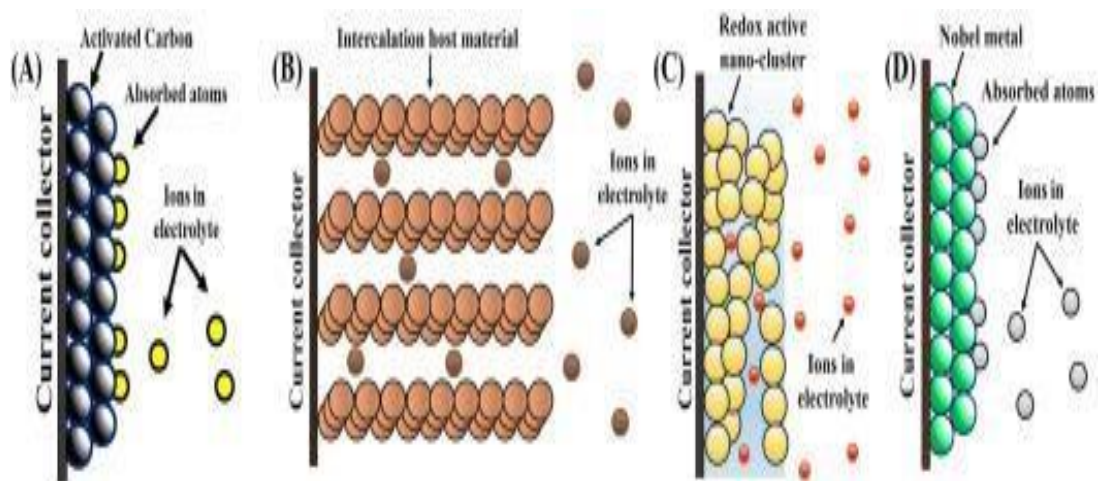
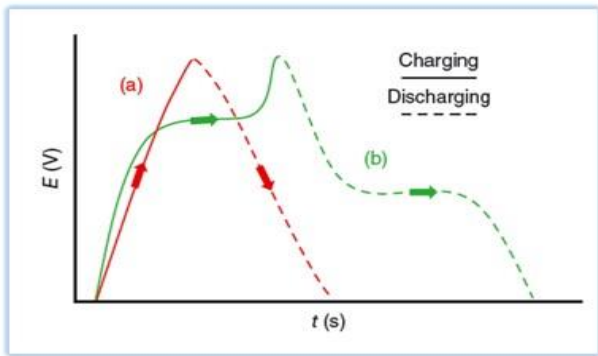


Figure 6: Reaction mechanism in Pseudocapacitor

Galvanostatic charge discharge



- a) Electrochemical Double Layer Capacitor.
b) Pseudo Capacitor.

Cyclic Voltammetry Curve

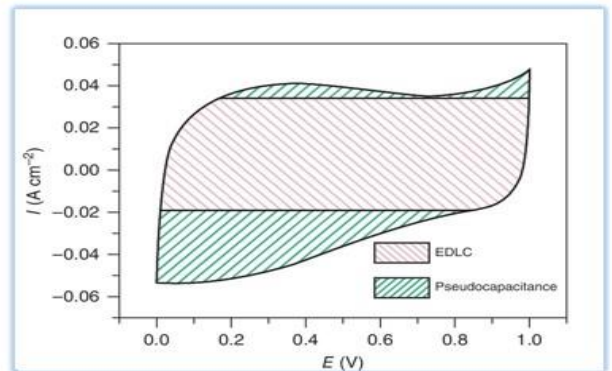


Figure 7: Galvanostatic charge discharge (GCD) and Cyclic Voltammetry (CV) curves of EDLC and Pseudocapacitor.

Literature Survey:

Parameters	EDLC	Pseudocapacitor	Hybrid Capacitor	Reference
Storage mechanism	Electrostatically	Electrochemically	Electrostatically and Electrochemically	R.S. Kate et al./ Journal of alloys and compounds 734 (2018) 89e11
Specific capacitance	Low	High	High	International journal of Hydrogen energy 34 (2009) 4889-4889
Energy density	Low	High	High	International journal of Hydrogen energy 34 (2009) 4889-4889
Power density	High	low	High	International journal of Hydrogen energy 34 (2009) 4889-4889

Electrode material	Activated carbons, carbon materials	Conductive polymers, metal oxides	Carbon based material + metal oxides/conductive polymers	Electrochemical Energy Reviews (2020) 3:155-186
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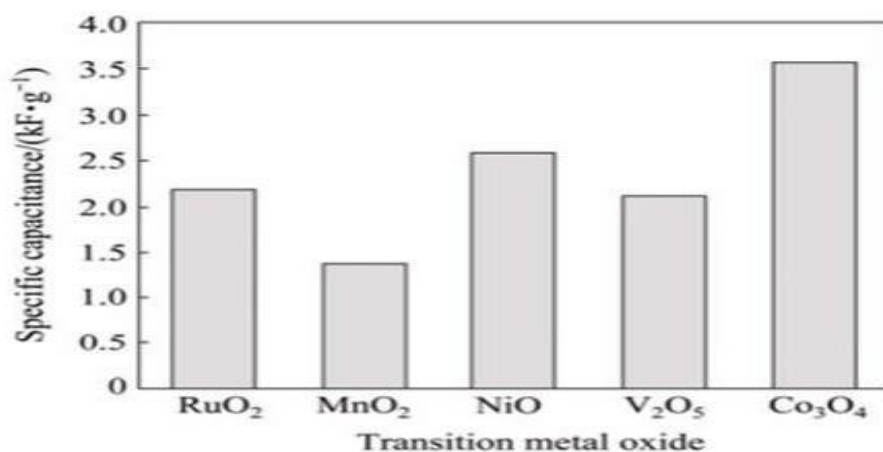


Figure 8: Specific Capacitance (Theoretical) of Transitional Metal oxides

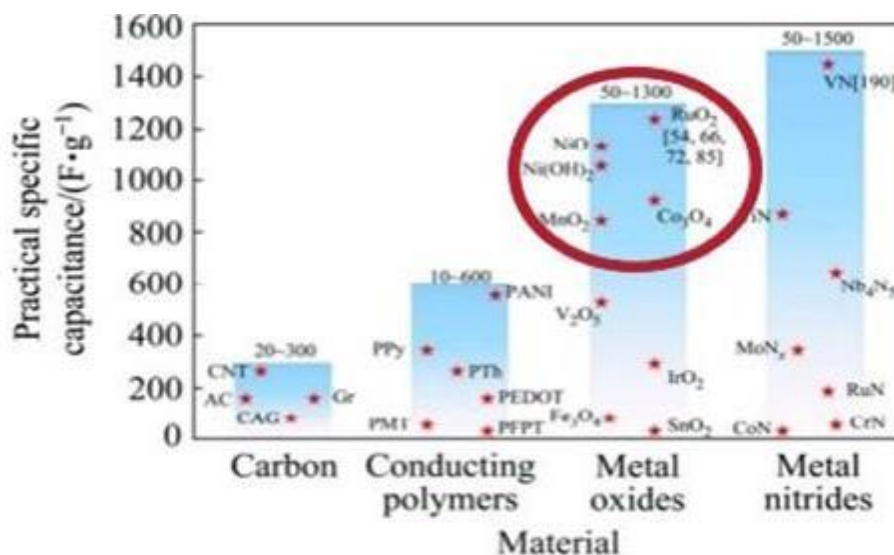


Figure 9: Specific Capacitance (Practical) of Transitional Metal oxides

The theoretical specific capacitances of transition metal oxides are 2200, 1370, 2584, 2120, 3560 F/g of RuO₂, MnO₂, NiO₂, V₂O₅, Co₃O₄ respectively. NiO exhibits high theoretical and practical values, surface properties, less toxicity, thermal and chemical stability various oxidation state for efficient charge transfer, excellent electrochemical properties, different nanostructured morphologies.

Synthesis of Nickel Oxide:

The nickel oxide has been synthesized using hydrothermal method by adding Ni(NO₃)₂·6H₂O and urea in 30 mL DI water and stirred it for 1 h, the Urea acts as binder to bind the particles of Nickel foam and in other beaker 30 mL of DI water and Glycine has been stirred for 30 min. The Glycine will control the structure. The composition of this precursor solution has been stirred for 2 h at 450 rpm.

The precursor solution transferred into teflon lined autoclave and nickel foam kept into that solution. The auto clave placed in oven for reaction at 130 °C for 12 h. After 12 h the nickel foam has taken out and kept in muffle furnace for calcination at 300 °C for 2 h. The reaching time is 1 h for muffle furnace for 300 °C, the OH bonds will break and nickel oxide is coated at nickel foam. After that the coated sample characterized with XRD, CV and FESEM.

Hydrothermal Method :

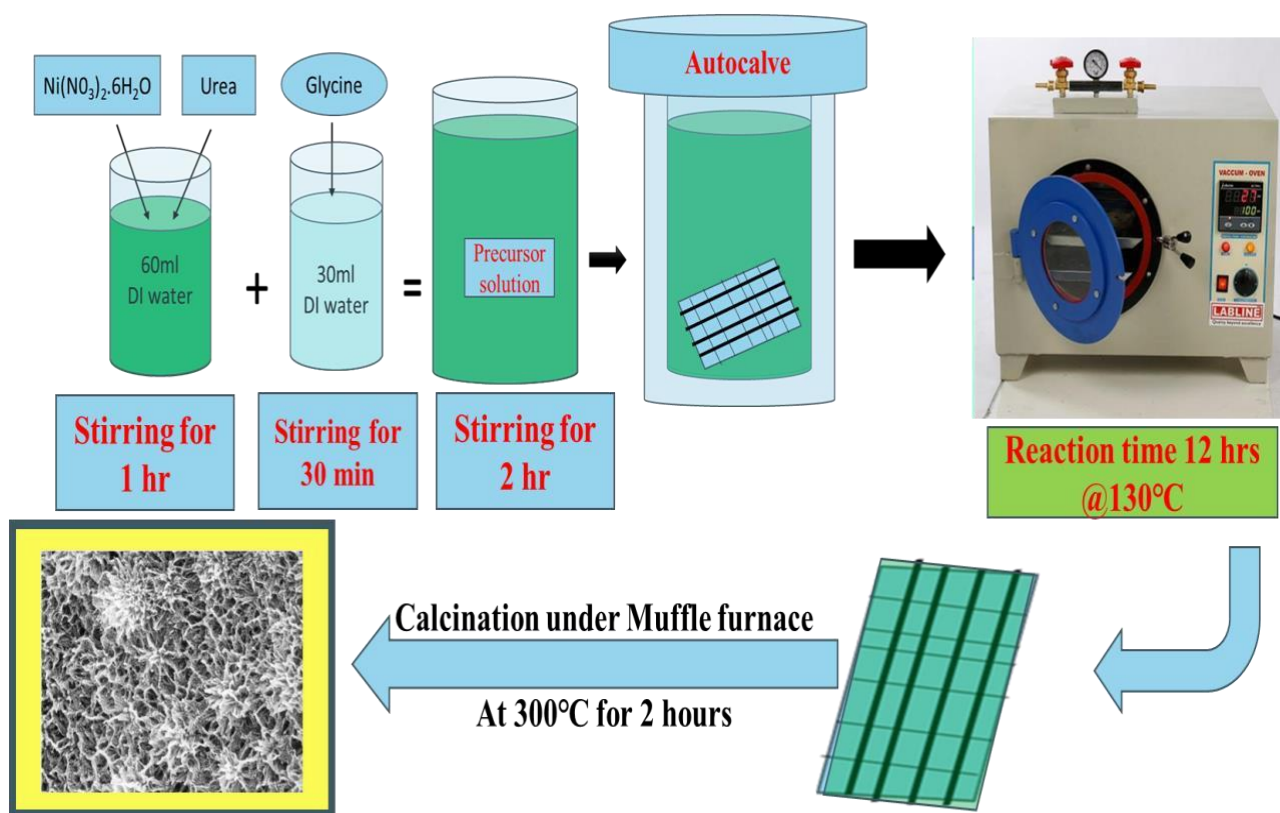


Figure 10: Hydrothermally Synthesized Nickel Oxide

Results and discussion:

1. X – Ray diffraction:

The growth orientation and crystal structure of hydrothermally synthesized NiO conformed by the XRD. Figure 11 exhibits the diffraction peaks 37.11° , 43.22° , 62.63° , 75.63° and 79.50° these are corresponded to the hkl planes (001), (200), (111), (021) and (002) and matched with JCPDS No (03-065- 6920). The highest intensity peaks are related to the nickel foam (NF).

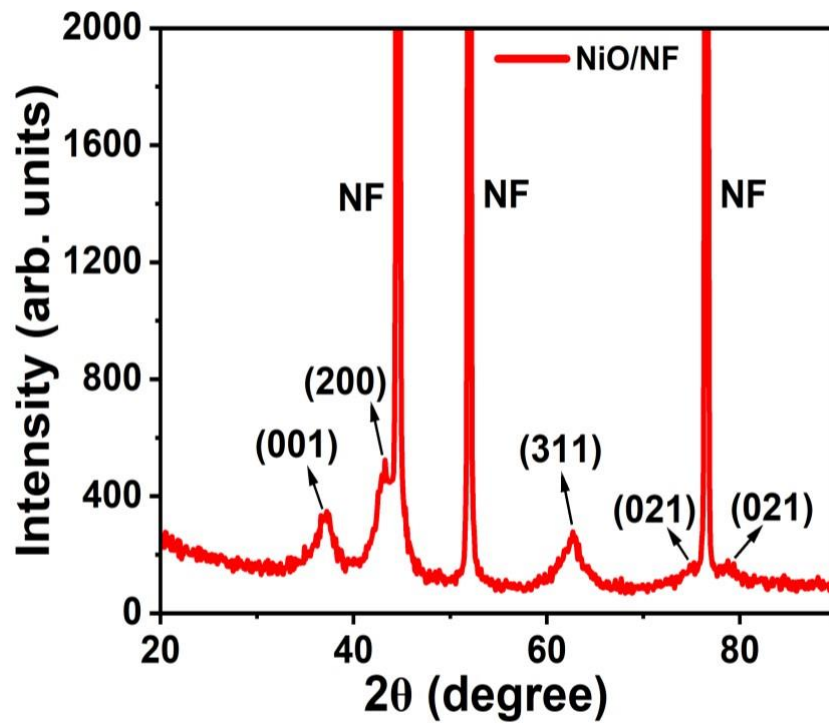


Figure 11: X – Ray Diffraction

2. Field Emission Scanning Electron Microscopy (FESEM):

The figure 12 shows the morphology of NiO using the FESEM. The FESEM of NiO exhibit the nanoflower like structure. This flower like structure act as ion diffusions paths during electrochemical reactions.

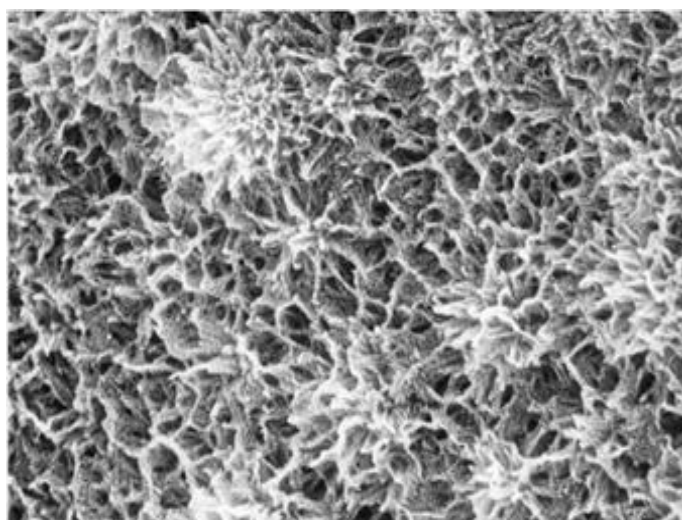


Figure 12: Nanoflower-like structure of NiO

3. Electrochemical Studies:

The electrochemical study is a three-electrode system, where we consider working electrode as NiO coated with nickel foam and counter and reference electrodes are silver and platinum electrodes. The graph of cyclic voltammetry curves (CV Curves) have been obtained at different scanning rates from 5 to 100 mV/s. CV curves as shown in figure 13 that the non rectangular shape, this is due to the Pseudo capacitive behaviour of the NiO electrode. When we are increasing scan rate from 5 mV/s to 100 mV/s area under the curve is increasing this is the capacitive nature of the electrode. Specific capacitance of synthesised NiO electrode is **1111 Fg⁻¹ at 5 mV/s**.

$$C_s = \frac{A}{m \cdot \nu \cdot \Delta V}$$

C_s – Specific Capacitance, A - Area under the curve, m – mass loading of the electrode, ν - scanning rate, ΔV - potential window.

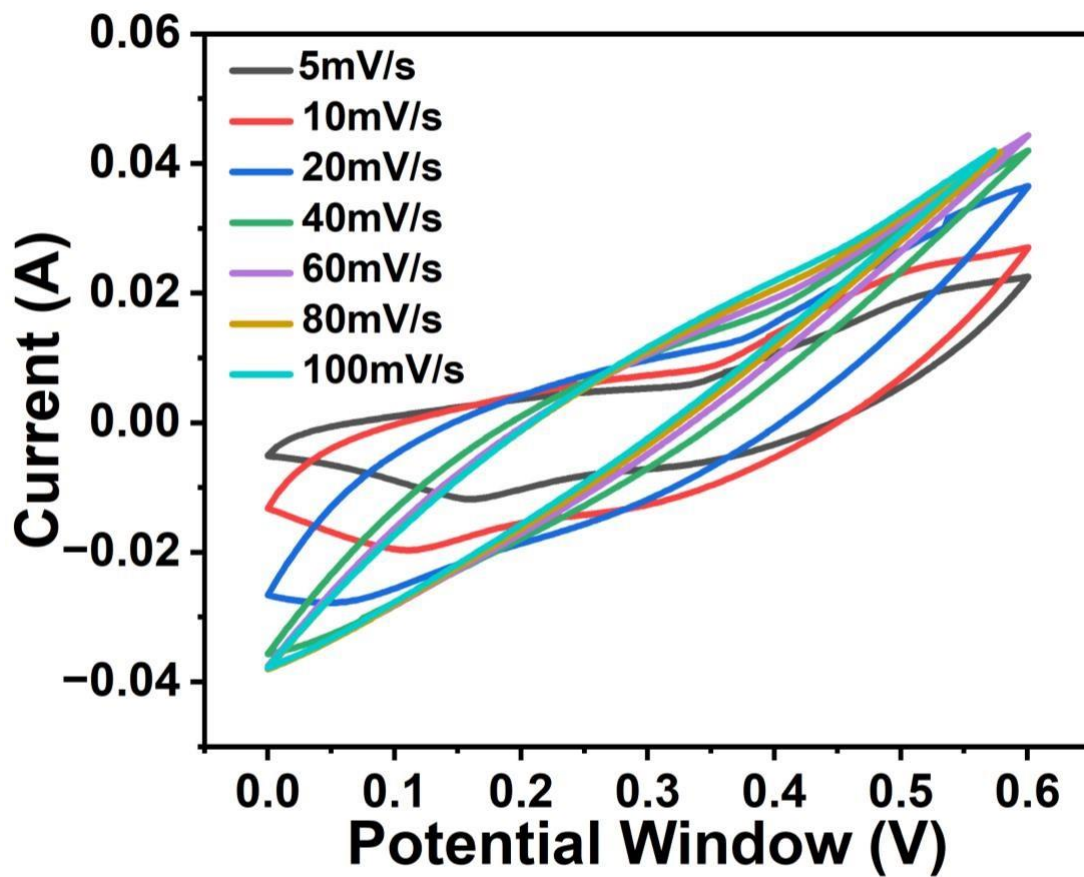


Figure 13: CV curves of NiO (scan rate from 5 to 100 mV/s)

Conclusion:

In Conclusion, the NiO nanoflower-like structure have grown on the nickel foam have been synthesized through hydrothermal method. The structure and morphology of the NiO was confirmed by using X-ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM). The FESEM shows the nanoflower-like morphology. The NiO electrode exhibits excellent electrochemical performance with a specific capacitance of 1111 F/g at 5 mV/s scan rate. The nanoflower like structure enhance the specific capacitance, this ascribed due to the huge surface to volume ratio. The hydrothermally prepared NiO electrode is beneficial for Supercapacitor applications.

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