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Engineering carbon and nitrogen intermingled three dimensional porous cobalt oxide polyhedrons/nanowires for energy storage

By

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The undersigned certify that they have read, and recommended to the Institute of Engineering for acceptance, a thesis entitled " Engineering carbon and nitrogen intermingled three dimensional porous cobalt oxide polyhedrons/nanowires for energy storage" submitted by Bishal G.C. , 074MSMSE018 in partial fulfillment of the requirements for the degree of Masters in Materials Science and Engineering.

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ABSTRACT

There is great demand in the development of efficient and economic energy storage devices to address the environmental and exhausting issues of fossil fuel. Supercapacitor, a promising energy storage technology for future generation, demands enormous improvement in its electrode such high specific surface area, high porosity, conductivity and proper architecture. Among various materials, cobalt oxide (Co_3O_4) has high capacitance but less stability and conductivity. Recently, metal-organic frameworks (MOFs) have been used to enhance the surface area and controllable porosity. However, there is still a challenge to design and synthesize assembly of nanostructure with proper architecture. Here, MOFs-based carbon and nitrogen intermingled highly porous three dimensional (3D) cobalt oxide polyhedrons have been assembled with their nanowires on nickel foam by a combination of hydrothermal, solution, carbonization and calcinations method. Here, MOFs ensured high surface area, high porosity and also contribute carbon and nitrogen required for enhancing conductivity of cobalt oxide. In this study, electrode material in a new architecture has been synthesized through the route of MOFs by simple laboratory methods. The materials have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), elemental mapping, energy dispersive spectroscopy (EDS). The electrochemical test shows the material is promising for its use as SCs electrode material.

Key words: Cobalt oxide, Metal-organic framework, Energy storage, Supercapacitor

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ABBREBIATION

SC	Supercapacitor
TMC	Transition Metal Compounds
CVD	Chemical Vapour Deposition
MOF	Metal Organic Framework
ZIF	Zeolitic Imidazolate Framework
NP	Nanoparticles
EDLC	Electrical Double Layer Capacitor
X-RD	X- Ray Diffraction
CHC	Cobalt Hydroxide Carbonate
EDS	Energy Dispersive Spectroscopy
LIB	Lithium ion Battery
CNT	Carbon Nanotube
SWNT	Single Walled Nanotube
MWNT	Multi Walled Nanotube
MEA	Membrane Electrode Assembly

HTC	Hydrothermal Carbonization
CV	Cyclic Voltammetry
GCD	Galvano Static Charge Discharge
MS	Metal Sulphide

CHAPTER ONE: INTRODUCTION

1.1 Background

Energy is necessary in everyday activities such as in IT and telecommunication, learning and in infrastructure development. It is essential for portable electronics, electrical vehicles as well as for life sustaining pacemaker (Haeberlin et al., 2014; Hasan, Mahmud, Ahasan Habib, Motakabber, & Islam, 2021). Fossil fuels such as coal and petroleum are primary sources of current energy sources. (Logan et al., 2020). But fossil fuels are limited and will exhaust soon. Moreover, they emit CO_2 which is responsible for global warming (Pasquini, 2022) (Florides & Christodoulides, 2009). For future use alternative, renewable and clean sources of energy has being developed such as bioenergy, hydrogen energy, solar energy , hydroelectricity and nuclear energy (Simanjuntak, Al-attab, Daryanto, Tambunan, & Sciences, 2022). Advantages of using renewable energies against the fossil fuel energies are low CO_2 production, low sulphur dioxide production and also renewable energy source reduces nitrogen oxide production. Along with these benefits renewable energies are economically feasible and are being run with the sources which are highly available in the nature (H.-r. Zhao, Guo, Fu, & Reviews, 2014). Energy obtained from renewable sources are intermittent and fluctuating. Mostly the energy is used in the residential, industrialization and urbanization purposes. According to (Nejat, Jomehzadeh, Taheri, Gohari, & Abd. Majid, 2015) top ten countries including India, US, Iran, Japan, Canada, UK, Germany, South Korea, Russia and China are responsible for two-third of the global CO_2 emission. Also residential area represents for the 27 % and 17 % of the global energy consumption and CO_2 emission respectively (Nejat et al., 2015). From industrial and urbanization point of view, as these two major developments increases the per capita and GDP of the country but this can only be achieved by exchanging the development with the available fossil fuels consumption (Sadorsky, 2014). (Gómez-Castro & Gutiérrez-Antonio, 2022) investigated that the increase in CO_2 emission was by 87 % from the year 1978 to 2018. Full dependence on fossils fuel is not a wise practice as the global distribution of these fuels depends on international trades laws along with many international diplomacy and the war existing in between big countries of fuel production (W. Zhong et al., 2017). The fossils fuels are deteriorating the environment thus, human civilization need to switch to the renewable energy source and we already discussed renewable energy sources are not available all the periods of time (Owusu & Asumadu-Sarkodie, 2016). Hence, energy has to be stored for its use when needed (Goodenough, 2015). Currently, two types of energy storage technology are in use mostly batteries and SCs (S. Liu, Wei, & Wang, 2020). Recently, the development of energy storage technique is being going on with proper recent and developments. Toward battery as energy storage device, Li ion battery has been proved as the most promising battery in comparison with the other conventional batteries. Li ion battery has light weight for the same power storage capacity than conventional batteries causing low cost in shipping and low space in installation (Xinghui Zhang, Li, Luo, Fan, & Du, 2022). It has high energy density. Hence, it is used mostly in the electric vehicles and solar photovoltaic energy harvesting (Trahey et al., 2020). According to certain scientific reports, the availability of fossil fuels (coal, oil) would persist for a maximum of 190 years and 290 years in the case of natural gases, respectively. Despite the fact that fossil fuels exist, renewable energy has only provided up to 16 % of the world's energy up until this point. However, the usage of renewable energy is rising steadily (Månberger, 2021).

Besides the advantages of the renewable energies there are some disadvantages as well. While fully depending on renewable resources that itself also depends on weather conditions makes long chain of dependency (Maradin, 2021). In case of no solar day, no wind day and also no tides day the electricity generation from their respective prime movers may become zero, in such cases renewable energy sources lack consumer/public interest. Efficiency of the renewable energy is less than that of the fossils fuel energy (Akram, Chen, Khalid, Huang, & Irfan, 2021). Data shows that the efficiency of solar cells is in between (15-20) % and the natural gas or coal efficiency reaches up to (40-60) % but with increase in efficiency the outcome of fossils fuel does emission of carbon and other greenhouse gases (Fathi, Ashena, Bahari, & Consumption, 2021). During harness of renewable energy the whole energy harness setup need to be large enough i.e the surface area/ renewable energy catchment areas must be large (Młyński, Operacz, & Wałęga, 2020). Without any subsidy from the government or public sector sides the initial cost of renewable energy source is high that cannot be affordable by the normal people of the related country ("What are the Pros and Cons of Renewable Energy," 2021).

1.2 Supercapacitor (SC)

A typical capacitor (originally known as condenser) is a passive two-terminal electrical component used to store energy in an electric field. SCs are such type of energy storing material which are broadly investigated nowadays in the world's research and development perspectives. SCs can replace the conventional capacitor and also the batteries as well, if a good SC with high energy density on addition to its high power density capability is investigated (Q. Lu et al., 2011). According to (Obreja, 2008) a EDLC SC has capacitance up to thousands farads in comparison to same size of conventional capacitor and also the specific energy of the market available SCs is from 5-6 Wh kg^{-1} while market available batteries have specific energy of lower limit from 35-40 Wh kg^{-1}. These energy storage system also will replace the fossil fuel consumption and can fully depend on renewable energy resources (Halper & Ellenbogen, 2006). Comparisons of various energy storages devices on the basis of power and energy densities can be understood by the figure 2. Here, SC has high power density among other storage devices like battery and fuel cells. But on the basis of energy density variations, SCs energy density is less than the other storage devices. Thus on the aspect of power density SC is superior but in energy density fields battery and fuel cell have high selections (Riaz, Sarker, Saad, & Mohamed, 2021). On basis of energy and power densities various energy storage devices are classified in figure 1.

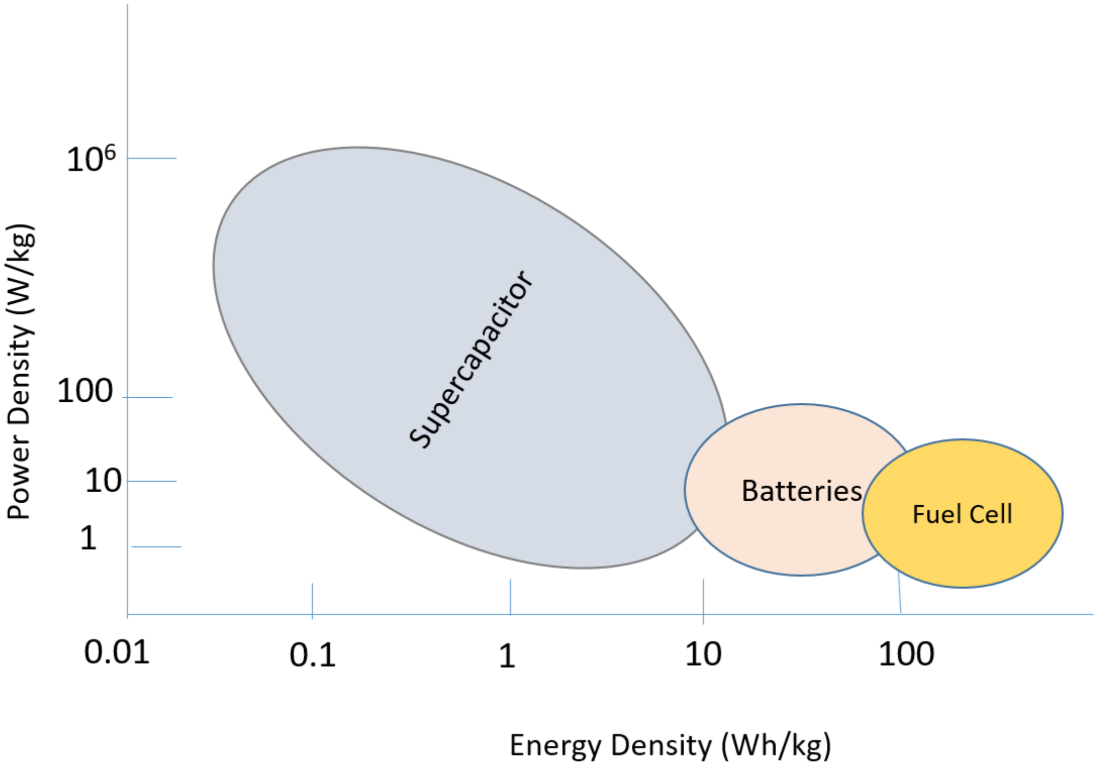


Figure 1 Comparison between different energy storage devices

SCs have energy densities greater than the conventional capacitors and the power density lower than the batteries (Halper & Ellenbogen, 2006). While comparing, a typical electrolytic capacitor will have a capacitance in the range of tens of milli farads. The same size super capacitor would have a capacitance of several farads, an improvement of about two or three orders of magnitude in capacitance but usually at a lower working voltage (Lokhande, Chavan, & Pandey, 2020). A general EDLC SC internal architecture is represented in figure 2.

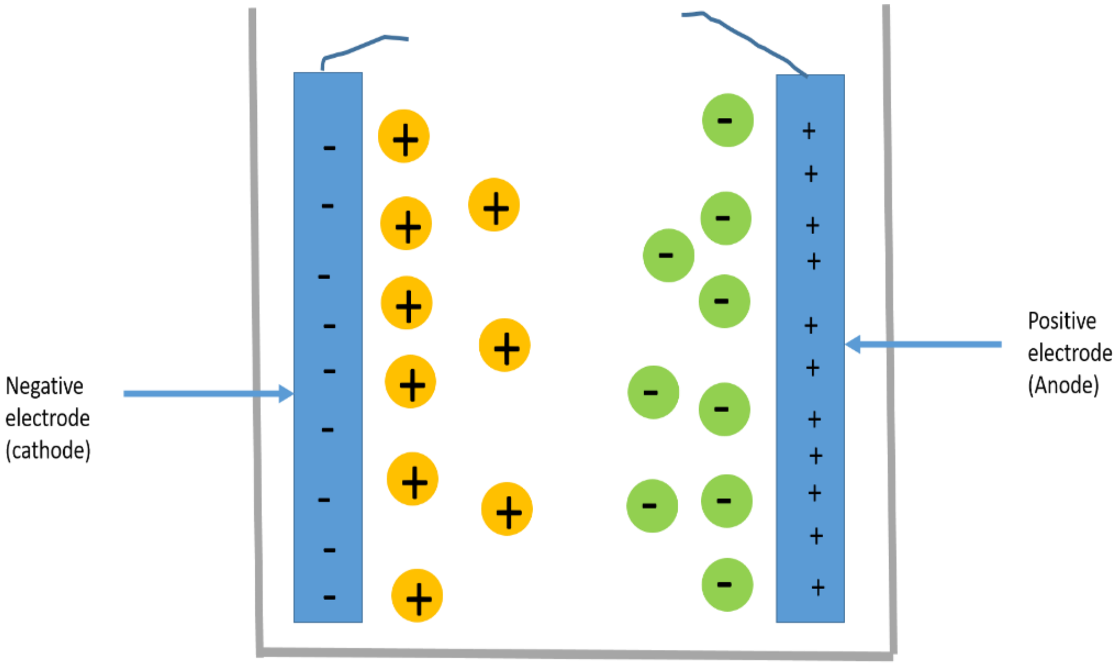


Figure 2 SCs internal schematic structure

Based upon the working parameters and internal reactions mechanisms, SCs can be divided into three types electrochemical double layer capacitors (EDLC), pseudo capacitors and hybrid capacitors. Faradic, non- faradic and combination of these two types of chemical reactions are the reactions that occurs internally in different types of SCs (Reece, Lekakou, Smith, & interfaces, 2020). In faradic process, oxidation and reduction reaction occurs where charge transfer in between electrode and electrolyte takes place. But no chemical reaction occurs in non faradic mechanism ie in EDLC SCs. In non faradic process only concentration of charges occurs physically near to the electrode where no chemical bonds get affected (Laheäär, Przygocki, Abbas, & Béguin, 2015).

SCs have attractive features such as fast charging, long life span and high power density(Wang, Wu, Han, & Li, 2021). However, low energy storing capacity per unit mass, volume and surface area is a major problem. Discovering a proper electrode material in proper architecture is a key issue for addressing this obstacle. Energy storing capacity of materials is proportional to its surface area, therefore, high specific surface area hence nano size is highly favorable to be a electrode material. Electrode requires high conductivity, high porosity and proper nanostructures. Electrodes transfer energy to and from the electrolyte through faradaic or non faradaic reaction to power the polarized device to which they connect (RICHARD, 2016). The materials studied for SCs electrode falls into carbon nanomaterials, transition metal compounds, conducting polymers and their nano composites (Najib & Erdem, 2019).

1.3 Materials used in SC electrode

1.3.1 Carbon Nanomaterials

Carbon based nanomaterials have been used as electrode materials for SCs. They include graphene carbon nanotube, carbon nanofibers, activated carbon, etc. (Azwar et al., 2018; Bokhari et al., 2020; Z. Yang et al., 2019). Carbon based materials have high chemical stability, very light, environmentally friendly, but the energy storage capacity is low (T. Chen & Dai, 2013). Carbon obtained from the organic wastes are taken to make activated carbon. The organic wastes like groundnut cells, coconut shells, walnut shells sugarcane bagasse etc. are taken and process until to get fine power. The fine powder are then taken for physical and chemical activation. Out of the many available reagents for chemical activation ($ZnCl_2$, H_3PO_4, $AlCl_3$, $MgCl_2$, KOH, NaOH, etc.), the most common chemical agents are $ZnCl_2$, H_3PO_4, and KOH, $ZnCl_2$ and H_3PO_4 act as dehydrating agents whereas KOH acts as an oxidant (Gao, Yue, Gao, & Li, 2020). Chemical activation has some benefits over the physical activation like i) it is usually carried out in a single step (lower time) ii) it has lower activation temperature iii) in chemical activation high level of carbon is produced iv) high surface area (up to 3600 m^2 g^{-1}) v) micro porosity is well developed with a well controlled distribution (Chikri, Elhadiri, Benchanaa, & El Maguana, 2020).

Given its high specific surface area, electrical conductivity, and chemical stability, carbon nanotube (CNT) SC electrodes have attracted a lot of attention in the last ten years (W. Lu & Dai, 2010). CNT-based electrodes can be further functionalized with substances like conducting polymers, metallophthalocyanines, or metal oxides (such as oxides of ruthenium, manganese, nickel, and zinc) that add a faradaic (charge transfer) component to the capacitor known as pseudocapacitance in addition to the electrochemical double-layer capacitance that CNTs provide. The performance characteristics of the electrode can be significantly enhanced with only a small amount of pseudocapacitive material (Fisher, Watt, & Jud Ready, 2013).

The first CNT material type that was explored for SC applications was randomly entangled CNTs because of its relatively simple production. CNTs have a moderate specific surface area when compared to activated carbons with a high surface area (Dai, 2010). It is found that higher capacitance has been demonstrated for CNTs, such as in study of Multi walled nano tubes (MWNTs), it has capacitance of 102 F g^{-1} (Niu, Sichel, Hoch, Moy, & Tennent, 1997) and in single walled nano tubes (SWNTs) it shows capacitance of 180 F g^{-1} (An et al., 2001) but while comparing with activated carbon, activated carbon has capacitance of only tens of F g^{-1}. It is generally acknowledged that CNTs have a special mesoporosity (the existence of a large population of mesopores) caused by tube entanglement, which leads to high electrolyte accessibility and high capacitance. Activated carbons have less mesoporosity than the carbon nanotubes which is also a strong reason behind having less capacitance than CNTs. As CNTs have high capacitance so these are used for making the SC's electrode. A SC electrode developed from a SWNT and KOH electrolyte shows a good power density of 20 kw kg^{-1} and energy density of 10 Wh kg^{-1} (An et al., 2001).

Another carbon nanomaterial- graphene is also been used for the preparation of electrode of SCs. Graphene is the monolayer of graphite and the graphene oxide is the multilayer of graphite that can be prepared through various techniques. Graphene shows high electrical conductivity, good chemical stability, tunable surface area and good mechanical strength; these all characteristics are best for the electrode's working purposes (Q. Ke & Wang, 2016). Research into graphene-based materials as a conducting network to enable the redox processes of transition metal oxides, hydroxides, and conducting polymers has been widespread. Because of the synergistic effect, these nanohybrid electrodes made of graphene and nanoparticles of transition metal oxides or hydroxides or conductive polymers result in effective electrochemical performance. Graphene layers help metal oxide or hydroxide nanoparticles evenly distribute and represent as a highly conductive matrix to increase electrical conductivity. Metal oxide or hydroxide or conducting polymers provide the desired pseudocapacitance (Q. Ke & Wang, 2016).

1.3.2 Conducting polymers

SC can be divided into two categories on the basis of charging of discharging mechanism, first type is electric double layer stage capacitor which is based primarily on high surface area carbon material, that uses electrodes/electrolytes to separate charges to produce capacitor. Second type is pseudo-capacitance, which is mainly composed of transition metal oxide and conductive polymer and it is generated by rapid reversible REDOX reaction on the surface of electrode (D Y Su, 2019).

Conducting polymer has several tunable characteristics for energy conversion and energy storage. Using conducting polymer efficient, reliable, low cost, conducting, stable and environment friendly energy system have been developed. Design, structure, composition and fabrication technique used for conducting polymer need to be focused to increase the commercialization and efficiency of SC/energy storage medium. Except in the SC, conducting polymer are also used in electrochemical devices like battery and fuel cells (Kausar, 2017).

Conducting polymer has drawn attention due to their useful mechanical, optical and electronic properties. They are used in electrostatic material, conducting adhesives, electromagnetic shielding against electromagnetic interference (EMI), artificial nerves, aircraft structures, diodes and transistors (Das & Prusty, 2012).

Conductive polymer is used as the electrode of SC. Due to the different doping forms of conducting polymers and different kinds of doped conducting polymers capacitor, SCs electrode can be made for different chemical, electrical and mechanical priorities. As shown in figure below, there are different types of conducting polymer SCs. First one of type I is composed of completely identical p type doped conductive polymer. The charge quantity released by this type I conductive polymer electrode is ½ and the difference of potential difference in between two poles is small. Similarly, the second type II conductive polymer which is made from different types of conductive polymers are doped with p type doping in both. Due to this different types of conductive polymer electrodes, the potential range of dopings are different so that the capacitor can have the higher voltage difference in the fully charged state. It has found that this type II kind of SC is not good enough to distinguish between the positive and negative and the capacitor cannot be reverse charge which then limits its application and shows impact on the life cycle of capacitors.

The last type III is composed of an n type doped electrode and a doped p type. In the fully charged state, the cathode of the capacitor is in completely n doped state while the positive electrode is in a fully p doped state, increase the voltage difference between the two electrodes. The main advantage of such a capacitor structure is the capacitive voltage is higher, charge release completely and charging two electrodes were incorporated, charge storage capacity. In addition, electron material holds high conductivity, small internal resistance of the capacitor and output power of large due to the two electrodes simultaneous doping.

In summary we can understand that with their quick doping and doping capabilities, charge-discharge kinetics, tunable morphological features, good mechanical strength, large specific capacitance, ease of fabrication and environment friendliness conducting polymers have been examined as one of the most favorable electrode materials (Dědek et al., 2022). Together, these features make conduction polymers an good electrode material (Kar, 2020). For the most part, polyaniline, polypyrrole, and polythiophene are used as electrode materials. Along with this, hybridization of conducting polymer with the MOFs give a new perspective to increase the electrochemical characteristic of the formed electrode (Dědek et al., 2022).

1.3.3 Transition metal compounds

Pseudocapacitor, a variety of SC, uses the transition metal compounds (TMCs) as the electrode material. In pseudocapacitors faradaic reactions take place where the electrons are adsorbed at or near the surface of the electrode through the electrolytes. Just like in a battery rapid and reversible faraday reactions take place in pseudo capacitor (R. Liu et al., 2021). The electrode, for undergoing these reactions, are made up of transition metal compounds and conductive polymers. During the intercalation pseudo capacitance involves the insertion of electrolyte ions into the voids or layers in active electrode materials along with a charge transfer process(R. Liu et al., 2021). Pseudocapacitive materials (TMC) like Nb_2O_5, MoO_3, TiO_2, WO_3, V_2O_5 etc. are capable of storing charge by pseudocapacitance so these materials can be used/fabricated as the electrode of pseudocapacitor (R. Liu et al., 2021). Because of their reported beneficial mechanical, structural or electronic properties as well as the high pseudocapacitances. Leading to the contribution of their multiple valence state changes, which are usually impossible with carbon materials, transition metal oxides are of great interest in the field of energy storage or conversion. Generally, transition metal oxides can be divided into two types as base transition metal oxide and noble metal oxides. Noble metal oxides includes RuO_2, IrO_2, etc. while base transition metal oxides for SCs are developing from monometallic oxides (like, NiO, CO_3O_4, Fe_3O_4 and Mn_3O_4) to single phase bimetallic oxides (like $NiCO_2O_4$, $MnCO_2O_4$, $NiMoO_4$, $NiFe_2O_4$, $CoMn_2O_4$)(Cui & Meng, 2020).

Out of other transition metal oxides, CO_3O_4 has excellent reversible redox behavior, high conductivity and good stability for SCs. CO_3O_4 nanostructures have been produced using a variety of methods, with morphologies varying from one to three dimensions. These approaches typically include two steps: precursor formation and calcination. A significant amount of effort has been put into the improvement of electrochemical performance of CO_3O_4 by constructing various morphologies and combining with other materials (Wu, Zhu, Ji, & Banks, 2016).

Its unique porous structure and hollow structure are what give it the better capacitive performance, which could speed ion and electron mobility, adequate strain tolerance and big surface area for reactions (Ma et al., 2021).

Besides the transition metal compounds (TMCs), metal sulfides are also used as the electrode material of the SC. Generally, there are two types of metal sulfides- layered metal sulfides and non-layered metal sulfides. Layered metal sulfides like MoS_2, WS_2, SnS_2, VS_2 and so on are arranged of three atom layer (S-M-S) connected by covalent bonds where the individual layers are held together through Van der Waals forces, whereas non layered MSs such as FeS_2, NiS_2, CoS_2, MnS and others have attracted researchers owing to their availability, low cost, eco friendliness and high theoretical capacity (Salele Iro, 2016). Due to the presence of sulphur, which makes it easier for electrons to transport, metal sulphides (MSs) or mixed MSs that are produced in redox reactions are known to have better electrical conductivity and flexibility than other frequently used materials like MOs and carbon materials (Barik & Ingole, 2020).

N-type semiconductors, which have both metalloid properties and good electric conductivity, are known to contain a number of metal phosphides (MPs). Moreover, they have a great abundance and an environmentally friendly nature. Therefore, a few of these metal phosphides make good candidates for use as electrode materials. They are kinetically more advantageous than transition metal oxides or hydroxides for the quick electron transport needed for high power density (Xin Li, Elshahawy, Guan, & Wang, 2017). Theoretically, transition metal phosphides, including those made of nickel and cobalt, have a significant energy storage capacity due to their strong redox activity and ideal electrical conductivity. They are abundant naturally and environmentally favorable. As a result, they attracted a lot of attention as a group of pseudocapacitive materials. Aluminium phosphide, Potassium phosphide sodium phosphide, zinc phosphide, calcium phosphide, magnesium phosphide, strontium phosphide, magnesium aluminium phosphide etc are some transition metal phosphides which are being studied for electrode material (Pu et al., 2020).

1.3.4 Nanocomposites

It is always important to keep in mind that the electrodes material and its contents elements are selected depending upon the electrical conductivity, stability, multiple oxidation number, high surface area and porosity and also superior electrochemical activity. Added advantage by using nanocomposites for SCs electrode is nanocomposite gives high specific surface area, shorter ion/electron diffusion paths eventually improving the specific capacitance of SCs (Ghuman, 2020). The nanocomposites offer larger SSA, shorter ion/electron diffusion paths, thus improving the specific capacitance of SCs.

Nanocomposites are materials which consist of distinct part of different materials in nanoscale level. So different materials composite will improve the mechanical properties like strength, flexural strength, hardness and toughness, thermal stability, elongation and stiffness as per the requirement in the final developed material. This, then formed composite will have reduced weight and the composite will be usable for various application. For easy understanding, nano-composites are materials with one bulk phase and other small nanoscale particles distributed in that bulk phase, which are utilized to enhance the bulk phase's characteristics (Ghuman, 2020). By controlling the nanoparticles we can control various parameters of the materials like its physical, mechanical, chemical, biological, melting temperature, thermal stability, magnetic and chemical properties including others qualities like, color, electronic and electrical characteristics, optical characteristics, charge capacity, superconducting qualities, thermal conductivity, corrosion avoidance quality, heat resistance roughness, gas barrier properties, catalytic properties, and refractive index etc (Ghuman, 2020). Nanocomposites are generally, superior to their individual materials, due to synergistic effect. Hence many nanocomposites have been studied for SC electrode materials (Idumah & Materials, 2022). Nanocomposites are generally prepared by mixing different materials by different methods. Composites of transition metal compounds with carbon nanomaterials have soon promising results for SCs. In such composites carbon materials contributes conductivity and transition metal compounds contributes high capacitance. Presence of carbonaceous compounds in pseudocapacitive material the specific surface area of thus formed nanocomposite increases which increases the capacitance of the nanocomposite. Various forms of nanocomposite are developed for the SCs electrodes like carbon-carbon composites, carbon- metal oxides composites, carbon-conducting polymer composites and MOs-conducting polymer composites. The specific capacitance of such categories of electrodes is found higher than individual carbon, conducting polymers, metal oxides electrodes etc (Ghuman, 2020; Vangari, Pryor, & Jiang, 2013).

1.3.5 Metal-organic framework (MOFs)

Metal-organic frameworks (MOFs) are one of the most advanced crystal materials assembled by organic ligands as linkers and metal ions as center ions, which can be used as excellent materials for batteries and SCs due to their high adjustable pore sizes, controllable structures, and specific surface areas.

Metal-organic framework, abbreviated to MOF, is a coordination polymer (or alternatively Coordination Network) with an open framework containing potential voids. MOFs are self- assembled metal clusters with organic ligands, are well known for their structure, permanent porosity, and tunable properties and have shown great prospect for various applications ("Introduction to Metal–Organic Frameworks," 2012).

Metal ions + Organic units → Coordination Polymers or
(linkers/bridging ligands) MOF materials

MOFs are structures made up of inorganic nodes, which can either be single ions or clusters of ions and organic linkers. They contain potential voids which can be used for various application.

Some features of MOFs are they have very low density and large voids, they are crystalline with significant Van Der Waals interaction and complex unit cell. Many potential applications of MOFs depend on the size and nature of the available free volume or pores within the frameworks structure. Tuning of the pores is typically achieved by variation of the metal ions or organic ligands. Also lengthening the organic chains can lead to increased pore size but is often limited by a decrease in stability of the framework (Ahmadi et al., 2021). MOF's surface area normally ranges from 1000 to 10,000 m^2/g and pore size can be adjusted as large as 9.8 nm by changing the organic and metal containing unit. The organic units are divalent or polyvalent organic carboxylates, which when linking to metal containing units (like Mg^{2+}, Co^{2+}, Al^{3+}, Ni^{2+}) can form 3D structures with notable pore size distributions (Y. Zhao et al., 2016a). The mostly used method for the synthesis of MOFs are hydrothermal and solvothermal processes (Y. Zhao et al., 2016b).

With no gas present, the thermal conductivity decreases with increasing pore size. In the presence of adsorbed gas, MOFs with smaller pores experience reduced thermal conductivity due to phonon scattering introduced by gas-crystal interactions. For larger pores (>1.7nm), the adsorbed gas does not significantly affect thermal conductivity. This difference is due to the decreased probability of gas-crystal collisions in larger pore structures (CHAKRABARTY, 2017).

Due to its distinctive characteristics, including high porosity, nanoscale periodicity, vast surface areas, and structural variety, MOFs have attracted a great deal of interest. Low electrical conductivity is a major drawback of MOFs for energy storage applications. Increase the specific capacitance and overall performance of electrode materials by combining MOFs with other (nano) materials is being carried out more (Shah, Tsapatsis, & Siepmann, 2017). MOFs has its demonstrated history in the field of general electro catalysis, fuel cells and batteries (Vaitsis et al., 2022). MOFs have low conductivity, in order to increase its conductivity MOFs have been entangled with other materials just to increase the charge transfers, they entangled with metal oxides, sulfides and phosphides. And these entangled material (metal oxides, sulfides and phosphides) are got in porous and high conductive form by calcination or pyrolysis of the MOFs (Vaitsis et al., 2022).

In current scenario many toxic organic pollutants like textile dyes, pharmaceutical contaminants and antibiotics into the water systems and also the emission of the greenhouse gases (CO_2, CH_4) has created many problems. Using sunlight through the photocatalytic techniques these aforesaid problems can be reduced (Hussain et al., 2021). MOFs have found its wide and very important application in the photo catalysis as well (Y. Chen, Wang, Deng, Li, & Technology, 2017). Under the presence of UV rays, MOF is investigated to complete photo catalyst process producing H_2 gas from the water (Shi, Yang, Cao, & Zhao, 2019).

In the mechanism of the photo catalysis, semiconductor (MOFs) mechanism is taken as the catalyst. When the UV or visible light strike on the semiconductor then it produces the photo generated electron. This generated electron is transferred to the conduction band (CB) leaving behind hole in the valence band (VB). Protons of H_2O accept the photo generated electron and then H_2 gas is formed. Also the combination of holes with H_2O molecules forms the oxygen. This mechanism needs a theoretical bandgap energy of 1.23eV (Shi et al., 2019). Photo catalysis equation of hydrogen generation can be clearly understood through these below three equations (Tasleem, Tahir, & Khalifa, 2021).

Transition metal oxide usage Nickel and cobalt-based MOF has discovered that their research into photocatalytic H_2 production is limited because the donor atoms of the linker occupy the active sites in the structure of MOF (Liao, Matsagar, & Wu, 2018). Cobalt is easily available so the use of costly and rarely available materials like Gold (Au), Ruthenium (Ru) and Palladium (Pd) can be replace by Cobalt TMC (Ning et al., 2017). Cobalt based MOF i.e. ZIF-67 is used for the H_2 extraction via photocatalytic effect.

The use of a photosensitizer RuN_3 led to an 86.9 % efficient transport of electrons from excited RuN_3 to ZIF-67. Moreover, due to effective energy transfer from RuN_3, this RuN_3/ZIF-67 hybrid system demonstrated significantly increased photocatalytic activity for the creation of H_2 from H_2O (S. Yang, Pattengale, Kovrigin, & Huang, 2017).

Due to their high porosity, surface area and good structure controllability MOF's have high preference to produce nanomaterials like porous carbon and metal oxide. These produced nanomaterials are widely used in energy storage applications in fuel cells, SCs and batteries (lithium ion, lithium sulfur, lithium air batteries) (Y. Zhao et al., 2016a). Besides the pure MOFs, derivative of MOFs like porous carbon and nanostructured metal oxide also shows good performance in energy storage and in energy conversion (Xu Zhang et al., 2019a).

A fuel cell is an electrochemical conversion device that runs continuously on an oxidant like oxygen, air or hydrogen peroxide as well as a fuel like hydrogen, natural gas, or methanol. An anode, a cathode, and an electrolyte make up each fuel cell which enable ions to travel between the fuel cell's two sides (Laberty-Robert, Vallé, Pereira, & Sanchez, 2011). Fuel cell also produces electrical energy from the electrochemical oxidation of hydrogen. It is constructed as a stack of identical repeating unit cells with a membrane electrode assembly (MEA) that reduces oxygen gas (O_2) on the MEA cathode and oxidizes hydrogen gas (H_2) on the anode, are pressurized by bi-polar plates that supply the MEA with gaseous reactants and coolants while pulling current from it. Each MEA electrode is linked to a solid polymer ion exchange membrane that transports protons but not electrons, where the electrochemical process occurs. On the surfaces of platinum (Pt)-based catalysts, the cathode oxygen reduction reaction (ORR) and the anode hydrogen oxidation reaction both occur. Pure water and heat are the byproducts (Y. Zhao et al., 2016a).

Fuel cells have zero carbon emissions so they are mostly used in transportation, mostly in buses. Along with this fuel cells are used for backup power supply in residential areas and also in the place where combined heat and power generation are required. Fuel cells are also been used in the portable power source (Abdelkareem et al., 2021).

The desired MOFs product can be developed with rich metal such as transition metal: (Co, Fe, Cu...), nitrogen and carbon sites by carefully selecting metal groups and multi-functional linkers and that would be beneficial for developing high-quality electrochemical catalysts (Y. Zhao et al., 2016a). Cu based MOFs, Fe based MOFs as well as MOF based graphene composite are promising catalyst for fuel cells with high chemical stability, good catalytic activity and methanol tolerance. Hence, for the fuel cells using MOFs as the precursor for preparation of electro catalyst, metal/metal oxide/nitrogen/carbon hybrids with good catalytic activity can be easily achieved. In summary we can say that best selection of metal clusters and multi-functional linkers, desired MOFs product can be developed with higher transition metal-nitrogen-carbon sites which will be best applicable for fabrication of good electrochemical catalysts (Y. Zhao et al., 2016a).

Like in SCs porous materials are widely used in Lithium ion batteries as well as they have large internal surface area of 100 to 1000 m^2 g^{-1} along with high porosity that favors in the electrochemical reaction and interfacial charge transport (F.-S. Ke, Wu, & Deng, 2015). Reason behind using MOFs are MOFs are porous crystalline materials with high surface are of up to 7000 m^2 g^{-1} **,** low density and controllable structure**.** The anode and cathode of Lithium ion battery (LIB) are found that they have low energy density and poor rate performance than expectations. However the SCs have high rate of performance but the energy density is still lower than the LIBs (F.-S. Ke et al., 2015). To overcome this disadvantages batteries are provided with new technique through using MOFs in electrode material synthesis or for better electrochemical reactions. Generally, LIBs are based on two redox reactions at the anode and cathode. While charging lithium ions move from cathode ($LiCoO_2$) to anode (graphite) via electrolyte ($LiPF_6$ in organic solvents) (Li Zhang, Wang, Chen, Wang, & Su, 2018).

While the designable components promise the incorporation of electroactive sites, setting new endless possibilities for the search of suitable candidate electrode materials for various battery systems, MOFs' intrinsically porous structure offers convenient electrolyte penetration and ion transportation. However, many MOFs have irreversible structural damage following the charge/discharge operations, weak electrical conductivity, and low tap density, which may limit their practical application (Xinlin Li, Yu, Gosztola, Fry, & Deria, 2019).

1.4 Hydrothermal process

Hydrothermal process is used to synthesize the nanostructures under high pressure and temperature from the aqueous solution. This process is bottom-up process in which the nano- crystal is formed by the combination of molecule by molecule or atom by atom (Xia, 2004). Autoclave material is inert and withstand high temperatures and pressures for prolonged periods of time. A temperature gradient is maintained between the opposite ends of the chamber. At the hotter end the nutrient solute dissolves, while at the cooler end it is deposited on a seed crystal, growing the desired crystal. Advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can be grown by the hydrothermal method (Gan, 2022).

1.5 Carbonization

By pyrolysing organic material, typically in an inert atmosphere, solid residues with an increasing concentration of the element carbon are created by the process of carbonization (Marsh & Rodríguez-Reinoso, 2006). Without reacting with oxygen or any other oxidants, pyrolysis is the heat breakdown of a solid (or a liquid) into smaller volatile molecules (Stauffer, Dolan, & Newman, 2008). Generally, carbonization under pressure is divided into three types, i) carbonization under pressure built up by the gases of precursor ii) carbonization under hydrothermal conditions and iii) reduction of CO_2 under pressure (Inagaki, Kang, Toyoda, & Konno, 2014). In our study we have used hydrothermal process for the carbonization.

It is possible to pretreat biomass with a high moisture content using a thermochemical method called hydrothermal carbonization, which can be used for a variety of tasks. It takes place for 5 to 240 minutes in a closed reactor with a temperature range of 180-280 °C and a pressure range of 2-6 MPa. Aqueous phases (rich in nutrients) and gas phases (mostly CO_2) are also produced as byproducts of hydrothermal carbonization in addition to the coal-like substance known as hydro char. This solid product has a higher energy density and can either be burned to produce energy or dumped as fertilizer to feed the soil. The feedstock and processing conditions have an impact on how these products are distributed. The essential steps in this process' mechanism are polymerization, dehydration, and decarboxylation (Funke and Ziegler, 2010). The wet biomass's high water content makes it a great solvent and reaction medium. Because its ionic product is maximum at temperatures between 200 °C and 280 °C, water can function as both a base and an acid. Additionally, water behaves more like a nonpolar solvent at these temperatures due to a reduction in its dielectric constant (Yoganandham, Sathyamoorthy, & Renuka, 2020). The benefit of hydrothermal carbonization is that biomass can be converted to carbonaceous solids without using an energy-intensive drying process. Compared to the beginning material, the energy-dense hydro char has a higher energy-to-weight ratio. Toxic chemical compounds and lingering micro pollutants are also broken down during the hydrothermal carbonization phase (Weiner et al., 2013).

1.6 Problem Statement

SCs are the energy storage devices that works with both characteristics of a capacitor and a battery as a whole we can say that it acts as the bridge in between the capacitor and battery functioning. SCs can store more energy than a normal capacitor and also supply the energy at higher power rates than batteries. SCs are used as primary power supply energy device with other batteries to provide high power at starting of traction motors, escalators, elevators and vehicles where high torque and high power is used at starting. In order to increase the performance of SCs, their electrodes must be of large surface area and high conductivity. Normally, in market available SCs, their electrodes are made up of highly porous activated carbon (Fierro, 2020).

To increase the efficiency of SC new materials have been searched, so that we can make the electrode of this found material. In our study we have used cobalt oxide intermingled with nitrogen doped carbon as the main material of the electrode. This will study on a different way about the porosity, conductivity, size and structure of the electrode. For fast charging and fast discharging the use of SC is always in first choice. However, these sudden supply and cut off of power will highly power on the equipment on short time but cannot sustain the continuous supply. In traction, automotive and hybrid buses, in order to ignite the high power engine or to start the electric system with high power spikes SC has required best characteristic (Naseri, Farjah, & Ghanbari, 2016). But to run the system/equipment in continuous flow, power is needed most. To overcome this short time power supplies, energy density of the super capacitor need to increase without effecting its power density (Habibzadeh, Hassanalieragh, Soyata, & Sharma, 2017).

To overcome with this process nitrogen doped carbon nanostructure is used with the Cobalt oxide to increase the capacitance, chemical stability and conductivity. After carrying on this process, the nano sponges and hollow voids (after getting MOFs) increases the energy storage capability. Hereinafter the problem of fast discharging will solved out to some extent (Ban et al., 2013).

1.7 Research objectives

General objective

The general objective is to synthesize cobalt oxide/carbon nanocomposite and to study its electrochemical performance for SCs.

Specific objectives

i) To synthesize cobalt hydroxide carbonate (CHC) nanostructures on nickel foam by hydrothermal process

ii) To convert cobalt hydroxide nanostructure into its MOF by solution treatment under different conditions.

iii) To carbonize the resulting nanostructures then calcinations to get Co_3O_4 nanostructures

iv) To characterize the material obtained in X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDS)

v) To test the electrochemical performance of samples

1.8 Rationale

The main purpose of this study has been to carry out the synthesis of electrode made up of cobalt oxide intermingled with nitrogen doped carbon sponges. The study of this kind of electrode will increase the charge adsorption capability of the electrode and also increases the energy density of the electrode. Cobalt oxide with carbon sponge will increase the surface area at the nanoscales making the material more porous so can adsorb more chemical energy from the used electrolyte. And also can supply/discharge the energy for more useful time.

1.9 Scope of this work

This study is mainly focused on the synthesis and development of the cobalt oxide electrode with nitrogen doped carbon sponges on it. Use of renewable energy is on most priority in the recent world’s scenario, in this context the SCs with high energy storage capacity has high scope in energy storage developments.

1.10 Limitation

Our study will only be based on the only one plate electrode of the SC, the electrolytes and their chemical reactions and results will not be encountered in our study works. Also the obtained chemical, physical, mechanical, electrical and optical characteristics of the obtained electrode may not be an ideal one. It is the practical study the result may be different than other’s studies till the end date of our study. Also the study on separator and dielectrics of the SC will be beyond our study.

CHAPTER TWO: LITERATURE REVIEW

2.1 Research gaps and literature review

The first SC based on a double layer mechanism was developed in 1957 by General Electric using a porous carbon electrode. It was believed that the energy was stored in the carbon pores and it exhibited “exceptionally high capacitance”, although the mechanism was unknown at that time (Şahin, Blaabjerg, & Sangwongwanich, 2022). It was the Standard Oil Company, Cleveland (SOHIO) in 1966 that patented a device that stored energy in the double layer interface. SCs are known for over 50 years. SCs exhibit very high degree of reversibility in repetitive charge-discharge cycling. Cycle life over 5,00,000 cycles demonstrated (Ciszewski, Koszorek, Radko, Szatkowski, & Janas, 2019).

Highest efficiency of SC can get by constant current charging, because of the serial and parallel resistance in SC, they will consume electricity when charging. The amount of charging current will affect the charging efficiency (Y. Zhong, Zhang, Li, & Liu, 2006). By constant voltage charging the efficiency of SC will be up to 50%. Many times experiments show that the smaller charging current can lead to higher efficiency (Park & Kim, 2021).

SC design advancements accelerated as the electrification trend began to dominate industrial developments. Global company like General Electric carried out research on SC design enhancements in an effort to cash in on the rising demand for SCs as a crucial facilitator of electrification in various industries. The Standard Oil Company of Ohio (SOHIO) is primarily responsible for the invention, which was initially commercially introduced to the globe by the NEC Corporation (Yadwadkar, 2019)

The popularity of the SC technology immediately increased after superconductors were discovered as a more effective energy storage solution. Since they were initially introduced for commercial use, SCs have undergone multiple rounds of design advancement. Research organizations and top power electronics firms are still concentrating on developing new manufacturing processes and components to raise the performance and cost-effectiveness of SCs (Yadwadkar, 2019). Numerous SCs electrodes materials have been investigated since long ago to get the better featured SCs. Some of the advancement in the SCs development in global market can be discussed as in February 2013, University of California, Los Angeles researchers developed a ground-breaking and affordable fabrication technique to create micro-scale SCs using a LightScribe DVD burner designed for home use. These one-atom-thick layers of graphitic carbon make up the micro-SCs, which are simple to incorporate into small electronic devices. Researchers were able to significantly lower manufacturing costs and broaden the range of applications for SCs by combining a two-dimensional graphene sheet with the new fabrication method (Yadwadkar, 2019). A novel technique for mass producing 3-dimensional mesoporous graphene nano-balls (MGB), which can be used in the production of SCs, was invented by researchers at Ulsan National Institute of Science and Technology (UNIST) in July 2013. The features of mesoporous graphene, according to the researchers, will increase the scalability, quality, and cost-efficiency of SCs, broadening the range of uses for them in electric vehicles. In order to increase SCs' energy density ten times over that of commercial devices, experts at Monash University in Australia created a revolutionary way of synthesizing the graphene inside of them in August 2014. Through a procedure similar to the typical paper manufacturing process, the engineers produced a macroscopic graphene substance. Additionally, they confirmed that the engineers might provide new opportunities for the commercialization of graphene and 10x energy-dense SCs by lowering the solution-based chemical graphite oxide in graphene (Yadwadkar, 2019). In August 2014, a team of researchers in South Korea made an extraordinarily inventive but incredibly useful alternative material for SC electrodes. They came up with a means to turn cigarette filters into a highly effective carbon-based material with high power densities that can be used in SCs. Researchers might effectively store more electrical energy using old cigarette filters than commercially produced carbon (Yadwadkar, 2019). One of the most crucial business strategies of SC manufacturing businesses is the development of SCs appropriate for electric or hybrid automobiles. On the other hand, automakers are competing to release the most effective electric vehicles, which has led to their search for superior energy storage technologies. This is finally reflected in the continuously increasing automobile industry's expanding potential for SC developments (Yadwadkar, 2019). Tesla Inc., a global powerhouse in the automotive and energy sectors, revealed in February 2019 that it has bought Maxwell Technologies Inc., a pioneer in battery technology, for around US$ 218 million. With this acquisition, the business hopes to integrate SC knowledge and take advantage of the lucrative potential for electric vehicles. This might speed up car charging times (Yadwadkar, 2019).

Transition metal compounds (TMCs), such as metal oxides, hydroxides, sulfides, and phosphides, have attracted great attention due to their high theoretical capacitance, abundant sources, low cost, etc. (Low et al., 2019). In this case, the studies of TMC-based SCs are rising up due to their obviously enlarged energy densities (approaching 102 Wh kg^{-1}). The energy storage mechanisms of TMC-based electrodes primarily involve the electron transfer in the process of redox reactions and valence state changes of transition metal ions, indicating that the ion diffusion rate and phase transformation due to the change of valence state are important for electrochemical properties (Quan et al., 2018). Such transformation generally leads to the sluggish bulk phase reaction and dramatic volumetric expansion/shrinkage during the energy storage process and finally resulting in the low chemical reaction kinetics and inferior cycle stabilities of TMC-based SCs (Dubey & Guruviah, 2019). Since rapid charge/discharge capability and long cycling stability of minimum 10,000 cycles are key criteria for SCs, the poor electrical conductivity, low power density, unsatisfactory mechanical/electrochemical stability, and some other problems, still limit their prospects of TMCs for large-scaled applications (Y. J. I. T. o. e. c. Cheng, 2009).

Various Transitions Metal Oxides (TMOs) with high electronegativity like IrO_2, NiO, Fe_2O_3, SnO_2, Co_3O_4, MnO_2, RuO_2 etc. are used as the electrode of pseudocapacitor (Luo et al., 2014). Out of these all TMOs, RuO_2 shows high theoretical capacitance of about 1358 F g^{-1}, high electrochemical stability and high electrochemical stability of about 300 S cm^{-1} these properties make RuO_2 as most promising TMO for SC electrode (G. Yu, Xie, Pan, Bao, & Cui, 2013) . Although RuO_2 seems more promising material but due to their toxic nature and also high cost they are not preferred wisely (Deng et al., 2014).

The cobalt oxides have also attracted a lot of interest in recent years due to their affordability, non-toxicity, simplicity of synthesis, and environmental friendliness. Theoretically, the cobalt oxides have high capacitance (CoO: 4.292 F g^{-1}, Co_2O_4: 3.560 F g^{-1}) (H. Cheng et al., 2010; He et al., 2012). Beside this, cobalt oxide exhibits excellent electrochemical behavior in alkaline as well as organic electrolyte. Furthermore, cobalt oxide can interact with the ions of the electrolyte at the surface or internally through the material (Y. Liu et al., 2013). Also by modifying preparative parameters such as reaction temperature, reaction time, solution concentration, complexing agent, etc., cobalt oxide' properties like as shape, structures, and dimension may be easily adjusted (Wei et al., 2015). The material's optimized microstructure and managed morphology will increase its specific surface area and pore size distribution, which will make it easier for electrolyte ions to move through the material (Meher & Rao, 2011). Recent years have seen the successful application of numerous new techniques for the synthesis of materials with meso and microporous nanostructures made of cobalt oxide, including the hydrothermal method (Meher & Rao, 2011), combustion synthesis method (Deng et al., 2014), hydrothermal precipitation method (Z. J. Yu, Dai, & Chen, 2009), chemical bath deposition method (J. Xu, Gao, Cao, Wang, & Chen, 2010) etc.

The transition metal oxides go for continuous faradaic reactions, leading to changes and destruction in the structure as well as phase changing during cycling (charging/discharging). These changes degrade the capacitance of the transition metal oxides. Due to these results concept of MOFs was investigated (Rahul R. Salunkhe, Kaneti, & Yamauchi, 2017). Metal-organic frameworks (MOFs) have had a significant impact on several areas of material science since their discovery in the late 1990s. They have drawn a lot of attention in recent years as starting points or models for the creation of porous metal oxide nanostructures and nanocomposites for use in next-generation supercapacitor applications. It is currently mostly unclear how these materials will play a significant part in the advancement of the supercapacitor industry, despite the fact that they have numerous uses and have undergone extensive structural and synthetic research (Rahul R. Salunkhe et al., 2017). Due to their highly customizable architectures, wide surface areas, and controlled porosity, MOFs have proven to be appealing starting points for the development of porous TMO materials (Kaneti et al., 2017). Because MOFs are composed of metal ion centers coordinated to organic linkers, controlled heating in air can cause the metal ions to oxidize and the release of gaseous CO_2 and NO_2 resulting from the breakdown of organic linkers, which can result in porous TMO nanomaterials during heating (Rahul R. Salunkhe et al., 2017). The form and porosity of the parent MOFs are often retained by the resultant nanoporous oxide materials, which is advantageous for achieving huge surface area.

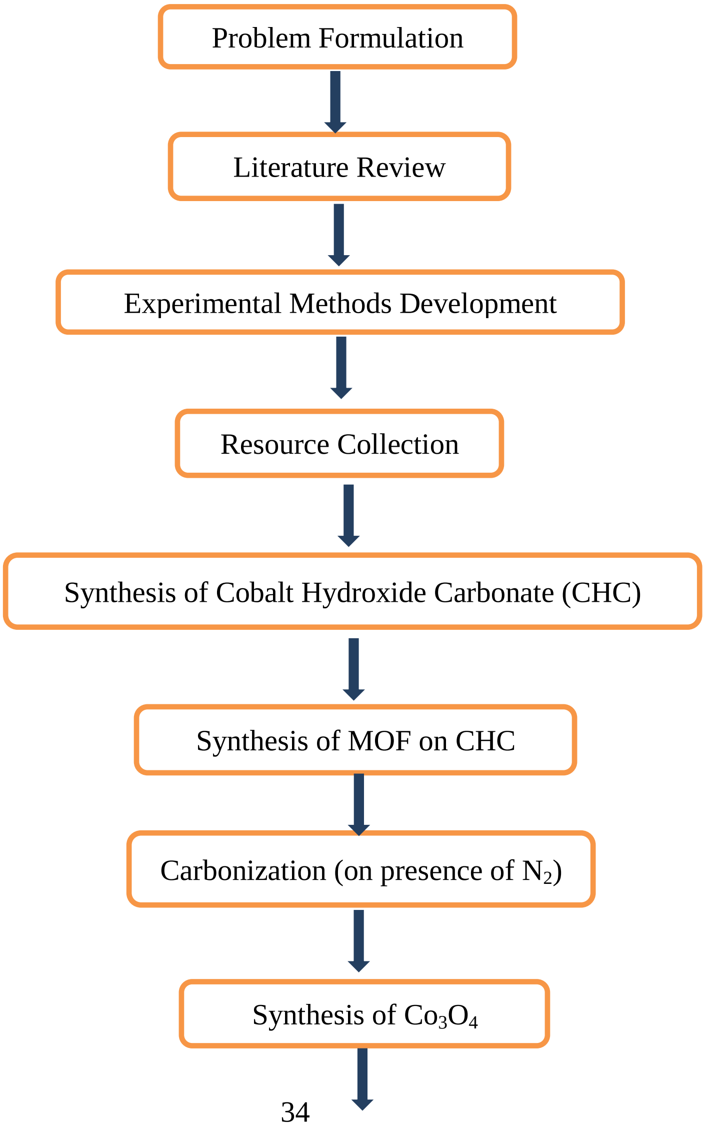
Various porous TMO nanomaterials, such as cupric oxide (CuO) (T.-T. Li, Qian, & Zheng, 2016), cobalt oxide (Co_3O_4) (Du, He, Lou, & Chen, 2017; Rahul R Salunkhe et al., 2015), cerium oxide (CeO_2) (Zeng, Chen, Chen, Xiong, & Wei, 2016), iron oxide (Fe_2O_3) (X. Xu, Cao, Jeong, & Cho, 2012; Lei Zhang, Wu, Madhavi, Hng, & Lou, 2012), titanium dioxide (TiO_2) (Xiu et al., 2015), magnesium oxide (MgO), manganese oxide (Mn_2O_3) (B. Zhang et al., 2016; Zheng, Xu, Yin, Zhang, & Lu, 2016), nickel oxide (NiO) (Han, Zhang, Shen, Li, & Li, 2017; Kong, Dai, Li, Sun, & Wang, 2015) and zinc oxide (ZnO),(Feng et al., 2017; Kimitsuka, Hosono, Ueno, Zhou, & Fujihara, 2013)

More interestingly, MOFs can be used to generate a variety of mixed metal oxides and metal oxide nanocomposites, including Cr_2O_3 on TiO_2 (W. Zhang et al., 2015), $Co_3O_4/ZnFe_2O_4$ (Hu, Liu, Qu, You, & interfaces, 2015), $Cu/Cu_2O@TiO_2$ (Mondal & Pal, 2016) etc. Therefore, these materials can be created to produce high-performance electrodes for supercapacitors by including numerous functions and high surface area.

CHAPTER THREE: RESEARCH METHODOLOGY

3.1 Methodology

This research is fully based on experimental tests and analysis consisting of qualitative and quantitative data. The methodology adopted in this research work is shown in flowchart below:



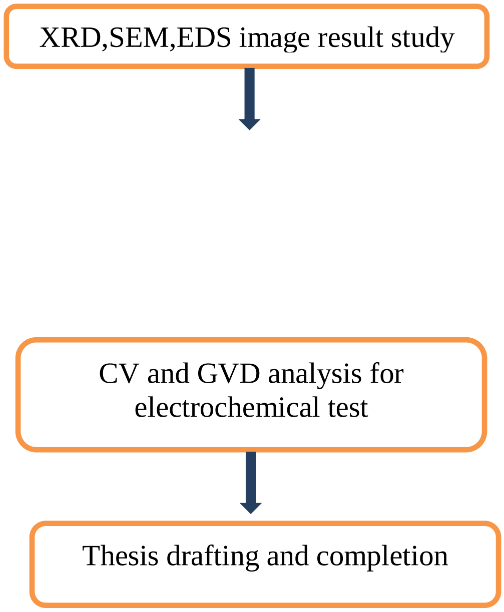


Figure 10: Flowchart of the methodology

SC has high uses to store the energy like a battery but with high charging rate than a battery. Similarly, the discharging rate is also very high than the batteries. So in order to increase the energy density new types of materials are in research and development phases to reduce the fast discharging rate. These new types of developed materials are generally used as the electrode material of SCs. In our study also, we tried to overcome this fast discharging problem by using a new type of material- cobalt oxide with coated nitrogen doped carbon sponges. This material have high nano surface area to absorb high chemical energy from the electrolyte.

With high study among all other possible materials we come to cobalt oxide as it shows high capacitance than others and also readily available in environment. After high literature review of our study we chose cobalt oxide as main material of electrode. To carry out experiments we have done our experiment in the research lab of IOE Pulchowk Campus. Chemicals and instruments for this study are provided by the Department of Applied Sciences and Chemical Engineering and by my thesis supervisor. For the experiments besides used chemical we have used furnace, magnetic stirrer, electric motor energized filtration method etc.

3.2 Materials

A Chemical solution was made by taking the following chemicals,

i) Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$)

ii) Ammonium Fluoride **(**NH_4F)

iii) Urea (CH_4N_2O)

iv) A piece of Nickel foam

3.3 Methods

Figure 3 below shows the overall laboratory works methods/process to produce cobalt oxide before the final calcination stage.

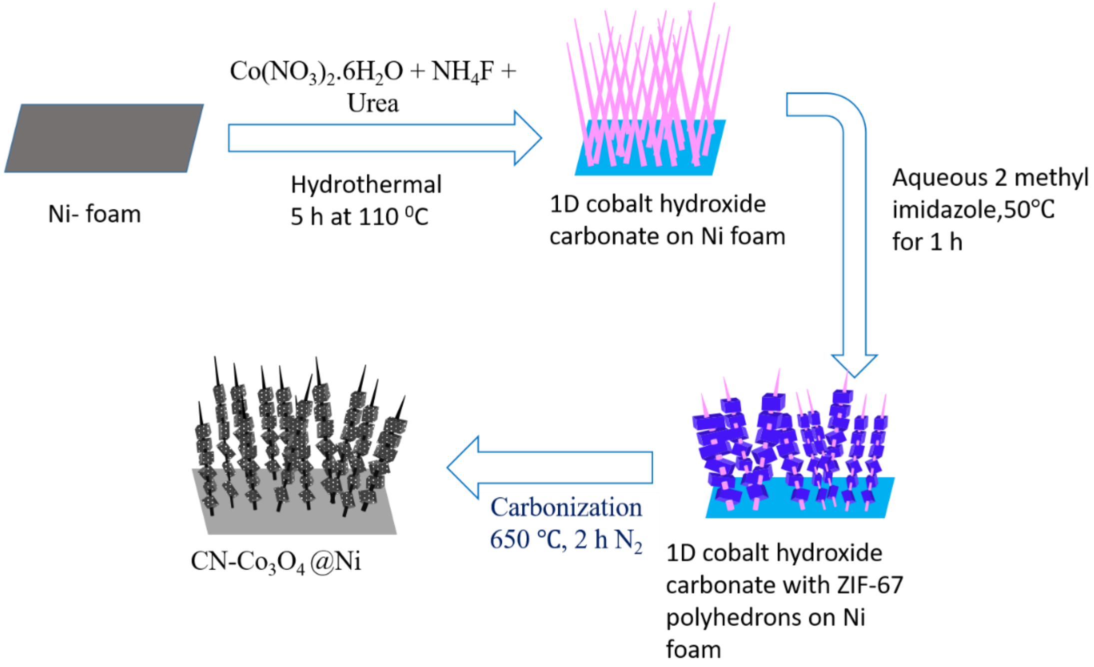


Figure 3 Schematic process diagram of lab work

3.4 Synthesis of cobalt hydroxide carbonate (CHC)

The quantity and the material listed under above topic (materials used) were mixed together in 100 ml of distilled water and stirred properly. Then the solution is taken for thermal decomposition in high pressure in a hydrothermal process at 110 ^{0}C temperature for 5 hours.

(a) (b)

Figure 4 (a) Autoclave after HTC containing solution (b)Pink colored solution taken after HTC

After then the solution's color turns into pink and then it is stirred on a magnetic stirrer. Washed the solution for multiple times and took out the sediment chemical and nickel foam separately. These two, chemical and nickel foam are kept in furnace at 50 °C temperature for 24 hours to make them dry.

3.5 Synthesis of Metal Organic Framework (MOF)

2% wt/wt concentration of 2-methylimidazole is made in 50 ml distilled water. Thus, 1.5 g of 2-Methylimidazole is taken and mixed with 50ml distilled water. The solution is then stirred in magnetic stirrer. Then after a small cut piece of 0.2291 g of above obtained Nickel foam is taken and mixed in the solution. This mixture is then kept in furnace at 50 °C for 1 hour. Then, the mixture is taken out and the nickel foam, which is acting as inactive material for the chemical reactions, turns into blue in colour with many sponges/small pores on it as seen in these figure below.

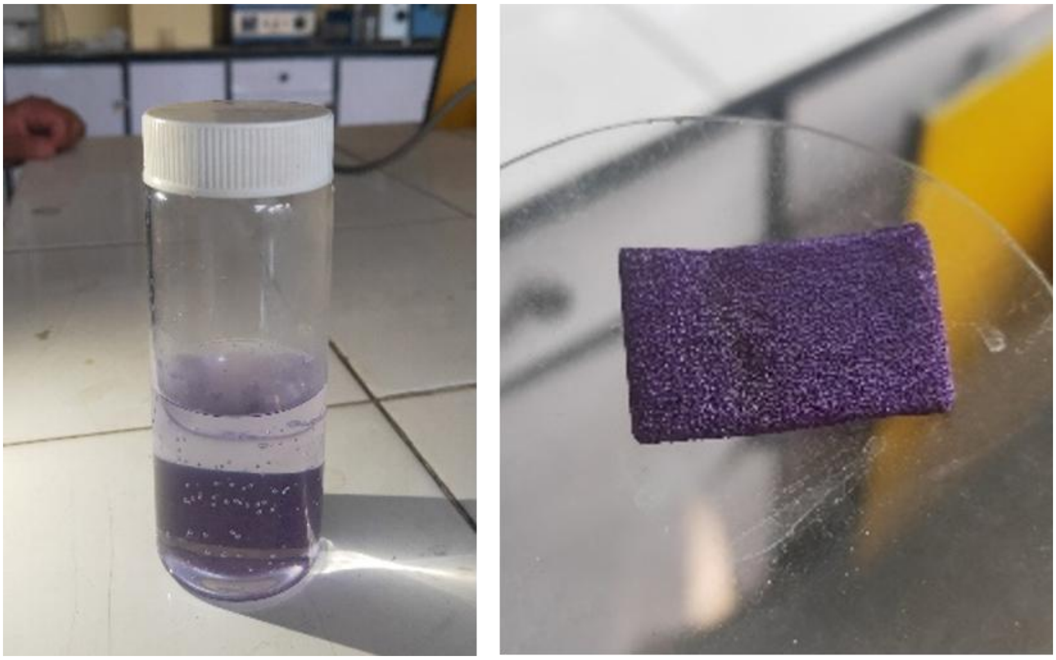


Figure 5 Synthesis of MOF on nanowire deposited on nickel foam

Then the taken nickel foam seen in fig above is mixed with 20ml ethyl alcohol and kept it for 24 hours in furnace at a temperature of 50 °C. After this we get the nickel foam with expecting electrode material on it.

3.6 Carbonization and calcination

As prepared MOF on Cobalt Hydroxide Carbonate nanowire deposited on Ni foam was subjected to carbonization in a tube furnace for about 2 h in nitrogen atmosphere at 650 ℃ . It is then subjected to calcination in a muffle furnace at 300 ℃ for 1 h to get carbon and nitrogen intermingled cobalt oxide polyhedrons (CN-Co_3O_4 on Ni).

3.7 Electrochemical test

The electrochemical test was carried out versa stat electrochemical work station. As prepared CN-Co_3O_4 @Ni was used as working electrode. Platinum wire was used as counter electrode. Ag/AgCl electrode was used as reference electrode. 3 M aqueous KOH was used as electrolyte. Cyclic voltammetry (CV) test was carried out in between 0.0 to 0.5 V and galvano static charge discharge (GCD) test was carried out between 0.0 to 0.45 V. CV was carried out at different scan rates and GCD was carried out at different current densities.

Specific capacity of faradaic material was calculated with the help of following equation

$$\boldsymbol{C = \frac{2 * I * \int V\, dt\ * 1000}{m * V * 60 * 60}}$$

where, C = specific capacity (mA h g^{-1})

t = discharging time (s)

I = discharge current (A)

V = voltage difference (V)

m = mass of the electrode material (g)

$\int V\, dt$ = integral area under discharge curve

3.8 X Ray Diffraction (XRD) analysis technique

XRD is a non-destructive technique that shows detail information about the crystallographic structure, chemical composition and physical properties of the material. This analysis is based on the constructive interference of monochromatic X-rays and a crystalline sample. As we know x- ray is an electromagnetic radiation having short wavelength which is generated when the electrically charged particle having sufficient is decelerated.

In XRD, the generated X-rays are collimated and directed to a nanomaterial sample, where the interaction of the incident rays with the sample produces a diffracted ray, which is then detected, processed, and counted. The intensity of the diffracted rays scattered at different angles of material are plotted to display a diffraction pattern.

Each phase of the material produces a unique diffraction pattern due to the material's specific chemistry and atomic arrangement. The diffraction pattern is a simple sum of diffraction patterns of each phase. Imperfection in the sample material would affect the pattern of the diffracted signal. In this case, the factors that contribute to the imperfection of the sample would be the composition heterogeneity, crystal structure defects, micro stains and crystallite size.

The peaks of the XRD pattern play a vital role in the identification of the phases as well as the properties of the nanoparticles. In this case, the width of the peak would reveal the average crystalline size of a nanoparticle where sharp peaks indicate a large size of crystallites, whereas broad peaks indicate smaller crystallites. (Pandian Bothi Raja, 2022)

3.9 Energy dispersive spectroscopy

The energy dispersive spectroscopy (EDS) technique is mostly used for qualitative analysis of materials but it is also capable to provide semi-quantitative results as well. Generally, the SEM instrumentation is equipped with an EDS system to allow for the chemical analysis of features being observed in SEM monitor. Simultaneous SEM and EDS analysis is advantageous in failure analysis cases where spot analysis becomes extremely crucial in arriving at a valid conclusion. Signals produced in an SEM/EDS system includes secondary and backscattered electrons that are used in image forming for morphological analysis as well as X-rays that are used for identification and quantification of chemicals present at detectable concentrations. The detection limit in EDS depends on sample surface conditions, smoother the surface the lower the detection limit. EDS can detect major and minor elements with concentrations higher than 10 wt % (major) and minor concentrations (concentrations between 1 and 10 wt %). The detection limit for bulk materials is 0.1 wt % therefore EDS cannot detect trace elements (concentrations below 0.01 wt %) (Seifollah Nasrazadani, 2016)

EDS technique is capable of producing elemental distribution maps, an example of which is shown in Figure 8 at result portion of this study where SEM image on the left corner shows patches of Cobalt oxide 3D porous polyhedrons intermingled with nitrogen doped carbon sponges that correspond to Co, O, N and C maps indicated in the dot coloured map images.

3.10 Material characterization

Transmission electron microscopy (TEM; JEOL, JEM-2010 instrument), scanning electron microscopy (SEM; Hitachi S-7400), and field emission scanning electron microscopy (FES-SEM; JEOL, JSM6701F) were applied to record the material morphologies. A Cu-sealed tube (λ =1.54056 Å)-equipped Rigaku X-ray diffractometer was used to record the X-ray diffraction (XRD) patterns. X-ray photoelectron spectroscopy was used to determine the chemical composition of the surface (XPS). Three-electrode cell electrochemical tests were conducted in 3 M aquatic KOH. The prepared mat (0.2291 g) served as the working electrode, with platinum wire serving as the counter electrode and Ag/AgCl serving as the reference electrode. From 0.0 to 0.5 V, cyclic voltammetry (CV) was measured. Between 0.0 and 0.45 V, galvanostatic charge discharge (GCD) was measured.

CHAPTER FOUR: RESULTS AND DISCUSSION

Cobalt hydroxide carbonate nanowires were grown on nickel foam hydrothermally. As prepared sample of cobalt hydroxide carbonate (CHC) on Ni foam was observed by scanning electron microscopy (SEM). The SEM image (6a) shows one dimensional (1D) structures uniformly grown on Ni foam. The 1D structures are in nanoscale level. Figure (6b) is the SEM image of the material in which MOF has been grown on 1D structure of CHC. MOFs are polyhedrons and uniformly grown on 1D nanostructures. SEM image (6c) shows the structure of carbon and nitrogen intermingled cobalt oxide polyhedrons (CN-Co_3O_4 @Ni) material after carbonization of MOF developed on 1D structures followed by calcination. There are uniformly grown porous nanostructures. The high porosity is clearly seen in its enlarged image (fig 6d). The high porosity is essential for increasing the surface area as well as effective transport of ions and electrons. Doping of nitrogen in the prepared compound CN-Co_3O_4 @Ni is observed in its elemental mapping (figure 7)

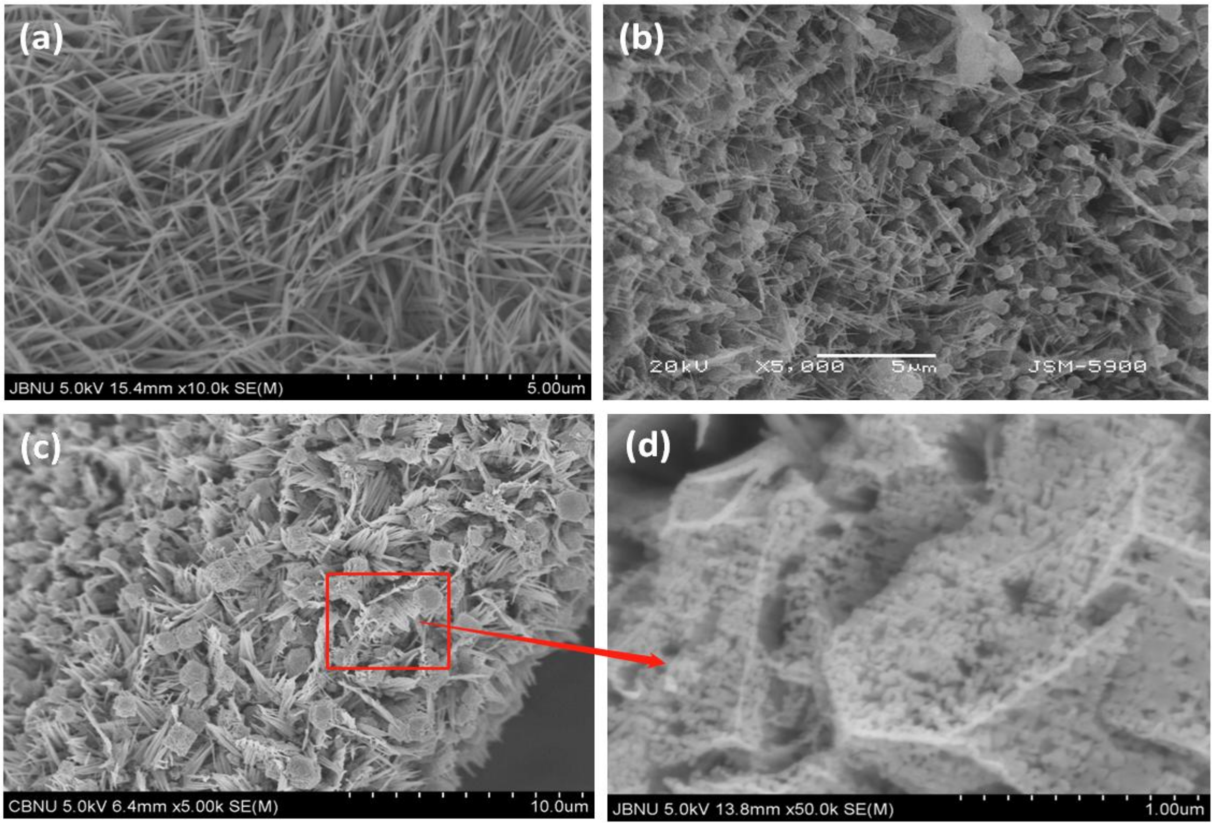


Figure 6 (a) 1D cobalt hydroxide carbonate on Ni foam (b) 1D cobalt hydroxide carbonate with MOF polyhedrons on Ni foam (c) CN-Co_3O_4 on Ni and (d) a portion of (c) showing high porosity

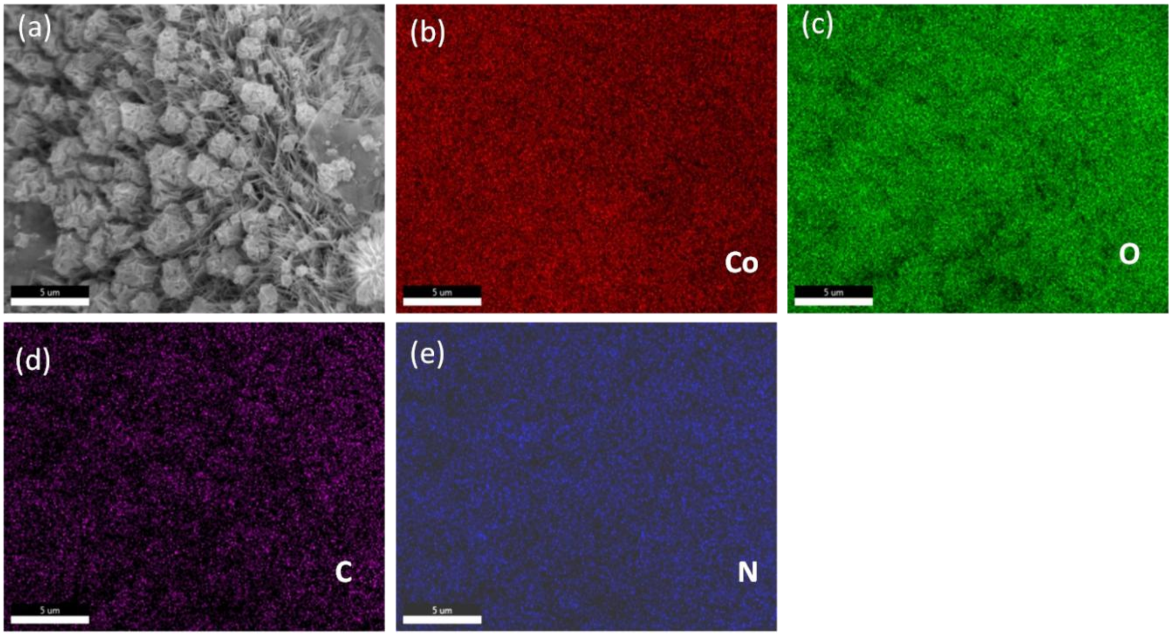


Figure 7 Elemental mapping of CN-Co_3O_4 on Ni

Energy dispersive spectroscopy (EDS) of the material shows that the material contains 6.4 % by weight of carbon, 2.5 % by weight of nitrogen, 34.7 % by weight of Oxygen and 56.3 % by weight of Cobalt. It shows that nitrogen is present on the sample. The source of nitrogen is obviously the ligand 2-methylimidazole (Z. Zhao, Kou, & Wu, 2020).

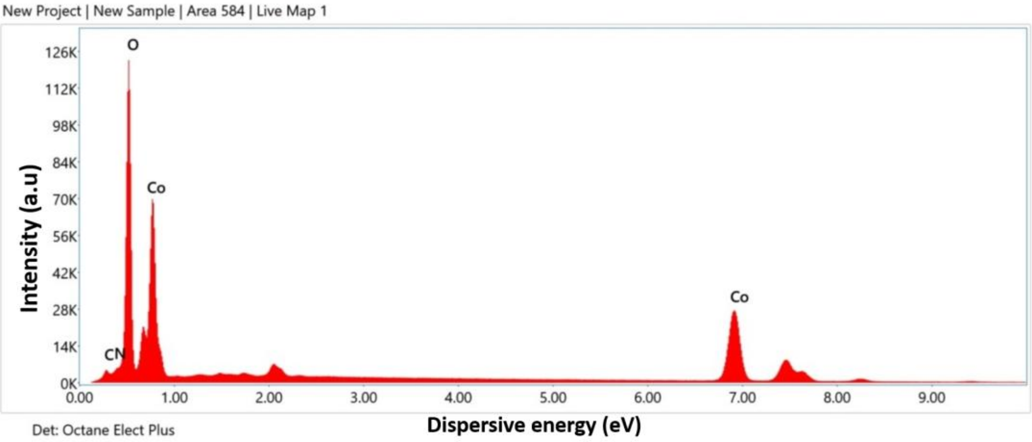


Figure 8 Energy Dispersive X-ray spectroscopy (EDS) of CN-Co_3O_4 on Ni

Table 1 EDS output result

Element	Weight %	Atomic %
C K	6.4	13.9
N K	2.5	4.6
O K	34.7	56.5
Co K	56.3	24.9

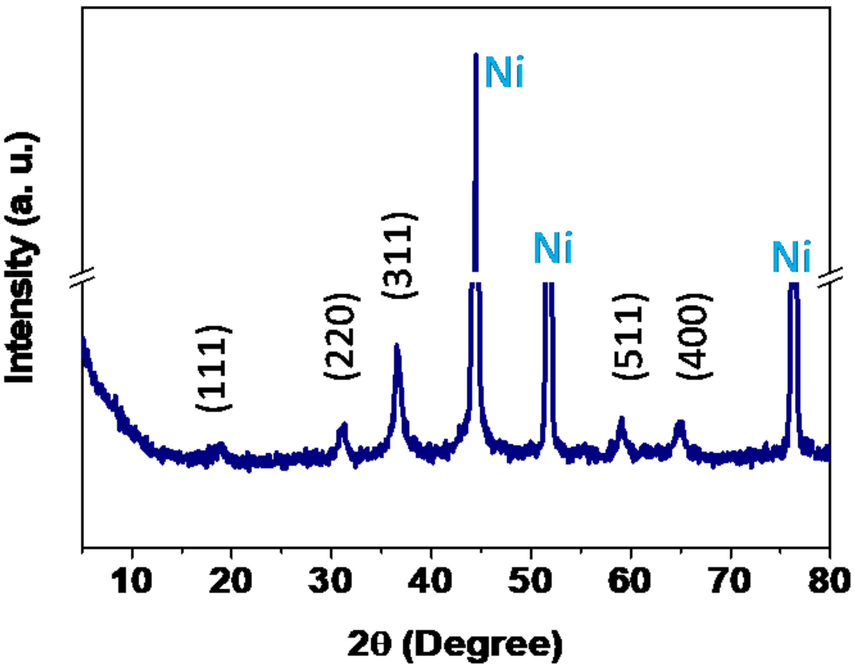


Figure 9 XRD pattern of 1D/3D CN-Co_3O_4 on Ni

XRD graph shown above shows that the cobalt oxide formed is crystalline in nature. It is found that there are peaks at 2θ values of 31.30, 19.01,36.84, 65.08 and 59.20 which belongs to (220), (111), (311), (511) and (400) respectively (Mukhiya et al., 2020). This confirms the successful formation of cobalt oxide. The peaks for carbon cannot be seen probably due to high intensity of peaks for cobalt oxide and nickel. However, the carbon content in the prepared material can be seen in its EDS data (figure 8) and table 1 as well as in elemental mapping of figure 7. Also the peaks at 2θ values of Ni are found at values 45, 52.3 and 77.4 (Taghizadeh, 2016).

For SC electrode, the electrochemical performance of the synthesized CN-Co_3O_4 on Ni material was investigated. Against an Ag/AgCl electrode, the material's CV test ranged from 0.0 to 0.5 V (figure 14). At 5 mV s^{-1}, 7 mV s^{-1}, 10 mV s^{-1}, and 20 mV s^{-1}, CV curves were evaluated. Current in the material likewise rises as scan rates are increased. The oxidation and reduction peaks can be seen in the CV curves. These peaks demonstrate the faradaic nature of the charge storage in the CN-Co_3O_4 on Ni material as it has been prepared. The CV curves can be analyzed here below in figure 10.

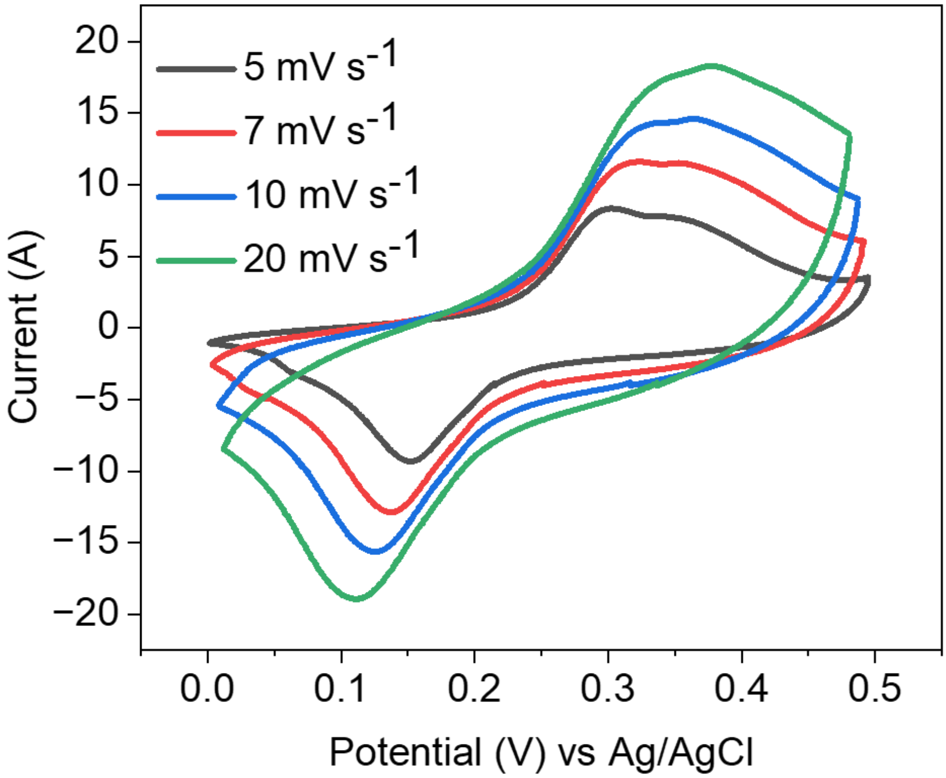


Figure 10 CV curve of CN-Co_3O_4 on Ni

Galvano static charge discharge (GCD) of as prepared CN-Co_3O_4 on Ni material was carried out in between 0.0 to 0.45 V. GCD was carried out at different current densities. Figure 11 represents the GCD curves at different current densities. It shows the specific capacity of the as prepared CN-Co_3O_4 on Ni is 155 mA h g^{-1} at current density of 1 A g^{-1}. At current density of 2 A g^{-1}, the specific capacity decreases to 132 mA h g $^{-1}$. At current density of 5 A g^{-1}, the specific capacity reached to 83 mA h g^{-1}. This means specific capacity still retains to 46 % when current density is increased to 5 times.

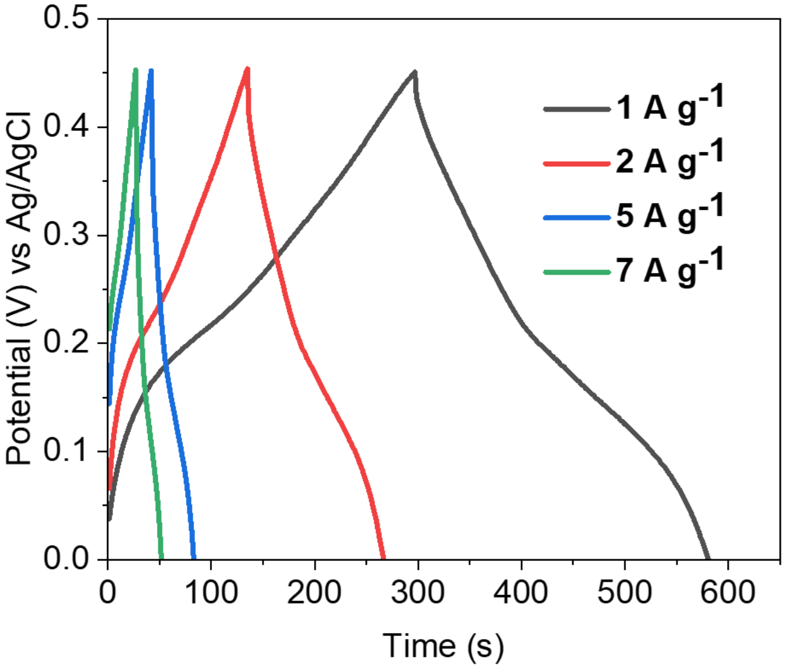


Figure 11 GCD curve of CN-Co_3O_4 on Ni

The energy storing capacity of as prepared CN-Co_3O_4 on Ni material is due to high surface area of the material. MOFs derived materials inherently furnished high surface area and high porosity (Xu Zhang et al., 2019b; Zou & Li, 2018). The highly porous material is suitable for storage and transport of electrolytic ions (W. Li et al., 2021; Yan, Liu, Liu, Yan, & Huang, 2022). Such structures enhance the ionic mobility and the capacitance of the material. The material is carbonaceous and doped with nitrogen. The source of carbon and nitrogen are MOFs. Carbon and nitrogen are responsible for providing the conductivity of the as prepared material CN-Co_3O_4 on Ni .This enhances the conductivity of cobalt oxide nanostructures which has high energy storing capacity (Shinde, Mahadik, Gujar, & Lokhande, 2006). In overall the synergistic effect of carbonaceous material and cobalt oxide nanostructures in a 3D porous morphology is effective and promising for high energy storage capacity for supercapacitor (Dong et al., 2020).

CHAPTER FIVE: CONCLUSIONS

In summary, this research work is focused in the fabrication of metal-organic frameworks (MOFs) based highly porous carbon and nitrogen doped cobalt oxide polyhedrons. For this, cobalt hydroxide carbonate nanowires were uniformly grown on nickel foam by hydrothermal method. MOFs polyhedrons were assembled on nanowires by solution method. Carbon and nitrogen intermingled highly porous three dimensional (3D) cobalt oxide polyhedrons (CN-Co_3O_4 on Ni) was prepared by carbonization and calcination. As prepared CN-Co_3O_4 on Ni was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), elemental mapping, energy dispersive spectroscopy (EDS). The electrochemical test of the as prepared CN-Co_3O_4 on Ni material exhibits a specific capacity of 155 mA h g^{-1} at current density of 1 A g^{-1}. The high energy storing capacity is due to high surface area and porosity of MOF based cobalt oxide nanostructures.

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