

# **Synthesis and Characterization of Iron-Cobalt Oxide imbedded PANI Composite for Supercapacitors**



**By**

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# **Synthesis and Characterization of Iron-Cobalt Oxide imbedded PANI Composite for Supercapacitors**



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**This thesis is submitted as a partial fulfilment of the requirements for the degree of**

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## **DEDICATION**

My humble efforts for this dissertation and all of my academic achievements are dedicated to my father, Mr. Mirza Jamil Nawaz, mother Mrs. Aqeela Jamil, husband Mr. Hammad Ahmed Khan and my beloved son Zayyan Mustafa Khan; whose examples evolved me to think about character values, resilience, grits, patience and determination. Which were the skills that actually helped me to navigate my life and develop myself intellectually and personally.

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## **Abstract**

Nanostructured Iron cobalt oxide composite with polymer PANI has been established as a promising electrode material due to synergistic enhancement effect. Iron cobalt oxide was synthesized by using a facile hydrothermal route followed by annealing and further in situ polymerization of PANI to make their composite. For comparison pure PANI was also synthesized by the same method. The synthesized samples were characterized by versatile techniques such as XRD; for structural analysis, SEM for morphological analysis; Galvanostatic charge discharge; CV and GCD for electrochemical studies. These tests affirmed the developed iron cobalt oxide nanoparticles composite with PANI for supercapacitors. The composite exhibits the specific capacitance of  $1283.5 \text{ Fg}^{-1}$  at  $2 \text{ Ag}^{-1}$ .



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## List of Abbreviations

CO -----Cobalt Oxide ( $\text{Co}_2\text{O}_4$ )

PANI -----Poly-aniline

FCO -----Iron Cobalt Oxide ( $\text{Fe Co}_2\text{O}_4$ )

Ppy -----Poly pyrrole

XRD -----X-ray Diffraction

CV -----Cyclic Voltammetry

GCD -----Galvanostatic charge discharge

# Chapter 1: Introduction

## 1.1 Introduction

Millions of years ago due to high pressure and temperature deposits of coal, natural gas and oil were produced deep in the layers of earth, by the process of anaerobic decomposition of dead bodies. Petrochemical industries, plastic and fertilizer production, and many such valuable uses of the renewable resources increased each decade [1]. Rapid industrial development and global population required greater energy demand since past few years and results in diminishing the limited natural resources that are used to meet this increased demand. An alarming signal has been raised on the existing energy resources due to their dramatic increased consumption[1]. Fossil fuel resources quality production has declined a lot compared to the case decades ago. Industrial utilization of fossil fuels results in global warming due to the release of GHGs in the environment [1]. its urgent and challenging to develop alternate energy storage system as the energy crisis are seriously increasing now [2].

Although the renewable energy resources are natural but hundreds of years required replenishing the store limit their supply [3]. Finite nature of fossil fuels and global warming both the challenges are important to be dealt with and fundamental advances in energy storage and energy conversions are required[4]. Both government and non-government organizations are working to conserve the natural resources by reducing their irresponsible use[5].

To fulfil high energy demands petroleum-based fuels are used which have a serious effect on the environment. The whole infrastructure of energy production is dominantly affected due to insufficient energy generation compared to energy demands across the world[6]. A shift towards sustainable and green energy products is needed in this hour of energy crisis [7]. Increased energy and power density is demanded in portable energy devices due to increased energy demand[8]. A lot of cost-effective storage materials are exploited providing renewable energy[9]. In a range of electrical devices, Supercapacitors, lithium ion batteries and fuel cells, unique combination of properties is provided by the Nano materials as Nano electrode and

Nano electrolyte[10]. Serious efforts are made to make efficient energy storage devices for improved energy conversion device efficiency.

The established energy-generating sources are not enough to accommodate energy demand in the rest of the globe[11]. These factors had a prominent effect on the energy production infrastructures. Petroleum-based fuels have used elevated energy requirements that affect the environment to overcome this problem. Usage of the renewable energy source is therefore vital for sustainable revolutions and storage to overcome this problem [12].

We need to produce efficient methods for energy generation which are cost effective and efficient both from renewable energy sources as well as from energy storage devices[13]. Most of the energy sources are depleting and are of sporadic nature, hence, energy conversion requires efficient energy storage devices. Now a days, energy conversion devices such as Sodium ion batteries, Lithium ion batteries, Lithium air batteries, Zinc air batteries, Zinc ion batteries and Lithium Sulphur batteries are used [14]. Supercapacitors also called ultracapacitor are also used as highly efficient energy storage device. Some of the features including rapid charge-discharge, fast processing, and long-term cyclic stability up to millions of cycles, of supercapacitors make them superior energy storage device as compared to batteries[15]. Charge storage phenomenon of supercapacitors is different than that of batteries[16]. First supercapacitor that was fabricated efficiently accumulated charge due to carbon-based electrode material providing high surface area. Batteries Process by faradaic reactions and provide Better energy density as compared to supercapacitors, hence low energy density is a major drawback in super capacitors[17]. High energy and power density are the required in portable energy devices. To overcome this challenge asymmetric devices are used which work by faradaic reactions and electrostatic charge storage and hence provide high power density and energy density[18].



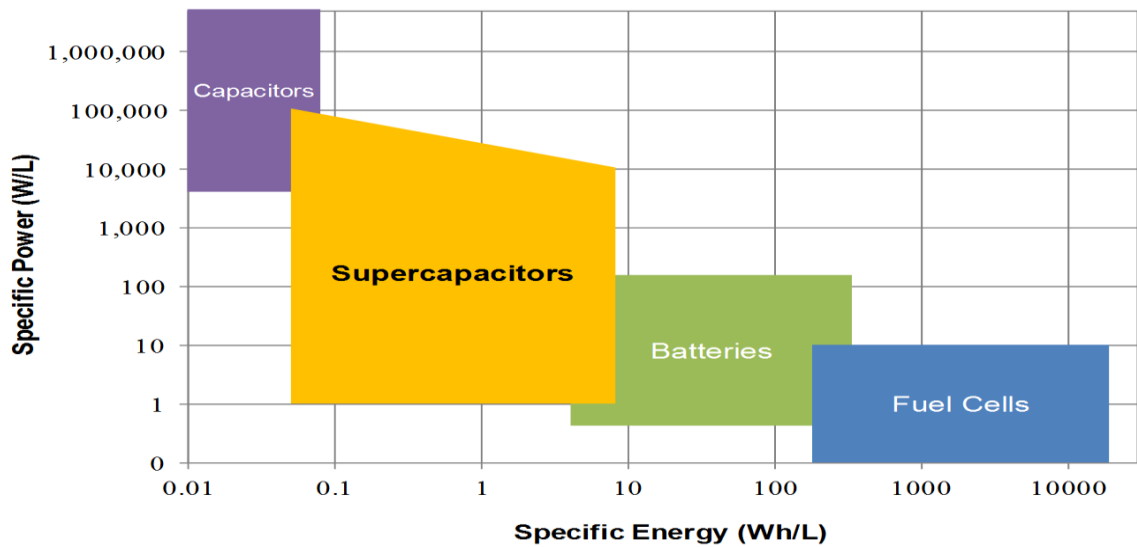


Figure 1.1 Ragone plot of Energy Storage Devices

## 1.2 Energy Storage

Based on energy storage mechanism multiple type of energy storage devices exist i.e; fuel cells store energy as fuel, electrochemical cells store energy electrochemically, and electric circuits store as charge[19]. Different energy storage devices are shown schematically as;

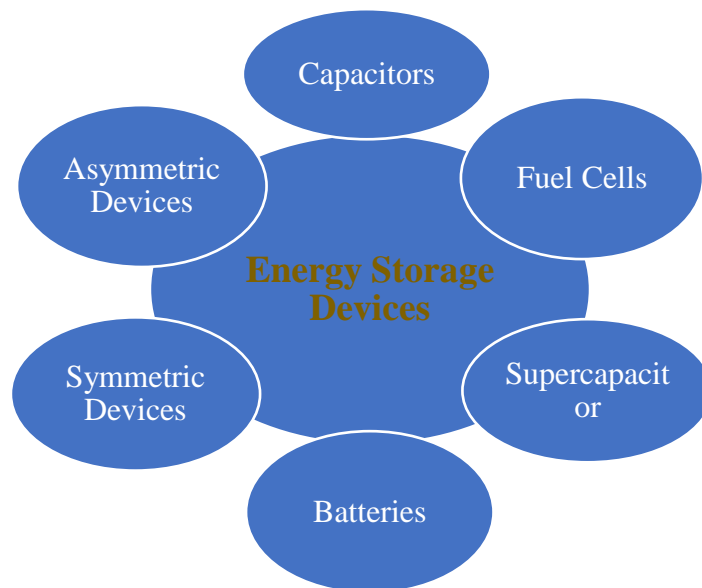


Figure 1.2: State of the art energy storage device

### 1.2.1 Batteries

Electrochemical cells or series of cells supply direct electric current to the batteries. A sequence of redox reactions converts chemical energy into electrical energy. In many industrial applications and consumer electronics most crucial energy sources are electrochemical batteries till now[20]. Many cells are used in a standard battery, each consisting of two electrodes and an electrolyte containing charged species. Polarity of a battery can be identified depending upon passage of ions. Redox reactions involving oxidation at anode and reduction at cathode power a battery. Near future, Li ion batteries are a good choice in industrial applications, electronics, and electric transportation[21]. Hybrid cars (Toyota Prius) are electric hybrid cars commercially available. adequate weight and high acceptable energy density of 115-170Wh/g is offered by Li ion batteries. However, a limitation in their performance is due to low power density and charge discharge rate. Schematic demonstration of lithium-ion battery is presented below in figure 1.3.

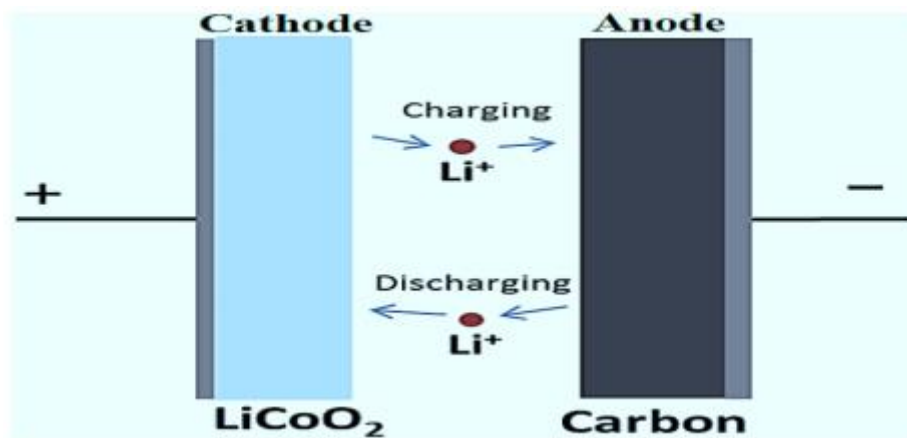


Figure 1.3 Schematic view of li-ion battery.

Different types of batteries are being used for energy storage applications. Two main categories of the batteries are:

- i) Primary batteries
- ii) Secondary batteries

### 1.2.1.1 Primary batteries

Mostly primary batteries are used in portable devices. One cycle of the lifetime is the key feature of the primary batteries[22]. Based on electrolyte being used in the batteries they are further classified. Both aqueous and non-aqueous electrolyte are used in these batteries.

### 1.2.1.2 Secondary batteries

Secondary batteries can also be known as electrochemical cells. These are rechargeable devices for multiple number of times. Solar cells operations, portable electronic devices and vehicles are the multiple fields using this type of batteries[23]. With the development of the electrode materials used in these devices batteries also develop. Based on electrode material used in the secondary batteries can be classified into different types. Lithium ion batteries, sodium batteries, lead batteries are some of the examples of secondary batteries[23].

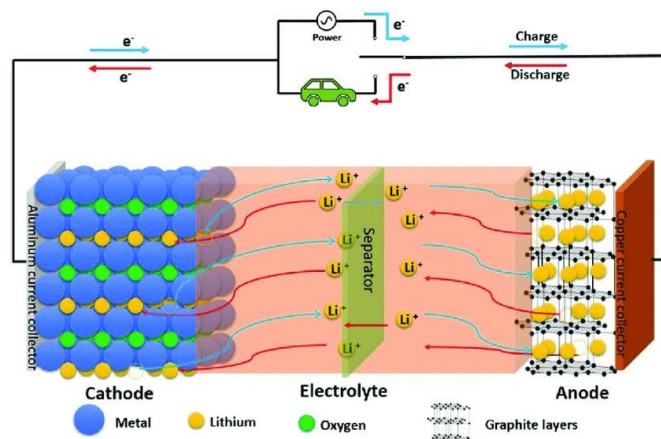


Figure 1-2: Schematic for working of batteries[14]

### 1.2.1.3 Working Principle

A standard battery is comprised up of one or multiple electrochemical cells, each cell holds two electrodes that are separated by an electrolyte inhibiting charged species. The polarity of a battery is recognized upon the transition of anions and cations inside it[3]. To power a battery two sets of redox reactions, take place i.e., Reduction at

cathode and oxidation at the anode. Figure 1.4 presents the schematic illustration of Li ion batteries.

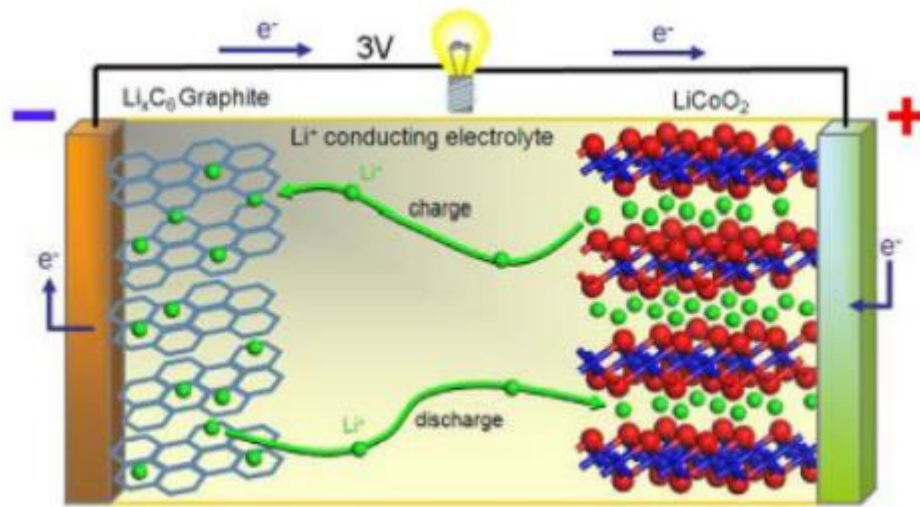


Figure 1.4 Working mechanism of Li ion batteries.

### 1.2.2 Capacitors

The capacitor is a device which stores electrical energy as the electric field made on its electrodes. It contains two plates relating to each other which is generally called cathodes and a dielectric material between the plates[24]. Capacitance is the tendency of a capacitor to store electrical charge which is controlled by:

$$Q = CV$$

The capacitors are requested in different sorts reliant upon conditions of electrodes used in the capacitor and the dielectric type. The most typical type of capacitor is parallel plate capacitor factors on which charge storage capacity depend are the plates area and the dielectric material used between the plates. Its capacitance is controlled by the formula[25]:

$$C = A\epsilon / d$$

### 1.2.3 Supercapacitors

The shortcomings confronted in the use of fuel cells and electrochemical batteries as energy source, such as low power output, costly components and inadequate lifespan stability, significant growth was given to supercapacitors to substitute for the lower power output characteristics of the batteries and fuel cells [26].

Supercapacitors are also known as electrochemical capacitors. As compared to fuel cells and batteries supercapacitors are the most suitable energy storage device due to their long cyclic life, low price, and stability[27]. Supercapacitors provide high power output and do not cause environmental hazards comparative to fuel cells and batteries. Schematic illustration of supercapacitors is shown in the figure 1.5.

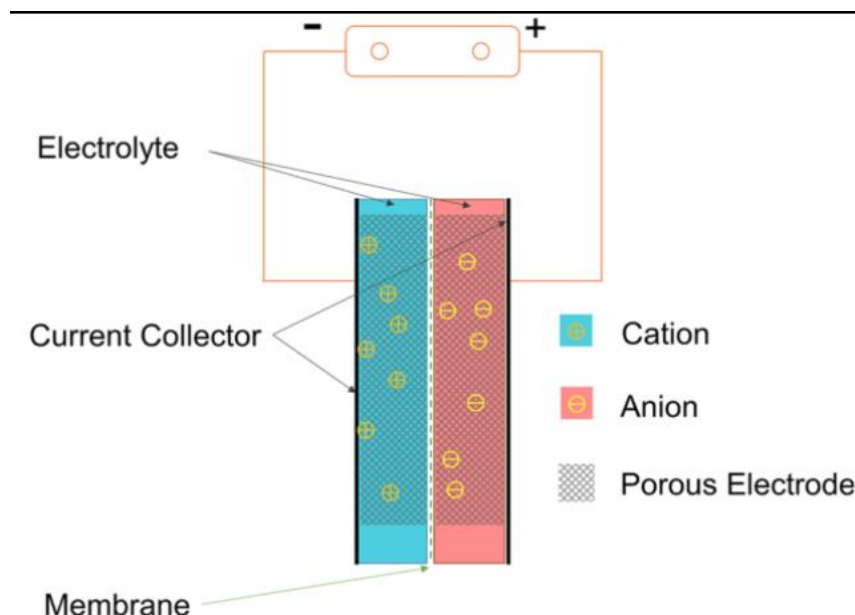


Figure 1.5 Schematic Illustration of super capacitor

#### 1.2.3.1 Working Principle

A supercapacitor rule is same as of standard electrostatic capacitors. A supercapacitor comprises of two anodes, an electrolyte, and a separator between the cathodes. At the point when a force source is applied on the contrary terminals of anode, charges start to assemble on the outside of the cathodes[28]. The ionic species present in the electrolyte overflow out of the separator film on account of law of fascination and enter the pores of the terminal material which if there should arise an

occurrence of supercapacitors is unnecessarily permeable. A significant part of supercapacitor anode materials is the plan designing[29]. It ought to be planned in a manner to forestall the undesirable recombining of particles. To get improved vitality thickness and high capacitance, materials with high porosity and more prominent surface territory with least separation between the terminals are good in supercapacitors. A significant part of supercapacitor's anode materials is configuration designing[30]. It ought to be designed so it gets a higher vitality thickness and high capacitance contrasted with that of customary capacitors. It is further categorized into three varieties based on the energy storage mechanism.

- i. Electrochemical double layer capacitor
- ii. Pseudo capacitors
- iii. Hybrid capacitors

#### **1.2.3.2 Electrochemical double layer capacitors (EDLC)**

In the EDLC, electrical vitality is put away by utilizing the system of charge gathering on the interface of cathode and electrolyte. In EDLC the anode material's surface zone is powerful on the vitality stockpiling capacities of the gadget[31]. The high surface territory connects between the dynamic material and electrolyte for charge continuing the interface. In charging cycle of electron twofold layer capacitor, the electrons move from cathode to anode by the impact of outer applied likely contrast and the cation move from the anode to cathode[32]. Electrons go in reverse during the releasing cycle. In this kind of supercapacitor, there is in no substance redox response include. The most well-known utilized materials in EDLC are carbon based, for example, graphite powder, MWCNTs, SWCNTs, actuated carbon and graphene and so on. A schematic diagram for the working of EDLC is shown in figure 1.5.

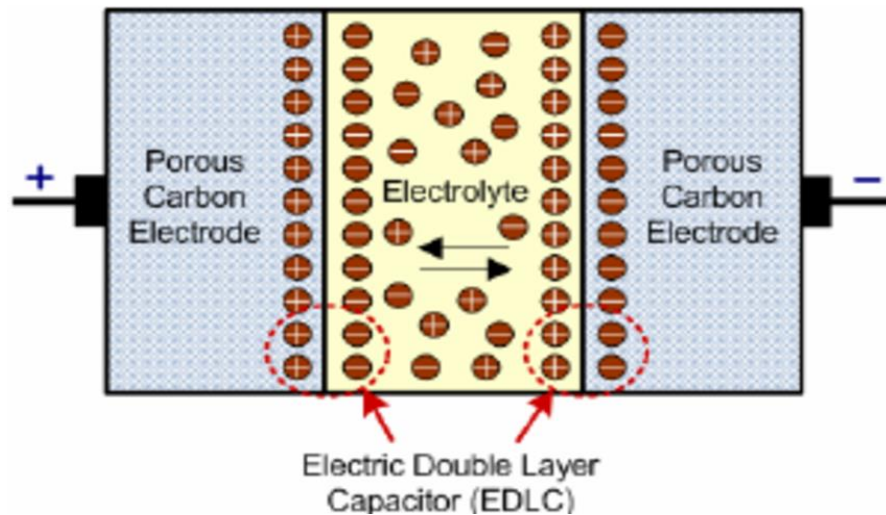


Figure 1.6 schematic illustration of EDLC supercapacitors

#### 1.2.4 Pseudo capacitors

This sort of supercapacitor is not quite the same as EDLC because of its working standard. In this sort, concoction redox responses are included at the interface of the dynamic material[33]. In selectivity of material for terminals of supercapacitor needs to have the option to show the redox response affected by remotely applied charge. There is 7 a huge assortment of material being utilized in pseudo capacitors, for example, natural materials (polyaniline and polypyrrole), metal oxides (NiO, Co<sub>3</sub>O<sub>4</sub>, CuO, FeCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> and so on.) and metal sulfides ( MoS<sub>2</sub>) and so forth[34]. A schematic diagram for the working of pseudo capacitors is shown in figure 1.7.

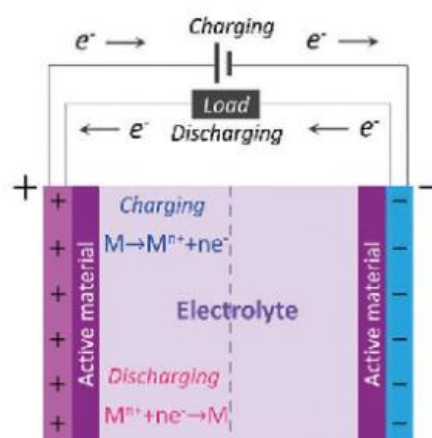


Figure 1.7 Schematic illustration of pseudo capacitors

Power density, high specific capacity and low expense are the attractions of pseudo-capacitors and limited stability, low performance, and high load / discharge cycle semi-conductors impede accelerated electron transport[35].

### 1.2.5 Hybrid Supercapacitor

Hybrid supercapacitors are the blend of both EDLC, and Pseudo capacitor as appeared in Figure 1.8. Crossover supercapacitor is various sorts by making composite of EDLC and a pseudo capacitor or by uneven in which positive terminal is pseudo capacitor and negative anode is EDLC[36]. The key attributes of hybrid supercapacitors are

- i. Excellent specific capacitance
- ii. Power Density
- iii. High Energy Density
- iv. Good cyclic stability

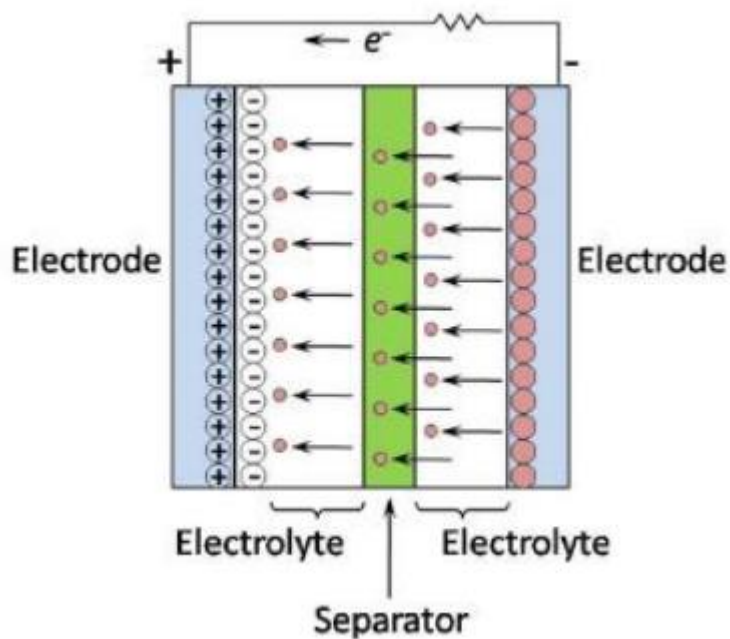


Figure 1.8 Hybrid Supercapacitor mechanism[37]



### **1.2.6 Asymmetric energy storage devices**

To achieve high energy and power density both fundamental principles of batteries and double layer capacitors are used in asymmetric energy storage devices and two distinct varieties of electrode materials are used. To provide high power density an electrode is made that provide high power density and the other electrode contain material having faradaic reaction which is used as anode to provide high energy density.

### **1.3 Applications of supercapacitors**

It has been a possible aspirant for several different structures, due to the substantial characteristics of supercapacitors. Some of the applications concerning supercapacitors are described below:

- i. Storage devices for memory
- ii. Computer systems such as cellular computing, electrical control, continuous power supplies (UPS)
- iii. Hybrid electric vehicles (HEV) and passenger vehicles
- iv. Commercial laser devices, medical equipment
- v. Electronic Power Supply [38]
- vi. Wireless method of contact [39]
- vii. Sustainable incorporation
- viii. Management of industrial resources

### **1.4 Research aims and objectives**

This project aims to prepare transition metal oxide nanoparticles  $\text{FeCoO}_4$  or  $\text{FeCo}_2\text{O}_4$  and its composites with PANI to investigate its charge storage application. The sequential targets were:

1. The synthesis of  $\text{FeCoO}_4$  (or  $\text{FeCo}_2\text{O}_4$ ) nanoparticles and PANI followed by the synthesis of their binary composite of  $\text{FeCoO}_4/\text{PANI}$ .
2. To modify the  $\text{FeCoO}_4/\text{PANI}$  or (or  $\text{FeCo}_2\text{O}_4$ ) composite with suitable carbon content material such as CNTs.

3. Structural characterizations of the synthesized composite by XRD, SEM, Raman, and FTIR.
4. Electrochemical study of the material for its faradic and capacitive behaviour by employing cyclic voltammetry, galvanostatic charge-discharge (GCD) response analysis.
5. Interpretation of the results for the use of synthesized material as electrode in batteries or/and supercapacitor devices.

## Chapter 2: Literature Review

The electrical energy produced from either of the sources can be stored electrochemically in two different ways. One is the “faradic process” which is the oxidation reduction of the electrochemically active material. This redox process leads to the electrical work which allows the charges to flow between two electrodes which are at different potentials. In the faradic reaction electrochemical conversion of material occurs such phenomenon is used in batteries. The second way is the “electrostatic” storage which is achieved by the charge separation at the polarized interface and the resultant device is nothing, but conventional capacitor also called electrolytic capacitor. However, conventional capacitor with the advantage of high cyclability is limited with its low energy density ( $\leq 10^{-2}$ W/Kg). When such capacitors are combined with liquid electrolyte and high specific surface area electrode material then they can achieve a high capacitance up to several hundred Farads per gram (F/g) in aqueous electrolyte. The combination produces another class of storage device called super capacitor or electrochemical capacitor (EC). Each of the three energy storage devices has its own merits and demerits and are used commercially in different applications. Till the mid of eighteenth century, emergence of different properties of supercapacitors were unknown. In early ages, it was witnessed that rubbing of different materials results I the innovation of charge potential over the conductive surfaces. Over 170 years ago, understanding at molecular level of electricity started and then with the study of J.J. Thomson, Millikan, and Michel Faraday. Supercapacitors lately have drawn more consideration from the specialists. Low energy density is the most important issue of the supercapacitor devices other than this issue ongoing headway in the electrode material and technology; they are filling the gap between the batteries and fuel cells. In association with the early investigations of reasons related with impacts of static electricity, the coming of Leyden container 1746 at Leyden in the Netherlands, the examinations of charge storage and separation mechanisms on the jar surface with glass as separator were of great significance in the field of study of power, electrochemical, electrical innovations and electronics. The device was known as "Condenser" in the early works, and it was attributed to Dignitary Kleist at Leyden and simultaneously to Kamin, Pomerania. Later, the condenser terminology was

changed and took the term of "Capacitor" in a wide range of epitomes and its potential as far as charge storage was replaced as "Capacitance" [40].

## 2.1 Transition metal oxides/ sulphides

Transition metal oxides are accepted to be one most encouraging class of electrode materials for supercapacitor application on account of certain benefits for example their high specific capacitance (because of the pseudocapacitive nature coming about because of faradic processes including synthetic responses and chemical reactions). Normal transition metal oxides which are concentrated as anode materials are RuO<sub>2</sub>[41], MnO<sub>2</sub> [42], Co<sub>3</sub>O<sub>4</sub>[43] V<sub>2</sub>O<sub>5</sub>[44], and NiO [45]. Among the other metal oxides, RuO<sub>2</sub> is quite possibly the most famous anode materials for its application in supercapacitors because of some remarkable qualities like high theoretical value for specific capacitance (1500 – 2200 for RuO<sub>2</sub>), a wide range of expected window, great electrical conductivity, and great reversibility[46]. Nonetheless, practical applications of ruthenium are restricted since ruthenium metal is harmful and costly (because of its restricted accessibility)[47]. This transferred the consideration of analysts on discovering minimal expense (MO<sub>x</sub>) choices for fruitful commercialization of supercapacitors. In any case, (MO<sub>x</sub>) based electrode material goes through volume instigated structural changes and extreme loss of capacity over delayed charge-release and they likewise languish execution misfortune over having lower electrical conductivity than carbon materials. The binary oxides with equation (AB<sub>2</sub>O<sub>4</sub>, for example, CuCo<sub>2</sub>O<sub>4</sub>, ZnMn<sub>2</sub>O<sub>4</sub>, MnCo<sub>2</sub>O<sub>4</sub>, and NiCo<sub>2</sub>O<sub>4</sub> shows unrivalled execution due to better performance by improved specific capacitance and have drawn in significant consideration among the researchers[48]. Metal oxides (MO<sub>x</sub>) and their composites with different materials like polymers are considered as one most encouraging electrode materials for supercapacitor applications. Progress metal sulfides-based cathode materials has gotten well known because of a portion of their novel attributes like minimal expense, wealth, high hypothetical capacitance, and more prominent ionic diffusivity [49]. Additionally, the electrical conductivity of binary metal sulfides is better a result of the inclusion of faradic responses and restricted band gap . In addition, their electrochemical movement is additionally more prominent considering the transfer of oxygen with sulfur particles that have more

noteworthy ionic conductivity [50]. Normal transition metal oxides that are at present explored for literature review chapter 2 are  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnO}$ . Consideration has been drawn on composites incorporated with electro conducting polymers, because of their scope of properties and minimal expense contrasted with valuable metals. Conjugated heterocyclic polymers, for example, polyaniline (PANI), polypyrrole (Ppy) and poly(3-methylthiophene) (P3MT) have been the subject of numerous examinations, because of their likely use in regions, for example, hardware [51], biosensors and actuators [52], electrochemistry and electrocatalysis.

These applications depend on the:

- i. electronic conductivity of these polymers
- ii. reversible changes of conductivity
- iii. different properties with a changing oxidation state (switching) [53].

Spinel iron oxides,  $\text{MFe}_2\text{O}_4$ , have gotten extensive consideration in light of the fact that their attractive properties can be differed deliberately by changing the character of the divalent  $\text{M}^{2+}$  cation (M: Mn, Co, Ni, Zn, and so forth) without changing the spinel crystal structure [4]. Spinel iron oxide particles have been created on a research center scale by strategies, for example, microemulsion synthesis [6], hydrothermal techniques [8], coprecipitation [5], and sol-gel synthesis [7]. Following hydrothermal route Nanostructured porous wires of  $\text{FeCo}_2\text{O}_4$  were developed on nickel foam and were utilized as additive/binder free electrode to explore the electrochemical conduction of  $\text{FeCo}_2\text{O}_4$  as electrode materials for supercapacitors. In initial cycling, a high specific capacitance of  $407 \text{ Fg}^{-1}$  at a scan rate of  $10 \text{ mV s}^{-1}$  was obtained. The exhibition of the pre-arranged  $\text{FeCo}_2\text{O}_4$  test is discovered to be obviously superior to the relating single oxides. Moreover, porous nanostructured  $\text{FeCo}_2\text{O}_4//\text{AC}$  asymmetric supercapacitors were gathered and could accomplish a high energy density of  $23 \text{ Wh kg}^{-1}$  and a power density of  $3780 \text{ W kg}^{-1}$  [54].

### **2.1.1 Cobalt Oxide:**

As far as energy applications are concerned, cobalt oxide has attracted great interest for batteries and supercapacitors as well [55]-[56]. Out of four states of cobalt

oxide two are required for energy storage. Cobalt (II) oxide, Cobalt (III) oxide, Cobalt (IV) oxide, and Cobalt (II, III) oxide.

#### **2.1.1.1 Limitations**

- i. High resistivity
- ii. Toxic nature of Co
- iii. Low charge ionic conductivity.

To resolve this issue researchers, try different strategies by making hybrid structure of Co or its composites with different metals or polymers. Poizot et al. utilize Co as the first run through utilized as anode for lithium-ion battery in 2000 [57]. In supercapacitor so many studies were done depending on the morphology since capacitance is morphology based.

#### **2.1.2. Iron (III) oxide Fe<sub>2</sub>O<sub>3</sub>**

Magnetic nanomaterials have attracted great attention due to their technological applications and physical properties. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), holds great importance among all the electrode materials due to its

- i. High theoretical C<sub>sp</sub>
- ii. Suitable potential window
- iii. Low cost
- iv. Abundance
- v. Non-toxic
- vi. High corrosion resistance and environment friendly properties.

For magnetic and structural phase transitions of nanoparticles, and polymorphism studies Iron (III) oxide Fe<sub>2</sub>O<sub>3</sub> is an important compound in basic research viewpoint. Amorphous Fe<sub>2</sub>O<sub>3</sub> and four of its polymorphs ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ) are well established and exist in nature. N-type properties are found in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and hence it is used for gas sensing, catalysis, medical fields, photo electrodes and electrode materials [58].

## 2.2 Conducting Polymers

Electronically directing polymers address a fascinating class of materials for use in electrochemical capacitors because of their qualities like eco-friendly, minimal expense, low obstruction, high conductivity in the doped state, wide potential window, faradic reversibility, high porosity, high stockpiling limit, and easy blend [59]. They are conductive because of the presence of formed frameworks that can move electrons along the polymer's spine. The primary procedures to orchestrate them are synthetic oxidation or reduction chemical testimony. These strategies are best a direct result of minimal expense and simple preparing [40]-[23]. The morphology of these polymeric materials can be altering the synthesis conditions bringing about various assortments, for example, nanowalls, nano powder, nanosheets, and so on. The most well-known conductive polymers, for example, polypyrrole (PPy), polyaniline (PANI), Poly (3,4-ethylene dioxythiophene) (PEDOT) and polythiophene (PTh) have been proposed by a few experimenters as anode materials for supercapacitors [57]-[58]-[59]. The electrical conductivity can be brought into polymers by the way toward doping. When framed, the polymers can exist in either p-doped, n-doped, or undoped state. At the point when the polymer backbone gets emphatically charged by oxidizing, the particles are moved to the polymer spine, known as a p-doped state with high electronic conductivity, ordinarily in the scope of  $1 - 100\text{S/cm}$ . At the point when the polymer spine gets positively charged by decreasing them, polymer discharge those particles into an electrolyte, known as a n-doped state, and this state likewise has critical electronic conductivity [60].

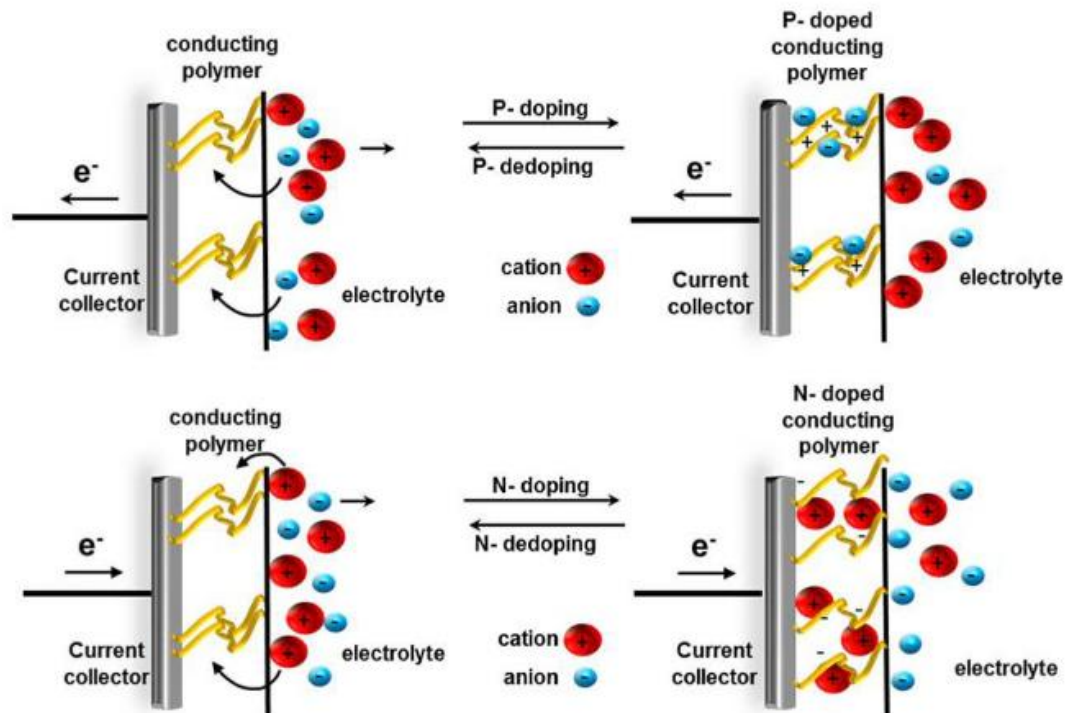


Figure 2.1 Charge/discharge process in p-doped & n-doped polymeric electrodes [61].

During fast charge-discharge cycles, large volume changes limit the long-term cyclic stability which can result in fetal degradation [62]. To resolve this issue transition metal chalcogenides or oxides can be added or by using polymers incorporated with carbonaceous materials due to which electrical conductivity of polymers and cyclic stability can be increased. So polymers are helping to enhance capacitive behavior of charge storage devices by making composites with the transition metals [63].

### 2.3 Polyaniline (PANI) based supercapacitors

Better conductivity and a great capacitive nature of conducting polymers have attracted great attention in energy storage devices as electrode material since 1960 [64]. Kaner and his coworkers used the polymer PANI for the very first time in supercapacitors [65]. some of the most important advantages of polymer polyaniline as listed as:

- i. Simple synthesis process
- ii. Efficient conductivity
- iii. Better flexibility



- iv. Multi-redox reactions
- v. At a very low price better specific capacitance [38]
- vi. Good electrochemical activity
- vii. High reversible pseudo capacitance
- viii. Stable thermal and environmentally friendly properties[66]
- ix. Great potential for supercapacitor applications
- x. Quick oxidation-reduction reactions [67]

After the Kaner, another gathering dealing with supercapacitors Rudge et al. thought the impact of doping on the presentation of PANI in supercapacitors applications [68]. Polyaniline (PANI) is the most guaranteed CP for application as an electrode in redox supercapacitors [69].

Conductive polymers/nanocomposites can be synthesized by two techniques; chemical strategy in which an oxidizing agent is utilized and in situ polymerization happens [20]-[48]. Another technique is electrochemical combination of conductive polymeric nano composites in which nano materials are scattered in a monomer arrangement and nanocomposite are framed by electro polymerization. Carbon materials are reasonable for the creation of PANI based composites because of their high stability, great conductivity, and huge surface region, which can support the structures of PANI during the doping and de-doping of counter particles [70]

### **2.3.1 Limitation**

Formation of polycations and loss of electron effect the charge storage mechanism in Conducting Polymers which triggers the anions present in the solution to take place in Conducting Polymer to provide electroneutrality. Due to the recurring charge-discharge process results in accumulation of stress on polymer, that is associated with poor life cycle. [71].

### **2.3.2 Improvement**

The key to this problem can be solved by applying nano materials to integrate nanocomposites. An entangled polymer matrix is formed by the solution of dispersed

nanoparticles and nano composites. The improvements significantly noticed in properties are:

- i. Flame retardants [17]
- ii. Electrical conductance [72]
- iii. Thermal conductance [48]
- iv. Impact strengthening.

## **Chapter 3: Experimental section**

### **3.1 Synthesis routes**

For the synthesis of perovskite nano crystals (NCs) both bottom up and top down approaches are being used. Most of the perovskite NCs were synthesized by bottom-up approaches and discussed in detail below:

#### **3.1.1 Top-down Approaches**

All the physical synthesis methods in which the bulk material break into small particles by using any form of energy like mechanical and chemical. Synthesis techniques are like ultrasonication, Ball Milling, sputtering etc. All these methods have a common disadvantage, lack of nanosized particles control.

#### **3.1.2 Bottom-up Approaches**

Bottom-up approaches in which material is synthesized by chemical reaction. These are widely used methods like hot injection method, Hydrothermal/ Solvothermal, Coprecipitation, Microemulsion method etc.

#### **3.1.3 Hydrothermal route**

Hydrothermal synthesis among all the synthesis methods is perhaps the most normally utilized techniques for arrangement of nanomaterials. It is essentially an arrangement response-based methodology. In hydrothermal synthesis, the arrangement of nanomaterials can occur in a wide temperature range from room temperature to exceptionally high temperatures. To control the morphology of the materials to be ready, either low-pressure factor or high-pressure conditions can be utilized relying upon the fume pressing factor of the fundamental arrangement in the response. Many sorts of nanomaterials have been effectively synthesized by the utilization of this methodology. There are huge benefits of hydrothermal technique over others. Aqueous union can create nanomaterials which are not steady at raised temperatures. Nanomaterials with high fume pressing factors can be delivered by the aqueous strategy with least loss of materials. The pieces of nanomaterials to be combined can be very much controlled in aqueous combination through fluid stage or multiphase

synthetic responses. This uncommon issue fills in as a gathering introducing the new exploration consequences of hydrothermal synthesis of nanomaterials.

### 3.1.4. Chemicals and Reagents

In table 3.1, all the chemicals that were used in the reaction are mentioned. No distillation or purification process was done, and all the reagents were used as purchased. Isopropanol was used to prepare all the solutions for synthesis and characterization process.

TABLE 3.1 CHEMICAL REAGENTS FOR THE SYNTHESIS OF COMPOSITE MATERIAL

Sr. No	Chemical Reagents	Chemical Formula	Molecular weight g/mole	Purity %	Source	Availability
1	Iron Nitrate	Fe (NO <sub>3</sub> ) <sub>2</sub> ·9H <sub>2</sub> O	403.9	100	DAEJUNG Company	NUST
2	Cobalt Nitrate	Co (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	290.93	100	UNI-CHEMICAL	NUST
3	Urea	CH <sub>4</sub> N <sub>2</sub> O	60.06	100	Fluka garantie	QAU
4	Aniline	C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	93.13	98	BDH Chemicals	QAU
5	Ammonium per sulphate	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	228.18	98	Sigma Aldrich	QAU
6	Sulphuric Acid	H <sub>2</sub> SO <sub>4</sub>	98.079	95.97	BDH Chemicals	QAU
7	Isopropanol	C <sub>3</sub> H <sub>8</sub> O	60.01	99	MERCK	NUST
8	Ethanol	C <sub>2</sub> H <sub>5</sub> OH	46.07	99	Sigma Aldrich	QAU

## 3.2. Hydrothermal Synthesis of Iron Cobalt oxide Nanoparticles

FeCo<sub>2</sub>O<sub>4</sub> was synthesized by a hydrothermal route. A schematic route for the synthesis of FeCo<sub>2</sub>O<sub>4</sub> is presented in figure 3.1. Firstly, 0.808g of Iron nitrate Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 1.164g of cobalt nitrate Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added in 30mL of Isopropanol, and stirred magnetically to make a homogeneous mixture. While magnetic stirring 7.2g of urea and 6mL of deionized water was also added in the mixture. After the addition of all the reagents the solution was stirred until a

homogeneous solution was formed. Then, this solution was shifted to Teflon lined stainless steel 100 mL autoclave and placed in an electric furnace for 16 hours at 140°C (for hydrothermal reaction). The autoclave was allowed to cool down at room temperature naturally after the completion of the hydrothermal reaction inside the autoclave. Then, the product formed was washed with deionized water using repeated centrifugation and at the end dispersed in water by sonication for 15 minutes. The product was filtered by the filtration assembly and washing with isopropanol was done thrice and once with deionized water, and then dried overnight in an oven at 50°C. After complete drying, the product was finely grounded using mortar pestle.

#### Solution preparation

- 0.808g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
- 1.164g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- 30mL of Isopropanol
- 6g of urea
- 6mL of deionized water

#### Stirring

- Magnetic stirring is done for 15 minutes to make a homogeneous solution.

#### Reaction

- Hydrothermal reaction was done in autoclave for 16 hours at a temperature of 140°C.

#### Filtration and washing

- The product was filtered and washed with isopropanol and deionized water multiple times.

#### Drying

- The product is dried overnight at 50°C.

#### Grinding

- Using pestle and mortar a fine powder was obtained.

*Figure 3.1 Hydrothermal Synthesis of  $\text{FeCo}_2\text{O}_4$ .*

### **3.3 PANI with FeCo<sub>2</sub>O<sub>4</sub> composite synthesis**

In situ polymerization of aniline with iron cobalt oxide (FeCo<sub>2</sub>O<sub>4</sub>) was performed to synthesize different ratios of the composite. About 10-12 different ratios of composite were prepared and the best electrochemical material was selected for the supercapacitor application. Different ratios obtained by the in-situ polymerization method are enlisted as:

- i. 10% PANI with 90% FeCo<sub>2</sub>O<sub>4</sub>
- ii. 20% PANI with 80% FeCo<sub>2</sub>O<sub>4</sub>
- iii. 30% PANI with 70% FeCo<sub>2</sub>O<sub>4</sub>
- iv. 40% PANI with 60% FeCo<sub>2</sub>O<sub>4</sub>
- v. 50% PANI with 50% FeCo<sub>2</sub>O<sub>4</sub>
- vi. 60% PANI with 40% FeCo<sub>2</sub>O<sub>4</sub>
- vii. 70% PANI with 30% FeCo<sub>2</sub>O<sub>4</sub>
- viii. 80% PANI with 20% FeCo<sub>2</sub>O<sub>4</sub>
- ix. 90% PANI with 10% FeCo<sub>2</sub>O<sub>4</sub>
- x. 95% PANI with 05% FeCo<sub>2</sub>O<sub>4</sub>
- xi. 98% PANI with 02% FeCo<sub>2</sub>O<sub>4</sub>

#### **3.3.1. 95% PANI with 5% FeCo<sub>2</sub>O<sub>4</sub> composite synthesis**

To synthesize 95% PANI with 5% FeCo<sub>2</sub>O<sub>4</sub> composite in situ polymerization of aniline was performed. To make 6g of the composite 0.3g of FeCo<sub>2</sub>O<sub>4</sub> was dissolved in 30mL of Isopropanol with continuous magnetic stirring and 5.7g of aniline was added drop wise by maintaining a chilling temperature and initiator Ammonium persulphate was added to initiate polymerization of aniline. The mixture was left for continuous magnetic stirring for about 18 hours and then filtered. Washing of filtrate was done thrice with DI water. Obtained composite was confirmed by performing characterization.

### Solution preparation

- 0.3 g of  $\text{FeCo}_2\text{O}_4$  was dissolved in 30 mL of isopropanol.

### Magnetic stirring

- homogeneous mixture is formed by continuous stirring.

### polymerization

- 5,7g of aniline was added drop wise.

### Initiation

- APS was added to initiate the polymerization reaction.

### Temperature maintainance

- chilled temperature of about  $15\text{ }^\circ\text{C}$  was maintained.

### Magnetic stirring

- continuous stirring was done for 18 hours.

### Filtration

- DI water was used to wash following filtration.

### Drying

- Filtrate was dried at  $50\text{ }^\circ\text{C}$  and product was obtained.

*Figure 3.2 Synthesis of 95% PANI with 5%  $\text{FeCo}_2\text{O}_4$  composite*

## Chapter4: Result and Discussions

This Chapter describes the results, the obtained data from therein, and their interpretation in the context of set objectives and hypotheses of the work.

### 4.1. X-ray diffraction Technique (XRD)

XRD is a rapid non-destructive method employed for the determination of crystal size(crystallinity) of compound equally applicable to liquid, powder, and crystals.

#### 4.1.1. Instrumental principle

X-ray diffraction works on the principle of constructive interference of X-rays and crystalline material. It is used for the crystal structure determination of the material. It is a non-destructive technique, and it provides fingerprints of Bragg's reflections of crystalline materials [73, 74].

$$2 d \sin\theta = n\lambda \dots\dots\dots (1)$$

This law gives the relationship between the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline material. Then detection of these diffracted rays processed and counted. Scanning at different  $2\theta$  angles is done due to the random orientation of particle diffraction in different directions is done.

These diffraction peaks are studied for the identification of the crystalline material because each crystalline material has its own set of particular d spacing. This identification process is done by comparing d-spacing with some standard reference patterns.

#### 4.1.2. Working

It consists of 3 main parts. A cathode tube, sample holder, and detector. X-rays are produced by heating filament element which accelerates electrons towards a target which collide with the target material with electrons. Crystal is composed of layers and planes "Diffraction" takes place, and it can be described as by Bragg's Law. These reflections' positions tell us about inter-layer spacing-ray diffraction tells us about the



phase, crystallinity, and sample purity. By this technique, one can also determine lattice mismatch, dislocations, and unit cell dimensions.

#### 4.1.3. Crystal Measurement

Size measurement of particles is done using the Debye Scherer equation as

$$D = K \lambda / \beta \cos \theta \dots\dots\dots (2)$$

D= size of particle,

K = shape factor = wavelength of X-ray,

$\beta$  = full wave half width and

$\theta$  is diffracted angel.

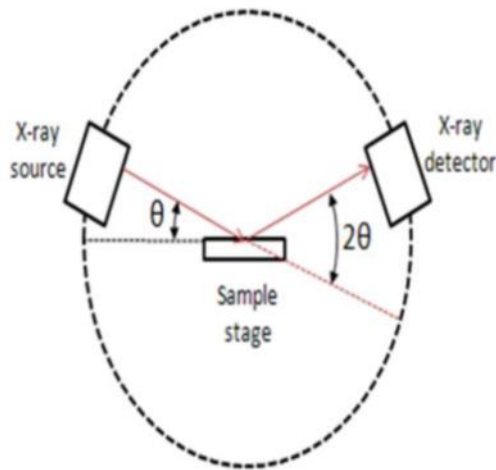


Figure 4.1 Schematic of XRD

#### 4.1.4. XRD analysis of Iron cobalt Oxide (FeCo<sub>2</sub>O<sub>4</sub>)

XRD was carried out to study the structural and compositional analysis of synthesized iron cobalt oxide (FCO). The results obtained by XRD analysis reveals the formation of the homogeneous cubic structure of Co<sub>3</sub>O<sub>4</sub> in complete agreement with JCPDS Card no. 01-080-1542. There are no peaks of any type of impurity detected in the XRD graph of Co<sub>3</sub>O<sub>4</sub>. This endorsed the successful replacement of

cobalt ions with iron ions in cobalt oxide. A slight peaks shift was observed toward lower angle in iron cobalt oxide. This peak shift is due to a slight difference of radius of iron ions as compared to cobalt ions. The increase in de spacing between the crystal plan was observed. The maximum x-ray diffraction was observed along the crystal plane (3 1 1) at  $2\theta = 36.6953$

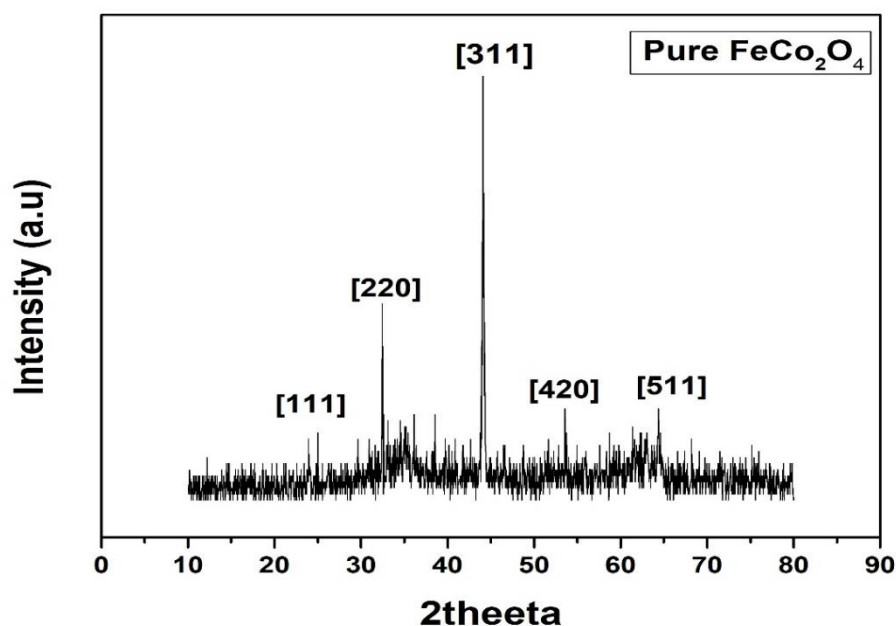


Figure 4.2 XRD of Pure Iron Oxide

#### 4.1.5. XRD Analysis of 95% PANI and 98%

The XRD was performed to investigate the crystal structure of the sample. This analysis confirms the presence of iron and cobalt ions in composite material. It was carried out to study the structural and compositional analysis of synthesized iron cobalt oxide. The XRD patterns of PANI doped by iron and cobalt oxide are shown in Figure. The results obtained by XRD analysis reveals the formation of the homogeneous cubic structure of  $\text{Co}_3\text{O}_4$  in complete agreement with JCPDS Card no 01-080-1542.

XRD pattern show that nanocrystalline iron cobalt oxide embedded into polycrystalline PANI to form crystalline nanocomposites. There are no peaks of any type of impurity detected in the XRD graph. This endorsed the successful replacement of cobalt ions with iron ions in cobalt oxide. Crystallite size of the  $\text{Co}_3\text{O}_4$  was

determined using Scherer's formula and found to be 35nm which closely agreement with that determined by Shambharkar [3]  $\text{Co}_3\text{O}_4$  nanoparticles with cubic structure.

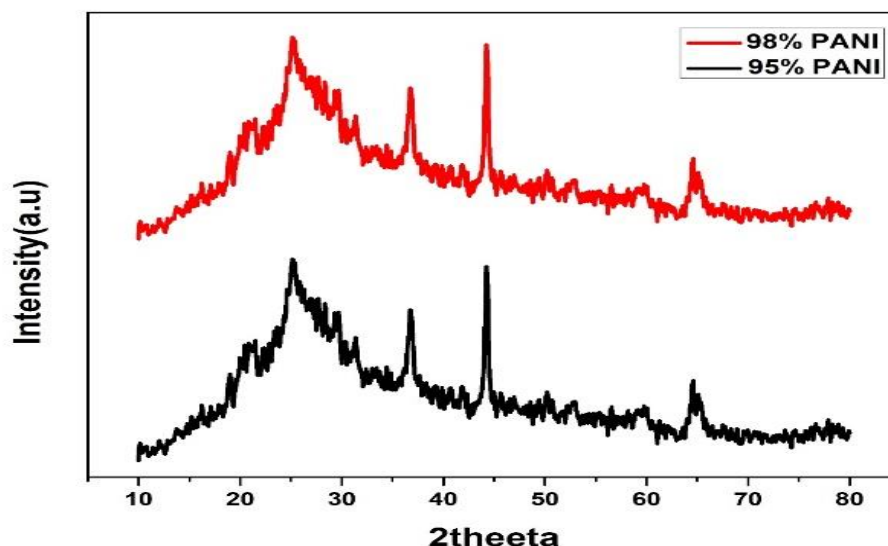


Figure 4.3 Xrd Spectra of  $\text{FeCo}_2\text{O}_4$  and 95% PANI and 98% PANI

A slight peaks shift was observed toward lower angle in iron cobalt oxide. This peak shift is due to a slight difference of radius of iron ions as compared to cobalt ions. The increase in de spacing between the crystal plan was observed. When nanoparticles are incorporated into PANI, the broad diffraction peaks of the PANI disappear gradually, which is possibly because the nanoparticles have acted as 'impurities' to hamper the growth of the PANI 'crystallites'.

## 4.2. Scanning Electron microscopy

In this technique, the fine beam of electrons is focused over a specimen's surface. Photons or electrons are knocked off from the material's surface in the result. These knocked off electrons are then focused on the detector. The output from the detector modulates the brightness of the cathode ray tube (CRT). Every point where the electron beams are focused and interact, it is plotted on the consequent end on CRT, and the material's image is produced [76].

The electron-surface interaction causes the release of secondary electrons (SE), backscattered electrons (BSE), and X-rays[5]. Secondary electrons are used for

detection. These electrons are emitted from the sample surface. So, a pronounced and clear image of the sample is obtained. It can reveal sample detail even less than 1nm in size. Also, the elastic scattering of incident electrons takes place and release backscattered electrons. They emerge from deeper locations as compared to secondary electrons. So, their resolution is comparatively low. When an inner shell electron knocks off from its shell, it emits characteristic x-rays [78].

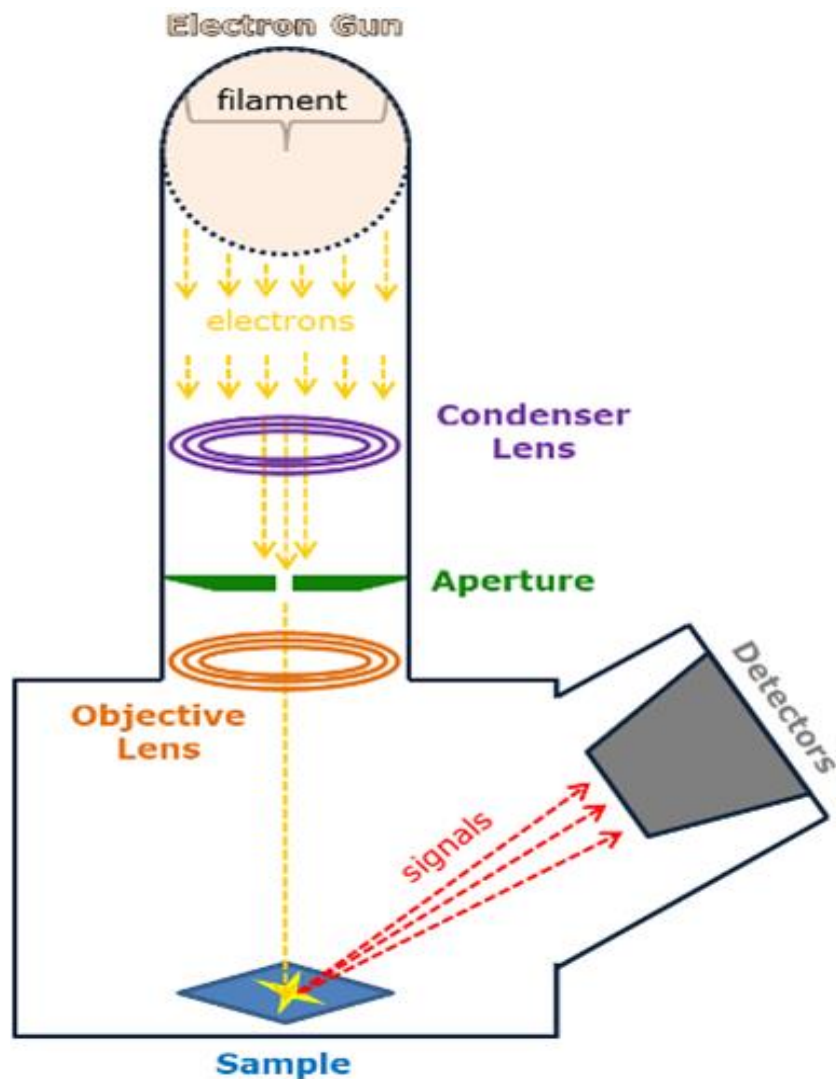


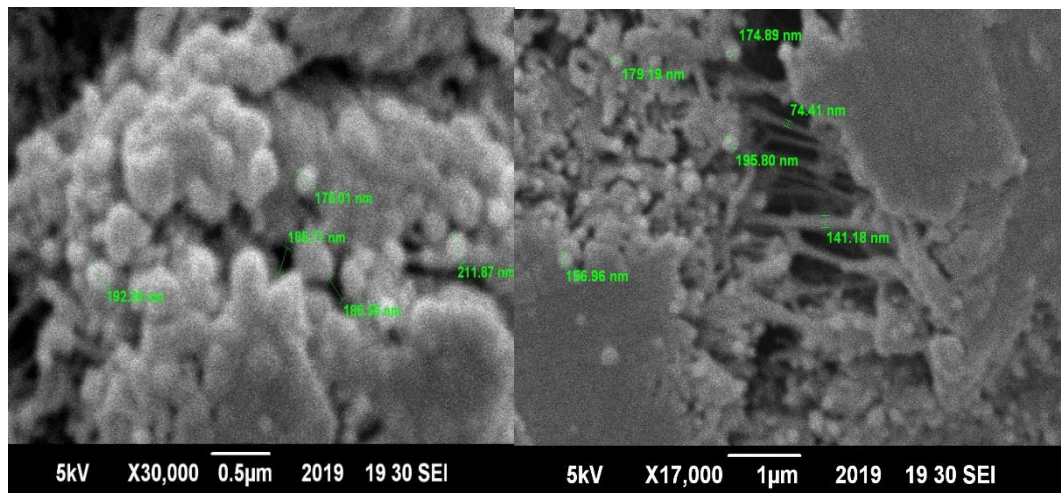
Figure 4.4 Schematics of SEM

#### 4.2.1. Analysis And identification of morphology of the sample

We use SEM as it has easy sample preparation, and we can figure our sample's morphology, chemistry, crystallography, and orientation of planes. Magnification of SEM can be controlled from 10 to 500,000 times. Morphology of the materials was

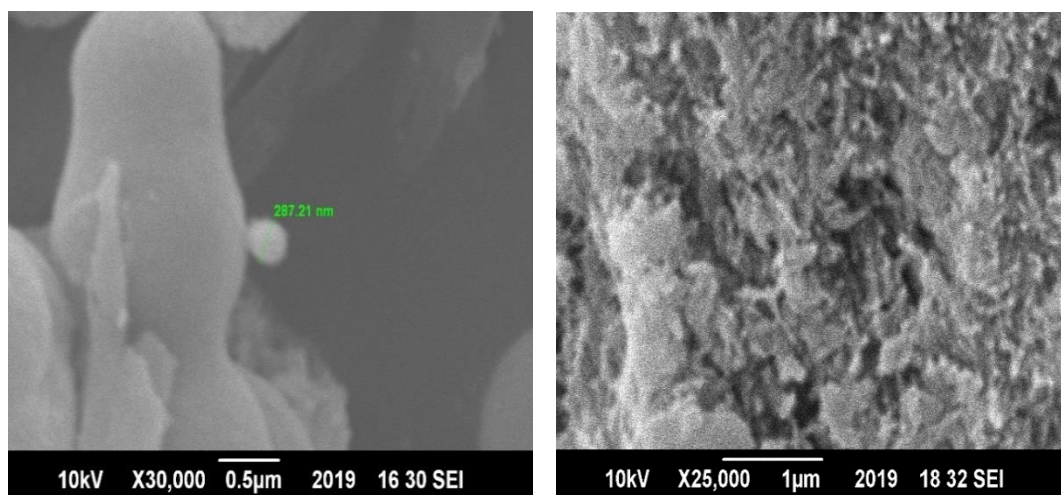
examined on (JEOL-JSM- 6490LA), The nanocomposites with an organized structure usually provide a new functional hybrid, with synergistic properties over their single component counterparts, which have attracted considerable attention for their potential application[79].

Figure 5a is a high-resolution SEM image of iron cobalt oxide. It revealed that our synthesized material consisted of nanosheets placed in vertically. This structure enhanced the surface area of iron cobalt oxide. This rise in surface area imposed a dominant effect on charge storage capabilities of composite material. Figure 5a is a SEM image of iron cobalt oxide with a high depth of focus. The morphology of of nanosheets help in movement of charges. This endorsed the charge mobility was enhanced due to vertical arrangement of sheets as shown in the figure 5.



(a)

(b)



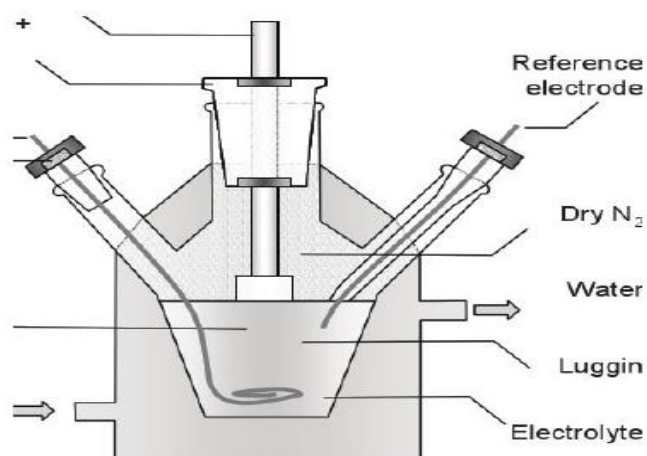
(c)

(d)

*Figure 4.5 (a) and (c) PANI and FeCo<sub>2</sub>O<sub>4</sub> composite at 0.5 μm (b) and (d) PANI and FeCo<sub>2</sub>O<sub>4</sub> composite at 1 μm*

#### 4.2.2 Electrode Preparation for testing electrochemical performance

For performing cyclic voltammetry, Glassy carbon electrode (GCE) was used as a working electrode. This GCE was modified with our synthesized material. In this modification process, 1mg of active material, 100 μL DMF, and 5 μL Nafion were sonicated for 20 minutes, and then 10 μL was drop cast on GCE and then dried. This was used as modified.



*Figure 4.6 Electrochemical workstation assembly*

#### 4.3. Cyclic Volta-metry

The cyclic voltammetry shows three pairs of characteristic peaks due to the redox reactions. It can be seen from figure 6.4 that the prepared electrode materials have better charge ad discharge reversible capacitance characteristics. The specific capacitances of samples are calculated from CV curves using the following equation.

$$C_s = \frac{\int idv}{mv\Delta V}$$

Where,

' $C_s$ ' is the specific capacitance

' $I$ ' is the current response density,

' $m$ ' is the mass of the active material, which is 1mg

' $v$ ' is the scan rate, and

$\Delta V$  is the potential window of discharge.

Specific capacitance decrease with the increasing scan rate due to limited faradaic redox reaction as less active sites available as compared to the lowest scan rate at which highest capacitance due to more redox-active sites.[8].This occurs because at low scan rate ions have maximum time for intercalation ,while at high scan rate ions have less time that's why specific capacitance becomes grater at lower scan rate.

#### **4.3.1. Cyclic Voltammetry of Pure FeCo<sub>2</sub>O<sub>4</sub>**

Figure 4.24 shows the CV curves for the iron cobalt oxide at the scan rate of 50,100 and 150 mVs<sup>-1</sup>. The CV was studied at the potential range of 0.1 V to 0.9 V. The non-rectangular graph of CV for iron cobalt oxide showed the pseudocapacitive type nature of FCO. The value of current in response to the applied potential difference increase with scan rate.

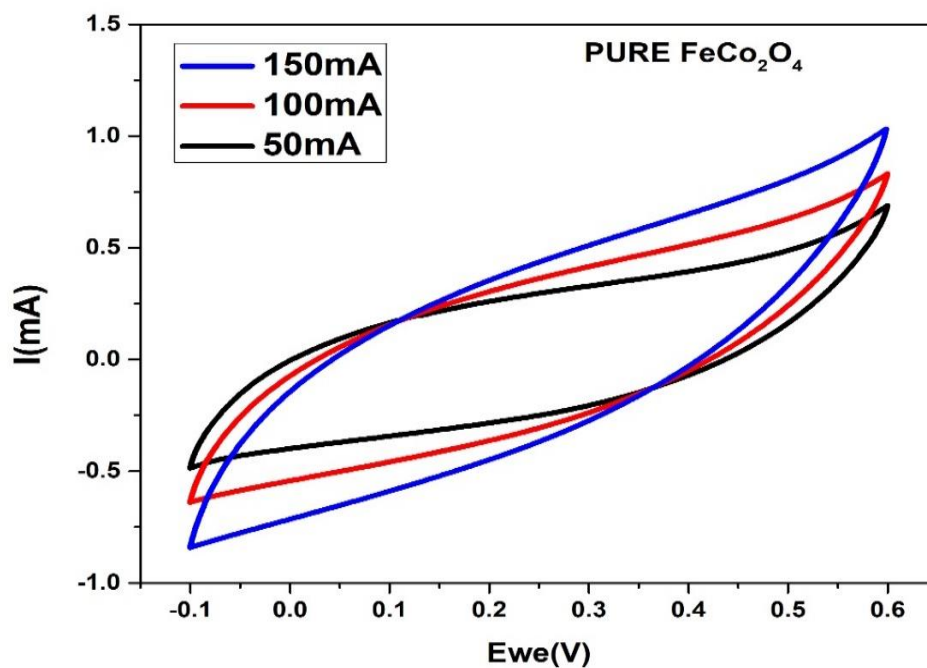


Figure 4.7 (a) CV of pure Iron oxide

Figure 4.7 (b) shows the CV curves for the 95% iron cobalt oxide and PANI composite at the scan rate of 50 mVs<sup>-1</sup>, 100 mVs<sup>-1</sup> and 100 mVs<sup>-1</sup>. The CV was studied at the potential range of - 0.1 V to 0.9 V. The non-rectangular graph of CV for cobalt oxide showed the pseudocapacitive type nature of iron cobalt oxide. The value of current in response to the applied potential difference increase with scan rate.



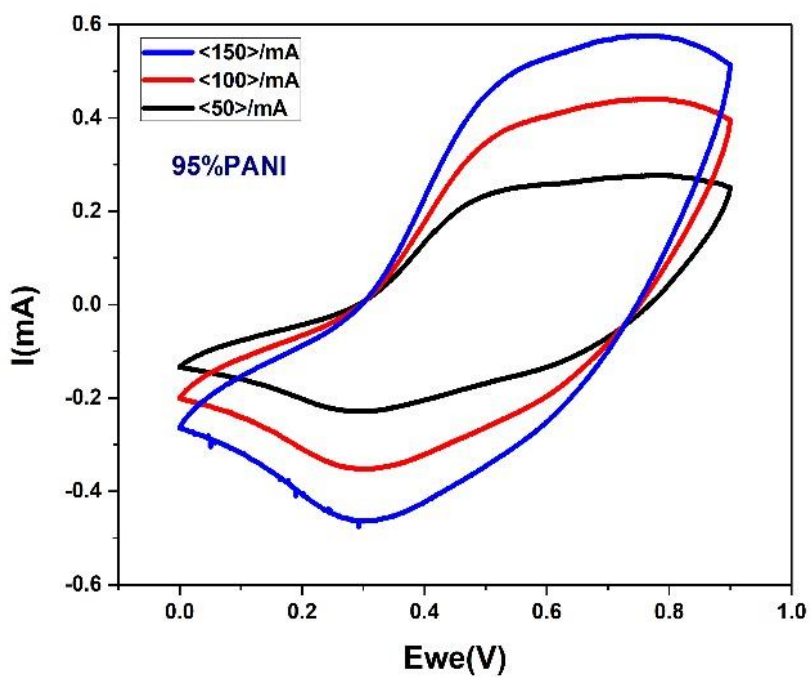


Figure 4.7 (b) 95% PANI

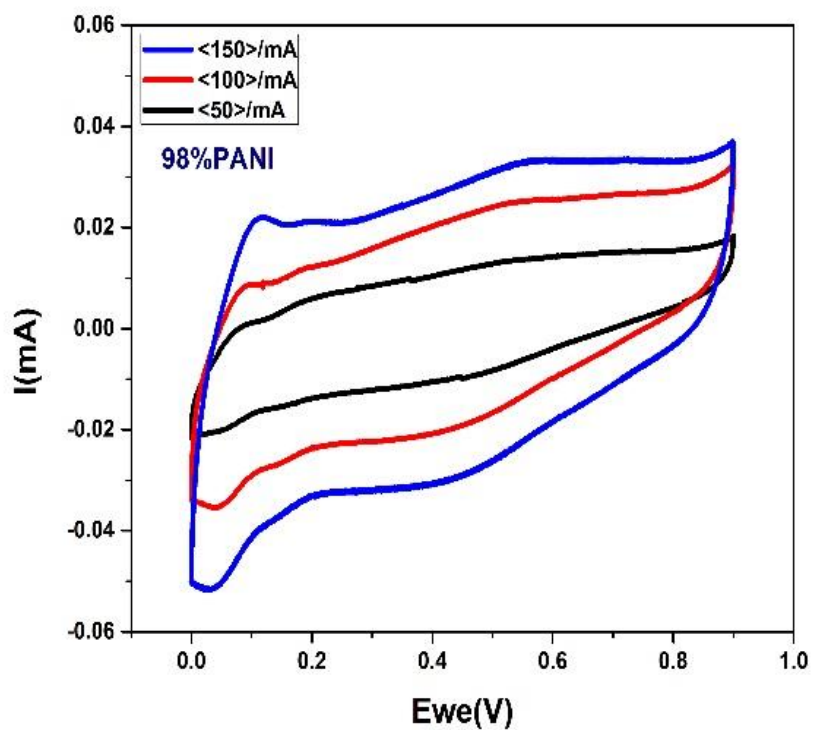


Figure 4.7 (c) 98% PANI

## Comparison of capacitance

TABLE 4.1 CAPACITANCE OF MATERIALS AT 50mA SCAN RATE

<b>Material</b>	<b>Scan Rate</b>	<b>Capacitance F/g</b>
Pure Iron-cobalt oxide	50mA	398.34
95 % PANI	50mA	1234
98% PANI	50mA	823

### 4.4. Galvanostatic Charge and Discharge technique (GCD)

GCD is the most common method to test the charging and discharging of the supercapacitors as well as batteries. GCD is used to measure the potential with time at constant current. Like CV, GCD curves of EDLC and Pseudo capacitor is different. EDLC materials GCD curve is linear whereas the Pseudo capacitor curve is not long showing the redox reaction occurs as shown in fig. It is a stable approach used for the electrochemical evaluation of materials. The GCD method is quite different from cyclic voltammetry because in this technique the current is controlled and measurement of voltage is done. The GCD approach is one of the most extensively used electrochemical techniques and it has the potential of extension from laboratory to industrial scales. These techniques are also some times termed as chronopotentiometry and it gives an insight of the following parameters such as

- i. Resistance
- ii. Capacitance
- iii. Stability

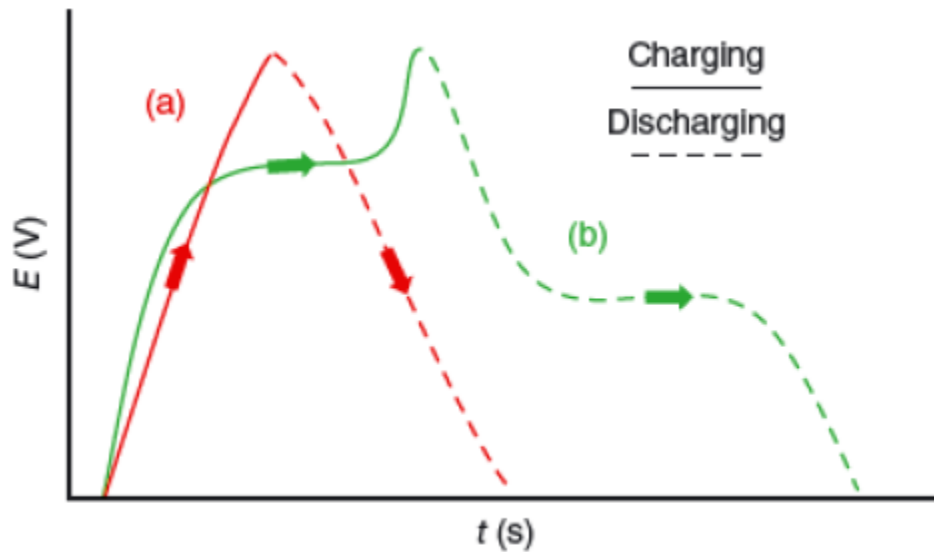


Figure 4.8 GCD curves of (a) EDLC (b) Pseudo capacitor [8]

The principle of GCD is based on the application of a current pulse to the working electrode WE and the measurement of resulting potential as function of time. The variation of voltage in a GCD test is given in the following equation

Here  $V(t)$  is the variable voltage, as a function of time,  $iR$  is the internal resistance,  $C$  is the capacitance and  $i$  is the current. it is clear from equation

$$C = I \Delta t \Delta V \dots \dots \dots (4)$$

**GCD of Pure iron cobalt oxide,**

**95% PANI and 98% PANI**

After visualizing the capacitive nature of cobalt oxide by cyclic voltammetry curve, we performed GCD to study the further capacitive properties of FCO. we performed the GCD at different current densities in order to study the abilities of FCO to sustain charge in detail as shown in fig. the maximum time for charge sustaining was observed on the current density of  $2 \text{ Ag}^{-1}$ .

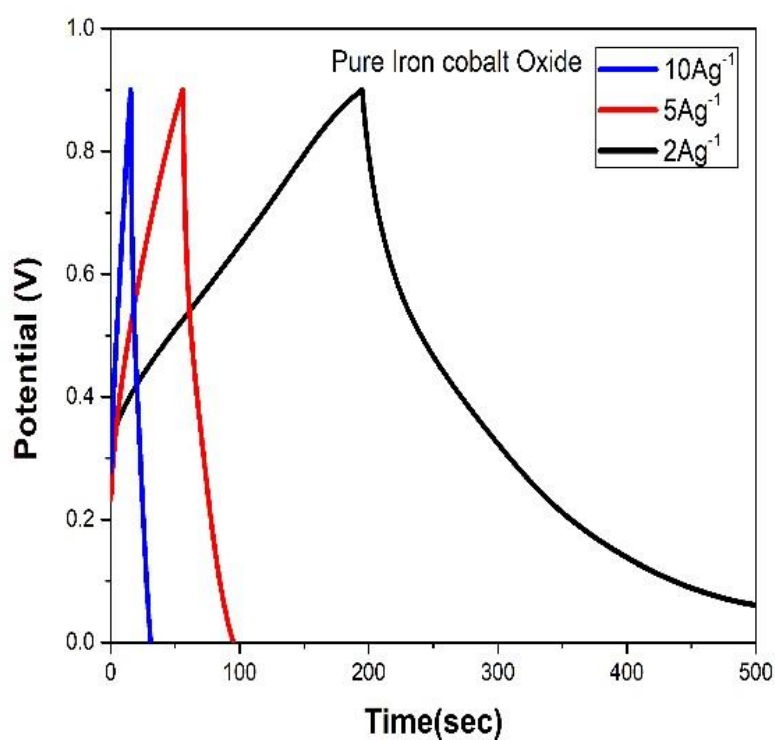


Figure 4.9 GCD of pure Iron Cocalt oxide

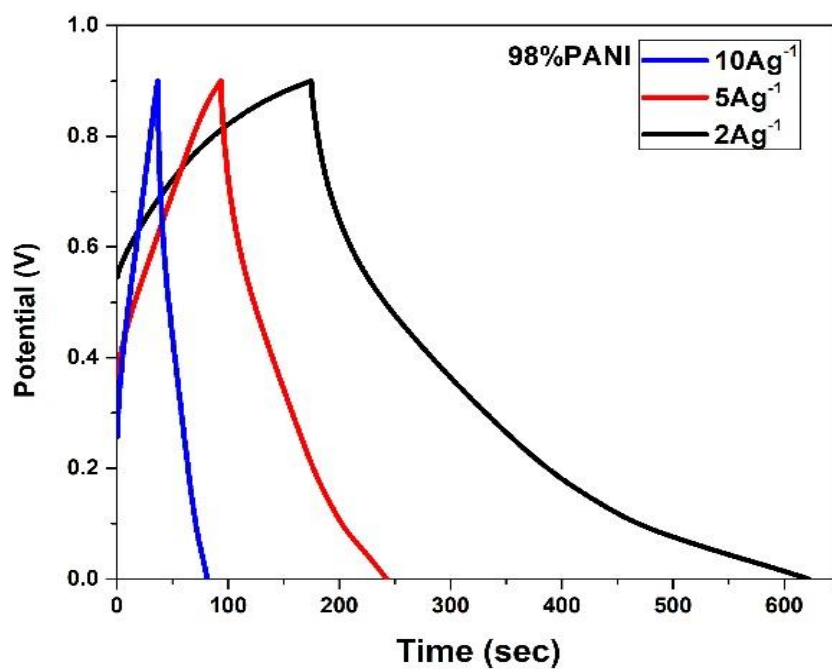


Figure 4.9 a GCD of 98% PANI

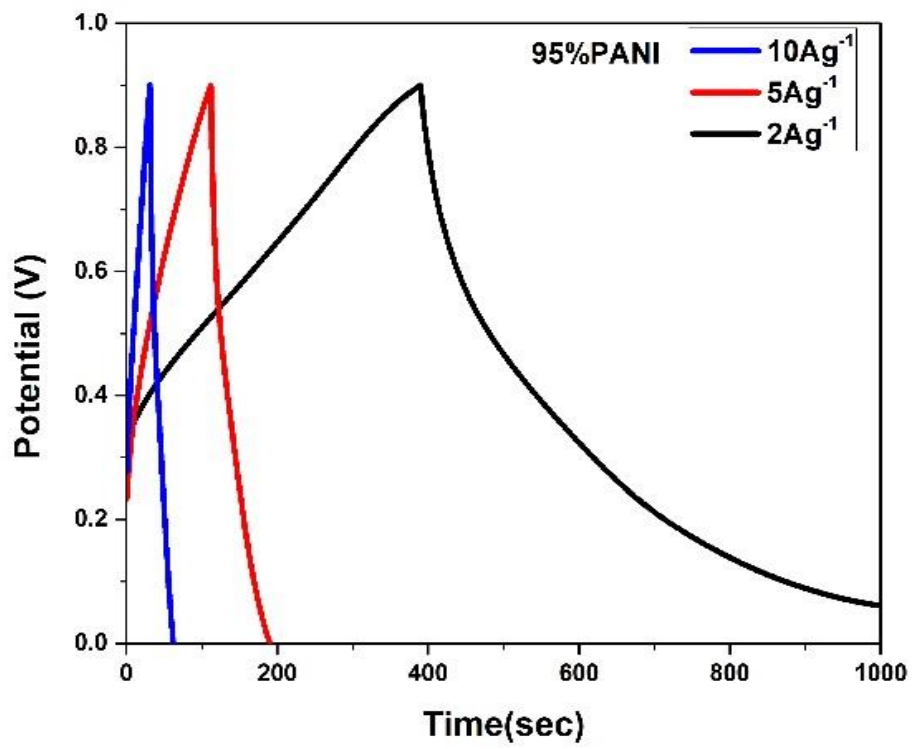


Figure 4.9b GCD of the 95% composite materials

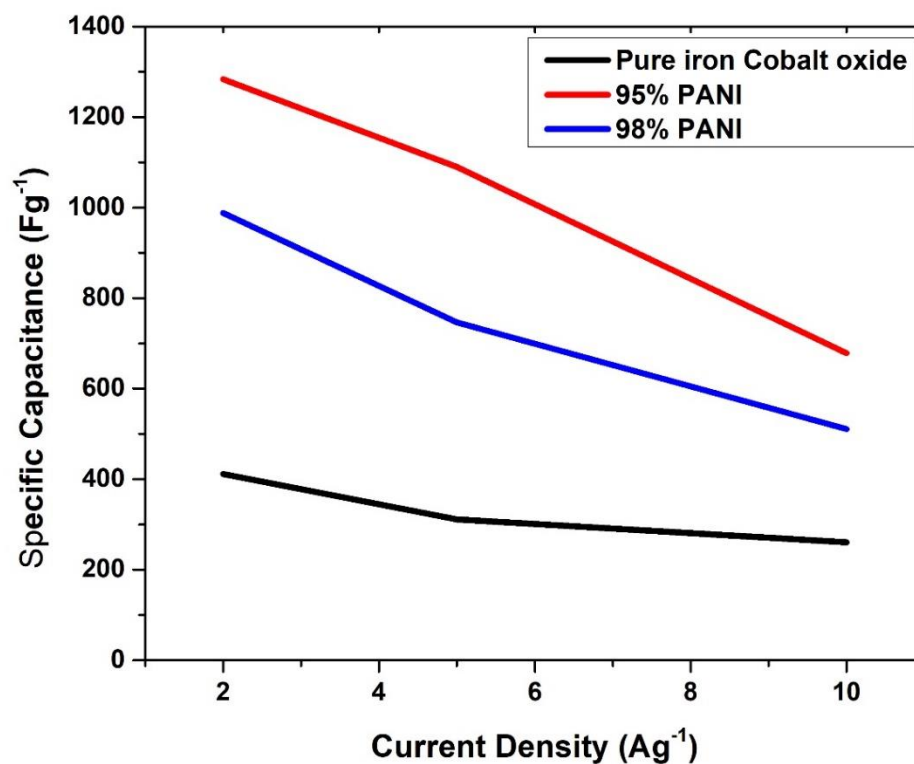


Figure 4.9c Comparison of GCD of Pre-Iron cobalt oxide with the composite material

TABLE 4.2 SPECIFIC CAPACITANCE OF MATERIALS AT 2, 5, AND 10 AG<sup>-1</sup>

Pure Iron cobalt oxide		95%PANI		98% PANI	
Current Density	Specific Capacitance	Current density	Specific Capacitance	Current Density	Specific Capacitance
Ag <sup>-1</sup>	Fg <sup>-1</sup>	Ag <sup>-1</sup>	Fg <sup>-1</sup>	Ag <sup>-1</sup>	Fg <sup>-1</sup>
2	411.1	2	1283.5	2	988
5	310.9	5	1090	5	746.5
10	260.9	10	678.56	10	510.8

## 4.5 Raman Spectroscopy

This is a modified form of FTIR technique with more efficient attributes than FTIR spectroscopy, which is non-destructive and more efficient. This technique is mostly used to determine the functional groups present in a compound. This technique is relying on observing the vibrations of chemical bond between the atoms. As each atom has different atomic mass, atomic radius, electro positivity and electronegativity. The vibrations between the atoms depend on these factors. So, it provides a unique fingerprint for each atom's bond vibrations which are used to determine the presence of atom. In this technique a monochromatic light falls on sample's specimen. The light interacts with vibrational frequency of chemical bond between the atoms. The light with similar wavelength to the bond get absorbed by the atoms and rest of the light transmit to the sensors placed in operating chamber to visualize the absorbed frequency by subtracting the received wavelength from source. The Raman shifts are mainly determined in terms of wave number ( $\text{cm}^{-1}$ ). There are three states of energy emission. due to the absorption of light. As a photon of infrared light is absorbed by material the

vibrating bond of material is able to emitted or scattered photon of same wavelength; this type of scattering is known as Rayleigh scattering.

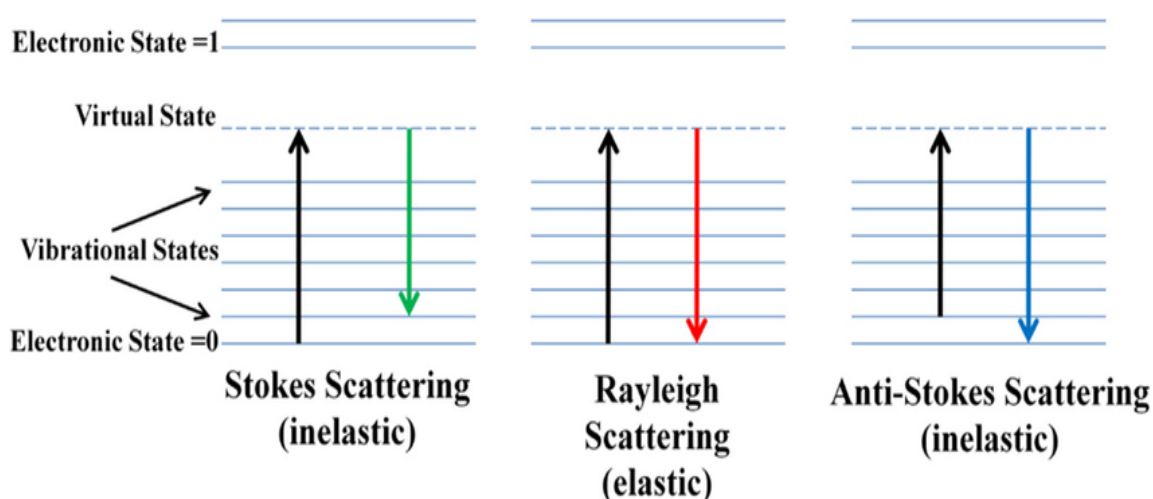


Figure 4.10 Energy level diagrams for Rayleigh scattering, Stokes Raman scattering and anti-Stokes Raman scattering.

#### 4.5.1. Comparison of Raman spectra

For further studies the properties of material were investigated by Raman scattering. The results in the figures shows the conformation of the iron and cobalt ion the sample. The peak shift from 600 to 1500  $\text{cm}^{-1}$  confirms Presence of composite material.

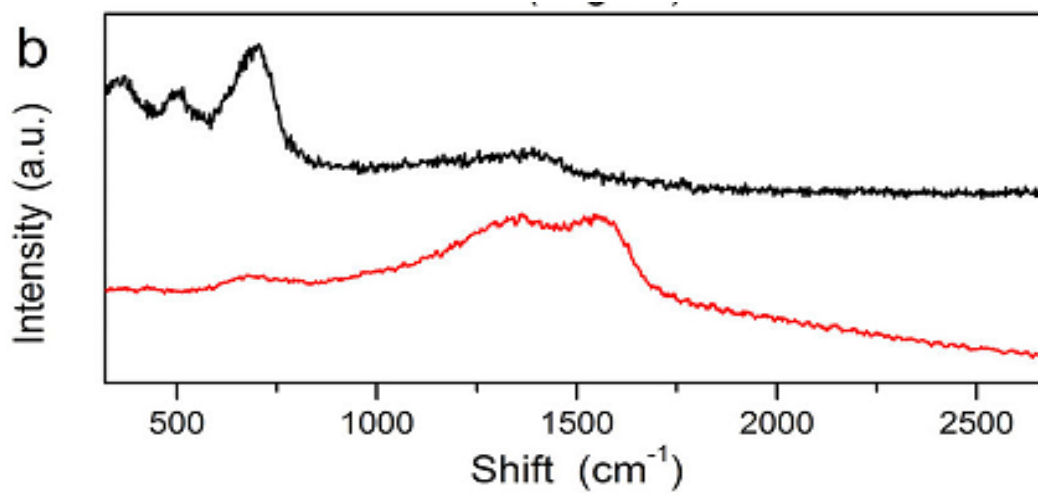


Figure 4.11 Raman spectra of composite material.



## **Conclusion**

Iron cobalt Oxide with PANI composite material were successfully synthesized. Excellent capacitance of  $1283.5 \text{ Fhg}^{-1}$  was achieved as well as it gives remarkable cyclic performance. Among both composite material 95% PANI shows excellent electrochemical properties. Superior electrochemical performance 95% PANI@IRON cobalt oxide illustrates that it will meet the modern-day energy applications demand and one of the desired materials for supercapacitors for flexible electronics. This material was first time tested for supercapacitors. The synthesized materials were employed as supercapacitor application.

In future, the same material will be coated on carbon fibers to fabricate the whole asymmetric device using electrolyte.

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