# Super-capacitive Properties of $Co_3O_4$/PPy/rGO Ternary Nanocomposites

Submitted By

**AZHAR RAZA**

(593-FBAS/MSPHY/F19)

Supervisor

**Dr. IMRAN MURTAZA**

Associate Professor

Department of Physics

Faculty of Basic and Applied Sciences

International Islamic University, Islamabad

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Polypyrroles

Graphene oxide

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# Final Approval

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It is certified that the work presented in this thesis has the title "**Super-capacitive Properties of $Co_3O_4$/PPy/rGO Ternary Nanocomposites** by **Azhar Raza,** Registration No. 593-FBAS/MSPHY/F19 fulfils the requirement for the award of the degree of MS Physics from the Department of Physics, International Islamic University, Islamabad, Pakistan.

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بسم الله الرحمن الرحيم

*In the name of Allah,*
*the Most Beneficent,*
*the Most Merciful*

**DEDICATED**

**To**

**My Beloved Parents And**

**Respected Teachers**

# Declaration of Originality

I, **AZHAR RAZA (Reg. No. 593-FBAS/MSPHY/F19)** student of MS Physics hereby declare that the work presented in the thesis titled **"Super-capacitive Properties of $Co_3O_4$/PPy/rGO ternary Nanocomposites"** in partial fulfilment of MS degree in Physics from International Islamic University Islamabad, Pakistan is my work and has not been published or submitted as research work or thesis in any form in any other university or institute in Pakistan or abroad.

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**Dr. IMRAN MURTAZA**
**Associate Professor / Incharge**
**Department of Physics**
**International Islamic University**
**Islamabad**

Dated: ________________

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**AZHAR RAZA**

# Abstract

In today's civilization, most energy consumers use non-renewable energy sources. Fossil fuels are finite in availability and bear the brunt of global warming. Solar, wind, hydropower and geothermal are cleaner alternatives to fossil fuels. Besides energy received from these resources, energy storage is also a big problem for scientific communities around the world nowadays. Energy storage is just as important as energy generation. Supercapacitors have acquired a lot of interest because of their great energy-delivering rate, extended life cycle and quick charge-discharge capabilities. Supercapacitors which will be employed in the residential, commercial and industrial sectors to improve energy storage, require economical and competent electrodes. Transition metal oxides, conducting polymers and reduced graphene oxide nanostructured materials have an enormous potential for energy storage devices owing to their high electrochemical performance and excellent stability. Herein, multiple methodologies were used to synthesize a ternary composite comprising cobalt oxide ($Co_3O_4$), polypyrrole (PPy) and reduced graphene oxide (rGO). In the first step, a simple hydrothermal approach was used to synthesize $Co_3O_4$/rGO and in the second step, PPy was incorporated by in situ polymerizing on the surface of $Co_3O_4$/rGO. X-ray Diffraction (XRD), which validates the cubical crystal structure of nanomaterials was used to study the structural analysis. Scanning Electron Microscopy (SEM) imaging showed that the particles were within the nanoscale. Energy dispersive X-ray (EDX) analysis reveals that there were no impurities in the synthesized materials. The synthesized $Co_3O_4$/PPy/rGO ternary nanocomposites have good electrochemical activity in redox reaction in sodium hydroxide electrolyte solution, demonstrated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) analysis. The Cobalt Oxide ($Co_3O_4$)/Polypyrrole (PPy)/Reduced Graphene Oxide (rGO) ternary nanocomposite electrode for Energy Storage Devices demonstrated the strong electrochemical activities of the electrode material determined from CV curves. With the modification in nanocomposite material concentrations in the electrodes for energy storage devices, electrochemical impedance characteristics were examined. By using CV, we found that $Co_3O_4$/PPy/rGO ternary nanocomposite having a high specific capacitance of 413 F/g with high cyclic stability.

# LIST OF CONTENTS

## List of Figures

# Chapter 1

# Introduction

## 1.1 The Need for Energy Storage:

Energy is now the most widely discussed topic at all levels of society and it is required in every field of life. The Nation's social and economic success has been dependent on the vast consumption of fossil fuels, non-renewable energy resources that easily existing carbon sources for the industrial revolution but with the increase in demand for oil, gas and coal consumption, there is a problematic situation for living creatures and with the use of these, environmental pollution increasing day by day and it is not less than a global warming situation for all living creatures. All of these energy resources due to their large amount of $CO_2$ emission create difficulties for all living creatures. In today's civilization, most energy consumers use non-renewable energy sources. Fossil fuels are finite in availability and bear the brunt of global warming. One of the key goals of scientific communities around the world is to find a lasting, clean and viable replacement for coal-powered energy. Therefore scientific communities all over the world are working on clean, sustainable energy sources like energy obtained from the sun, air and water because these energy resources have no negative impacts on living creatures also they have zero $CO_2$ emission [1, 2].

Solar, wind, hydropower and geothermal are cleaner alternatives to fossil fuels that are also eco-friendly and aid in the reduction of effects of certain pollutants in the environment. Besides energy received from these resources, energy storage is also a big problem for scientific communities around the world nowadays. Energy storage is just as important as energy generation.

Our modern civilization has recently demanded lightweight, flexible, affordable and environmentally friendly energy storage technologies to meet global concerns. Scientists have worked a lot on this issue. They developed a series of devices for energy storage like fuel cells, batteries, capacitors and super-capacitor but among all of this super-capacitor have great importance because they have extraordinary storage capacity as compared to others [3]. Supercapacitors have acquired a lot of interest because of their great energy-delivering rate, extended life cycle and quick charge-discharge capabilities [4].

## 1.2 Energy storage devices:

## 1.3 Fuel Cell:

A fuel cell produces electricity, water and heat without requiring combustion by mixing hydrogen and oxygen [5, 6]. As long as fuel and oxygen are obtainable, fuel cells can generate power. We can also say that with great efficiency and low pollutant emission, fuel cell convert fuel energy into electrical energy. A fuel cell is similar to a battery, but there is a significant difference: like a battery, a fuel cell does not store fuel and instead runs on a constant flow of fuel. This makes it comparable to engines, but unlike engines, it does not combust the fuel, producing gases; instead, it galvanically burns the fuel, producing water [7].

Hydrogen and oxygen are used as fuel and oxidants in the electrochemical process of a fuel cell. This procedure is unpolluted, soundless extremely effective than burning gasoline or coal. Fuel cells may be used across the whole energy demand range. Fuel cells may produce energy in the range of 1 W to 10 MW depending on the type, therefore they can be utilized for any energy demand. Domestic and public transportation are two of the most common uses for fuel cells, both as vehicle traction systems and as auxiliary power units. While batteries may serve the same purpose, their range is limited and they must be recharged before they can be used again. Furthermore, fuel cells offer far greater current densities than most currently available commercial batteries.

### 1.3.1 Working Principle of Fuel Cell:

Fuel cells consist of two electrodes anode and a cathode with an electrolyte between them. The electrode is connected through the load and the electrolyte may be hydrogen, aqueous alkaline solution, phosphoric acid or alkaline carbonate etc. The oxygen from ambient air is supplied to one side with hydrogen from the other.

The electrolyte has a unique property that enables positive ions to pass through while preventing electrons from passing through. The hydrogen gas flow across one electrode; referred to as an anode and is ionized into electrons and hydrogen protons in the presence of a catalyst.

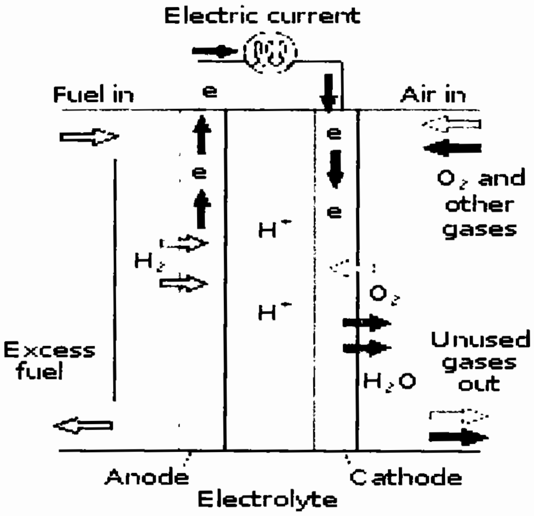

**Figure 1.1:** Fuel Cell

The positive ions of the hydrogen atom can pass through the electrolyte while electrons cannot pass through. However, the atoms need an equal charge, so to achieve this the electrons must change their path and this creates an electrical current. The positive ions by passing through the electrolyte reached the cathode, where these ions met with oxygen and electrons to generate water.

The oxidation and reduction reactions are as follows:

At anode

$$H_2 \rightarrow 2H^+ + 2e^- \qquad \text{(oxidation)}$$

At cathode

$$2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O \qquad \text{(reduction)}$$

The overall reaction of the fuel cell is as follows:

$$H_2 + 1/2O_2 \rightarrow H_2O$$

## 1.3.2 Types of Fuel Cell:

1 Alkaline Fuel Cells (AFC)
2 Phosphoric Acid Fuel Cells (PAFC)
3 Molten Carbonate Fuel Cells (MCFC)
4 Solid Oxide Fuel Cells (SOFC)

In AFCs alkaline electrolytes like potassium hydroxide is used. AFCs are high-performance fuel cells. In an alkaline fuel cell, we use compressed hydrogen and oxygen as fuel and potassium hydroxide (KOH) as an electrolyte. The efficiency of AFCs is 35-55% and the operative temperature is almost 60 °C-100 °C. By giving pure hydrogen fuel and platinum catalyst we can get almost 300 W to 20 kW output respectively.

The disadvantage of AFCs is that it is readily affected by carbon dioxide ($CO_2$). Tiny amounts of $CO_2$ in the air might degrade its performance, needing the purification of both the hydrogen and oxygen required. $CO_2$ can interact with KOH to yield potassium carbonate, which increases resistance. The cell's susceptibility to poisoning also impacts its longevity (the amount of time before it must be replaced), which adds to the expense.

In PAFCs anode is a finely dispersed platinum catalyst, the cathode is a silicon carbide structure and the electrolyte is usually phosphoric acid. Its operative temperature is 150 °C-200 °C [6] and has an efficiency of about 40-50%. The electrolyte is acidic and the catalyst used is platinum which is very expensive and raises the cost of the fuel cell.

In MCFCs molten carbonate salt is used as an electrolyte. Like alkaline, phosphoric acid fuel cells, to convert more energy-dense fuels to hydrogen, an additional reformer is required that molten carbonate fuel cells do not. This type of fuel cell can produce high power up to 100 MW also they can be used as high-power generators. Its operative temperature is up to 650 °C [6]. They are not so expensive in production and hence can be used for commercial uses. They have an efficiency of almost 55 %.

Solid oxide fuel cell (SOFCs) is unique due to their wide range of fuel uses. The majority of petroleum products may be used as fuel. The electrolyte used in this fuel cell is yttria-stabilised zirconia (YSZ). This electrolyte is suitable for large-scale power generation and possesses the same properties as the other electrolytes.

This is the most often used commercial fuel cell since it has the longest working life. It operates at an extremely high temperature of 1000 degrees Celsius [6]. However, some components of the fuel cell may be unable to withstand this temperature, making it exceedingly unstable. At high temperatures, the device may create water in the form of steam, which can then be readily transferred via steam turbines to generate more energy, enhancing the system's efficiency.

### 1.3.3 Application of Fuel Cell:

Fuel cells have been extensively and effectively utilised in spacecraft and attempts are currently being made to commercialize the fuel cell [6]. Fuel cells have several uses such as providing off-grid power supplies, in hybrid and electric vehicles, wastewater treatment plants and landfills, cellular phones, laptops and computers, credit card centers, buses, cars, planes, boats, forklifts, trains, vacuum cleaners, telecommunication and also used as power sources in remote areas.

## 1.4 Battery:

A battery converts chemical energy stored in its active components directly into electric energy [8]. In this type of reaction, an electronic route is employed to transfer $e^-$. A battery is a series-connected arrangement of multiple electrochemical cells that may be utilized as a source of direct electric current.

### 1.4.1 Working principle of Battery:

When two electrodes are dipped in a dilute electrolyte, oxidation and reduction responses occur in the electrodes, depending on the metal's electron affinity. As a result of the oxidation reaction, one electrode becomes negatively charged and is referred to as a cathode while another electrode becomes positively charged and is referred to as an anode. The battery's negative terminal is formed by the cathode, whereas the positive terminal is formed by the anode.

To effectively comprehend the basic principle of a battery, we must first understand the basic concepts of electrolytes and electron affinity. When two dissimilar metals are submerged in an electrolyte, a potential difference between these metals is formed.

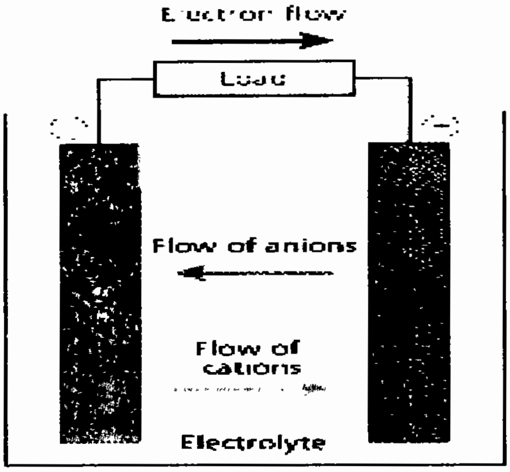

**Figure 1.2:** Battery Process

The electrodes are electrically linked via the electrolyte. The energy produced by a neutral atom after receiving an electron is referred to as electron affinity. Because various materials have distinct atomic structures, their electron affinity will differ. When an electrode dip in the electrolyte, oxidation/reduction occurs which means electrodes lose/gain electrons that depend on their electron affinity, also every material has different electron affinity.

The material with a low electron affinity will acquire electrons from the electrolyte. The metal with a high electron affinity, on the other hand, will emit electrons which enter the electrolyte solution and combine with the positive ions. As a result, one of these metals acquires electrons while the other loses electrons. The electron concentration of these two metals will differ and due to this difference in electron concentration, an electrical potential difference between the metals develops. This electrical potential difference also known as emf, can be used as a voltage source in any electronic or electrical circuit. This is a broad and fundamental principle of battery operation and it is how a battery operates.

### 1.4.2 Classification of Battery:

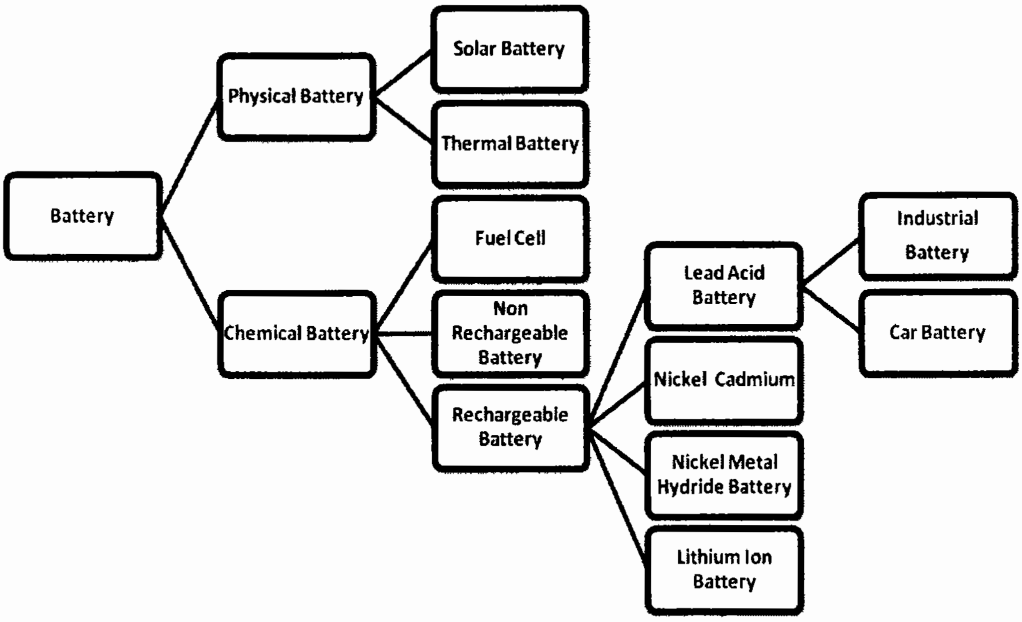

**Figure 1.3:** Classification of Battery

**The Battery is classified into two types:**

1. Physical Battery
2. Chemical Battery

**Physical Battery:**

Solar batteries and thermal batteries are examples of physical batteries that convert and deliver electrical energy directly.

Solar batteries collect sunlight and convert it to electricity. The photovoltaic effect uses an electrochemical mechanism to send the energy to the load.

A thermal battery is a physical battery used to store and release thermal energy. Thermal batteries are high-temperature molten-salt primary batteries. A solid, non-conducting inorganic salt serves as the electrolyte. Until the electrolyte melts, thermal batteries are entirely inert which gives them a long shelf life.

They are typically used for emergency-power scenarios like those in planes or submarines due to their ease of production and absence of maintenance requirements.

**Chemical Battery:**

Primary Batteries (non-rechargeable batteries), Secondary batteries (Rechargeable batteries) and Fuel cells are examples of chemical batteries. Chemical batteries use a chemical process to transfer chemical energy to electricity.

Primary batteries once discharged, cannot be recharged since the devices are not easily reversible and active components may not return to their original forms. Manufacturers of batteries advise avoiding charging primary cells. Throwaway batteries comprise the customary AA and AAA batteries found in electronic devices such as remotes, wall clocks etc. These batteries are known as throw-away batteries.

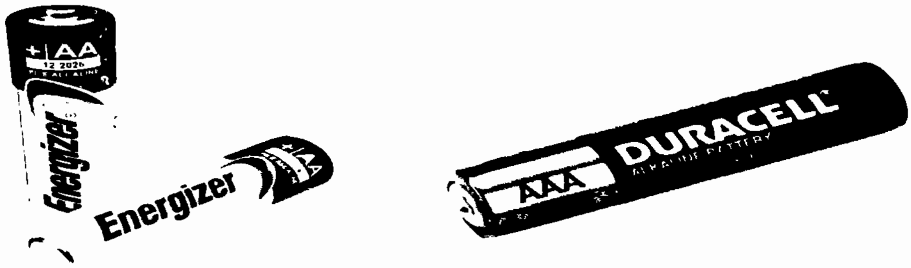

**Figure 1.4:** Non-rechargeable Battery

Secondary batteries may be used and recharged simultaneously and are frequently made of releasing active materials. Rechargeable batteries employ electric current to reverse the chemical reactions that take place during discharge. Devices that supply the required current are called chargers.

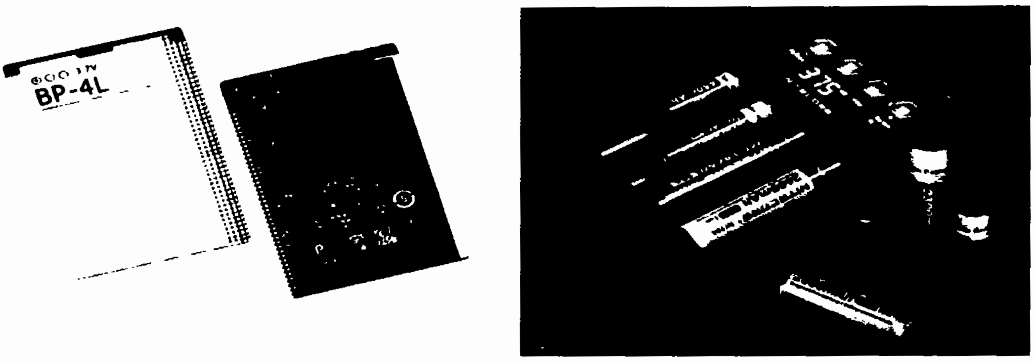

**Figure 1.5:** Rechargeable Battery

Such type of batteries is used in transportable phones, music devices and electronic devices etc.

### 1.4.3 Application of Batteries:

Batteries are utilised in a variety of household items. Remote controls, wall clocks, weight balance, laptops, mobile phones, tablets etc are powered by batteries [9].

Batteries play an important role in electric vehicles [10], aeroplanes, portable devices, grid energy storage [11], hospitals, health centres and other emergency services. Batteries are required for electrocardiograms, electrocardiographs, infusion pumps, glucose metres and other testing kits to work properly.

A radio is an emergency responder's most crucial gear. They provide a simple means of contact in areas where danger prevails. These radios are powered by high-quality big batteries that can carry a significant quantity of energy.

Batteries power other devices such as ECG monitors, metal detectors and spotlights. These technologies are critical for saving people's lives.

The most critical tool for armed troops is a utility tool and a set of batteries. Batteries may not be required in the military setting at first, but they are employed in a variety of ways.

## 1.5 Capacitor:

A capacitor stores electricity in the form of an electrostatic field rather than chemically as in a battery or fuel cell. It is made up of two conducting electrodes (plates) arranged close to each other and separated by a dielectric which can be a vacuum, air or any other insulators.

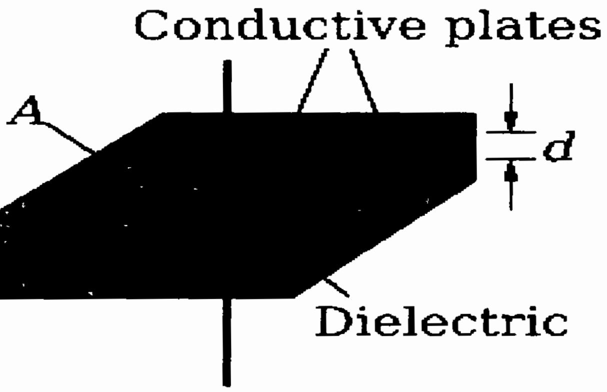

**Figure 1.6:** Schematic representation of a parallel plate capacitor

The capacitor is called a parallel plate capacitor because the electrodes are usually in parallel plate form. When the electrodes of capacitors are connected to a potential "V" of a battery, a potential difference is set up b/w the plates and +Q, –Q charges accumulates on their respective plates. The capacitor act as a voltage source when the two plates are charged and current flows until the charge balance is complete. As a result, its capacitance (C), which is measured in farads (F), is represented as the ratio of electric charge on each plate (Q) to the potential difference between them (V).

It is found that

$$C = Q/V \qquad 1.1$$

C is the constant of proportionality, it depends upon the geometry and the medium between the plates. It is a measurement of the capacitor's capacity to hold charges. The more charge per unit of voltage that a capacitor can store, the greater its capacitance.

For a parallel plate capacitor, the capacitance depends on the permittivity of dielectric material ($\varepsilon$), the area of the plate (A) and the separation between the plates (d) [12].

$$C = \varepsilon_o \frac{A}{d} \qquad 1.2$$

Where "C", "$\varepsilon_o$" and "A" is the capacitance in farads (F), the permittivity of free space ($8.85\times10^{-12}$ Fm$^{-1}$), the area of each plate and "d" is the distance between the two plates. If the two conductors are occupied by an insulating material, then the charge storage is

$$C = \varepsilon\varepsilon_o \frac{A}{d} \qquad 1.3$$

Where "$\varepsilon$" is the insulating substance permittivity. Its value is always greater than 1. So the capacitance of the capacitor can be enhanced when we use dielectric materials instead of free space. We can say that the capacitance depends on the permittivity of dielectric material ($\varepsilon$), the area of the plate (A) and the separation between the plates (d) respectively [12].

The two key properties of a capacitor that can be expressed as a quantity per weight or unit volume are power and energy densities. The opposed charges accumulated on the two plates create an electric field, which stores energy in a capacitor. The electric field is concentrated within the dielectric and is represented as lines of force between positive and negative charges.

The energy stored in a capacitor is proportional to the capacitance of the capacitor and also to the square of the potential

$$E= \frac{1}{2} CV^2 \qquad 1.4$$

Power (P) is the energy delivered rate with time. When calculating $P_{max}$ for a certain capacitor, the equivalent series resistance (ESR) of internal parts such as current collectors, electrode materials, and dielectric must be taken into account. Maximum power ($P_{max}$) is defined as follows:

$$P_{max} = V^2/4ESR \qquad 1.5$$

Where ESR determines the extreme energy and power of a capacitor by producing a voltage drop respectively.

## 1.6 Supercapacitor:

A supercapacitor has a higher energy density than a standard capacitor. Furthermore, as compared to the standard capacitor, supercapacitors achieve capacitances that are several orders of magnitude higher. Supercapacitors have higher power densities than batteries and higher energy densities than conventional capacitors [13].

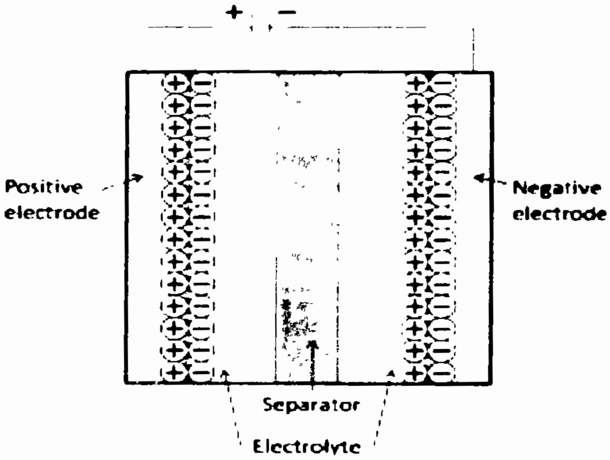

**Figure 1.7:** Schematic representation of Supercapacitor [14, 15]

Common capacitors accumulate charges on plates with a small surface area and are frequently graded in the microfarad and milifarad choices. Supercapacitors on the other hand, store charges in an electric double layer formed by ions at the interface between electrodes having a large surface area and electrolyte [16]. As a result, SCs can have ratings thousands of farads greater than a common capacitor [17].

The charging time and cyclability, both of which are influenced by the charge migration mechanism, are also different. Supercapacitors may be charged in seconds due to the rapid electrostatic charge transmission. Because electrostatic reactions are reversible, supercapacitors have a high cyclability and thus have a long life [17].

The mode of energy storage is the primary distinction between supercapacitors and batteries. Chemical reactions that are generating charges are used to accumulate energy in batteries. However, Due to the development of a double layer in the electrode/electrolyte interphase, supercapacitors continuously collect energy in the form of an electric charge [18].

On the other hand, Batteries take many hours to charge due to their slower redox processes because these processes are not fully reversible, and secondary batteries have a lower cyclability than supercapacitors. Supercapacitors are frequently employed in short-term energy storage applications, such as when power must be held or provided quickly. Furthermore, by balancing brief power peaks, supercapacitors can be utilised to support batteries or extend their life [19].

The material's apparent area and hole size govern the distinctive capacitance of an electrochemical capacitor. Carbon in its varying forms has a huge surface area (3.270 $m^2$ $g^{-1}$) particularly compared to transition metal oxides and conductive polymers [20].

## 1.7 Types of Supercapacitor:

Depending on the energy storage system and the electrode type employed, supercapacitors are categorized into three types that are as follows:

(1) Electrochemical Double-Layer Capacitors (EDLCs) (2) Pseudocapacitors

(3) Hybrid Capacitors.

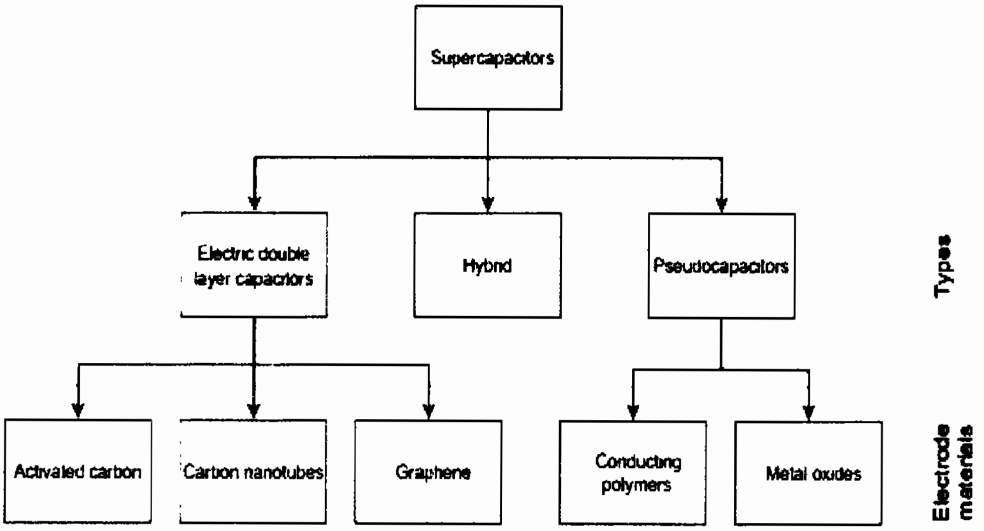

**Figure 1.8:** Types of Supercapacitors [21]

### 1.7.1 Electrochemical Double-Layer Capacitors (EDLCs):

Electrochemical Double-Layer Capacitors (EDLCs) are energy storage devices which possess high energy storage rate than a common capacitor and a high energy delivery rate compared to batteries. Distinct traditional energy storage devices, which use no organic responses and store a lesser amount of energy by actually keeping electronic charges b/w two conductive plates when an electrostatic response is applied, these energy packing devices use special electrodes and electrolytes and has a long cycle life (> 100 000 cycles) [22, 23].

The bulk separation and transportation of charges in electrochemical double-layer capacitors is the energy storage mechanism. Electrostatic charge transfer is fully reversible, resulting in devices that are very efficient and long-lasting. The charge that accumulates on the electrode-electrolyte interface is used to store energy.

Supercapacitors are made up of two metal plates, an electrolyte and a separator that permits charges to pass between the electrodes while providing insulation (used to prevent short circuits). The gap between the electrodes is filled by electrolytes. As supercapacitor electrode materials, a variety of materials have been employed, including different activated carbon materials, carbon nanotubes and graphene respectively [24].

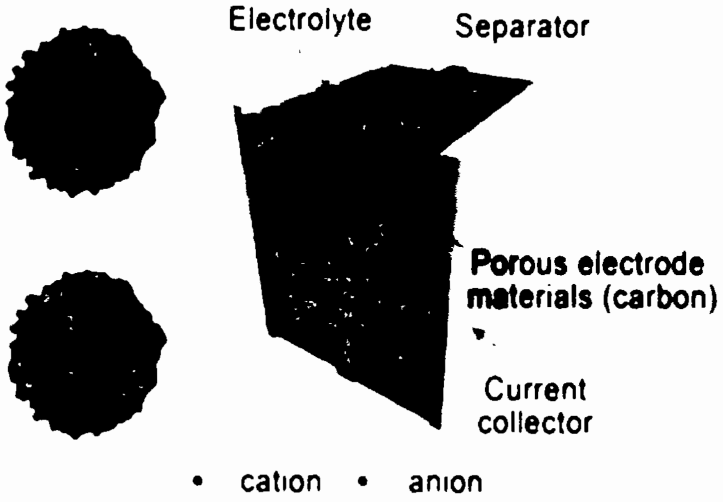

**Figure 1.9:** Schematic representation of electrochemical double-layer capacitor (EDLC) [25]

The most extensively used electrodes are carbon or its derivatives, metal oxides and conducting polymers. In recent years, graphene has been considered a viable capacitor electrode material due to its excellent chemical stability, high electrical conductivity, and enormous surface area [26].

When voltage is applied in electrochemical double-layer capacitors, charges move towards their respective electrodes throughout the solution. Between the electrode/electrolyte interface charge accumulates, generating two charged layers with a very short distance. EDLC stores charge on the electrode material's surface in a non-faradaic manner, meaning that no charge is transferred through the electrode-electrolyte interface. Because of their porosity, the carbon employed in capacitors constructs a high external area having a distance in a few angstroms (0.1nm). As a result that capacitance is a measure of surface area and is the inverse of the distance that separates two layers, high capacitance values may be acquired in a relatively tiny space.

### 1.7.2 Pseudocapacitors:

Energy storage in pseudocapacitors is based on an electrochemical procedure that takes place on materials of the electrode surface. The electrochemical procedure is so quick that the electrochemical characteristics of the device are similar to a carbon-based capacitor. They carry out reversible redox reactions on the electrode surface [27].

In addition to electrostatic charge separation, pseudocapacitors can perform electrochemical activities, which increases their energy storage capacity. Faradic capacitors, also known as pseudocapacitors, may store charge in a faradic manner. Charge transfer appears in redox reactions occurring at the electrode-electrolyte interface. Electroactive material redox reactions, intercalation, and electrosorption on the electrode surface all contribute to pseudocapacitance. The majority of electrodes are composed of conducting polymers or have transition metal oxides. Although faradaic processes in rechargeable batteries are slower as compared to pseudocapacitors, but are greater than electrostatic charge separation in EDLCs.

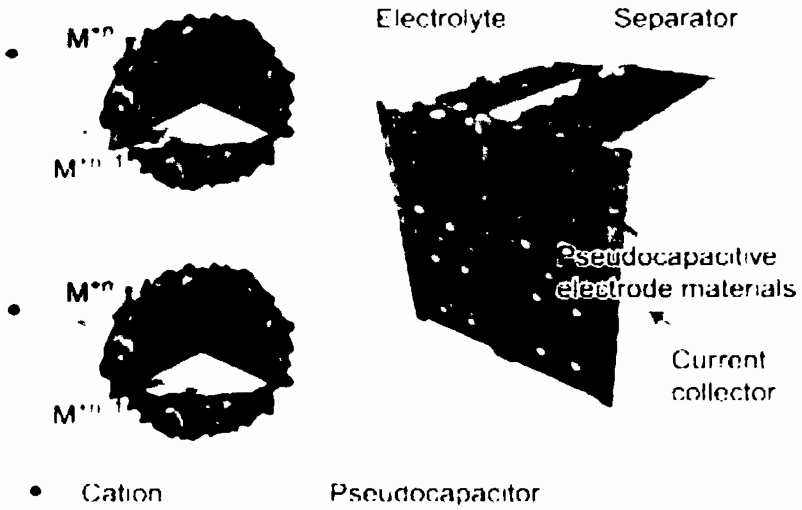

**Figure 1.10:** Schematic representation of Pseudocapacitor [25]

Pseudocapacitive procedures have few reaction products, they are more reversible than rechargeable batteries, but EDLCs do not undergo phase transformation and hence have the longest lifespan.

On the other end, pseudocapacitive processes enhance the supercapacitor's capacitance. On the accessible surface, EDLCs have stored charges at the rate of 0.17 to 0.20 electrons per atom, whereas PCs have around 2.5 electrons per atom. The energy accumulated by PCs is 10 to 100 times more than that of carbon-based EDLCs of the same mass or volume. The PCs electrochemical procedure, on other hand, causes less strength and life cycle. Cs and Es are higher in PCs as compared to EDLCs due to ions involved in redox reactions [26].

### 1.7.3 Hybrid supercapacitors:

When electrostatic and faradaic energy storage methods coexist in a device, it is referred to as a hybrid capacitor. Asymmetric setups, in which the anode and cathode materials are different, are employed in hybrid capacitors, due to the larger operating window.

Due to two different electrodes employment, each of which can work in a different operating window, boosting the device's overall operational voltage.

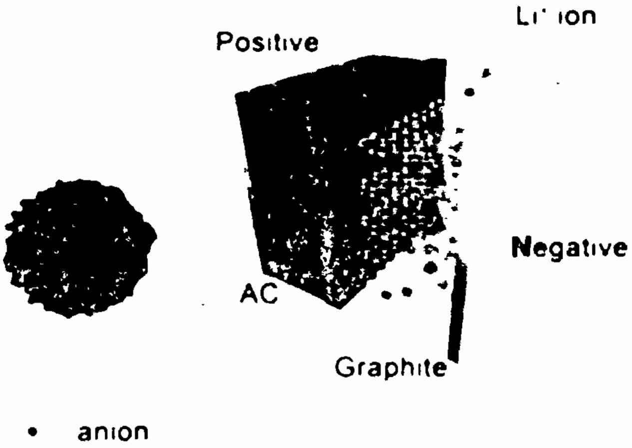

**Figure 1.11:** Schematic representation of a hybrid supercapacitor [25]

EDLC electrodes (usually activated carbons) and battery-type electrodes are used generally in the most asymmetric system. In a hybrid, one electrode exhibit electrostatic property while the other exhibit electrochemical property.

Both Faradic and non-Faradic charge storage strategies at the electrode/electrolyte contact relate to the specific capacitance of hybrid supercapacitors [20].

## 1.8 Electrolytes for supercapacitors:

Supercapacitors (SCs) most important constituents are the electrolytes (liquid, ionic or solid) since they provide ionic conductivity throughout the charging and discharging procedure. The supercapacitors electrolytes ionic conductivity can affect the ESR and the electrochemical stability window (ESW) which determines SCs operating voltage, are the two key features of electrolytes for supercapacitors. Electrolytes with a larger ESW and ionic conductivity are preferred choices for greater capacitive performance in supercapacitors. Electrolytes in supercapacitors facilitate the stabilisation of other critical supercapacitor properties. Interior opposition, operative heat, lifecycle, discharging, and poisonousness are all factors to examine when using supercapacitors in practice. The figure is made up of three concentric circles: the inner circle contains electrolytes and electrochemical supercapacitors and the centre circle contains the material goods of the electrolyte that influence the factors in the outer Circle shown in the figure.

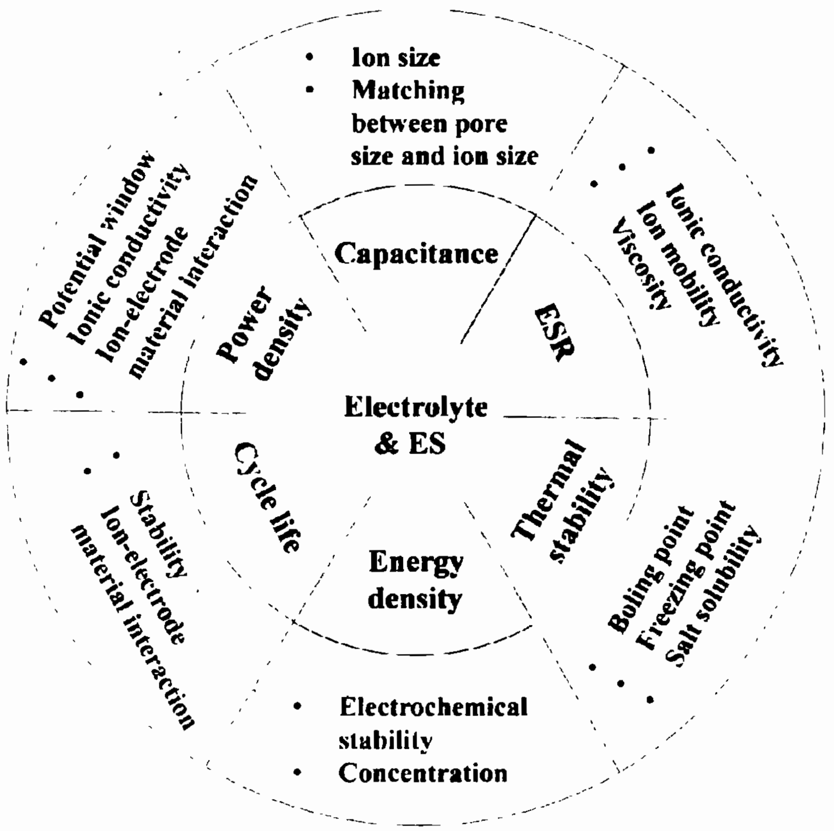

**Figure 1.12:** Effects of electrolyte properties on different parameters affecting the performance of supercapacitors (SC) [25]

Some of the important electrolytes are aqueous Electrolytes, Organic Electrolytes and Ionic Liquid Electrolytes.

### 1.8.1 Aqueous Electrolytes:

Supercapacitors with this electrolyte have higher ionic conductivity and capacitance than supercapacitors with solid electrolytes. However, the restricted breakdown of electrolytes limits its ESW, resulting in poor energy density devices. Acid, alkaline, and neutral electrolytes are the three types of aqueous electrolytes.

Aqueous electrolytes because of their low energy density is a poor selection for industrial use in SCs. It has been extensively employed in research because they are affordable and easy to handle, making construction and assembly easier. Furthermore, they have better conductivity than other electrolytes [28].

In acidic electrolytes, $H_2SO_4$ is the most widely utilised electrolyte due to its increased ionic conductivity, which is useful for lowering the ESR and hence boosting the power density of SCs. It has been found that acidic electrolytes, motivated electrodes of carbon have the maximum capacitance between 100 and 300 $Fg^{-1}$ in SCs. It has been observed that the specific capacitance of pseudocapacitors with $H_2SO_4$ electrolytes can be improved due to quick redox reactions on the carbon electrode surface [29, 18].

In alkaline electrolytes, Potassium hydroxide is also the most commonly utilised electrolyte as compared to other alkaline electrolytes. NaOH and LiOH, two more basic electrolytes, have also been studied [30].

Sodium chloride, potassium chloride and lithium chloride have attracted much attention in recent years because they have a larger operative possible window (1.5-1.6 V) and have low susceptibility to erosion [31].

### 1.8.2 Organic Electrolytes:

Organic electrolytes due to their high ESW now dominate the commercial market. As linked to aqueous electrolytes organic electrolytes have a much high energy storage rate and energy delivering rate. However, they are employed in SCs, there are a few things to keep in mind. When compared to aqueous electrolytes, they have a higher cost, poorer specific capacitance, lesser ionic conductivity, higher flammability, volatility and toxicity [17, 18].

Organic electrolytes also have a bigger solvated ion size and a lower dielectric constant than aqueous electrolytes, resulting in reduced capacitance in SCs. To create an organic electrolyte with ionic conductivity, conducting salts must be dissolved in organic solvents. Tetra-ethyl-ammonium tetrafluoroborate ($TEABF_4$) liquefied in acetonitrile (AC) or propylene carbonate (PC) is a common organic electrolyte for SCs. With these electrolytes highest capacitance, power densities and energy can be stored.

Several factors determine the ESW of an organic electrolyte. Among them are conductive salt, solvent, and contaminants, particularly tiny amounts of water. Undesired redox processes at the electrode materials may occur in some situations when organic electrolyte-based SCs are charged above the typical limits of ESW (2.5-2.8 V) [23] producing selfdischarge. This causes organic electrolyte-based SCs to fail in terms of long-term performance and safety [32].

### 1.8.3 Ionic Liquid Electrolytes:

It is salt in a liquid state (molten salt) at room temperature. It consist of a large asymmetric organic cation and an inorganic/an organic anion and this special combination of certain cations and anions contributes to a low melting point. The electrochemical stability window for ionic liquid is between 2-6 V. They have high thermal and chemical stability. They are non-toxic and have low flammability. This types of electrolytes can be classified as aprotic, protic and zwitterionic electrolytes respectively. It is a combination of a wide range of cations (+) and anions (-) combinations respectively, but due to their several main drawbacks such as high viscosity, low ionic conductivity and high cost it is restricted for practical use in electrochemical applications respectively.

# Chapter 02

## Literature Review

Carbon-based polymers that conduct electricity are known as conducting polymers (CPs). Conducting polymers is very important due to their economic importance, greater stability, reduced weight, higher workability, corrosion resistance and excellent electrical conductivity but tend to have low cycle strength and a volatile structure. Conducting polymers has inspired a lot of attention in the supercapacitor field due to their great charge density (relative to graphite) and minor price.

Conducting polymers are lighter, take up less space, and are less expensive to manufacture than other available technology. Polymers naturally are insulting materials.

Wrapping metal wires in plastic shields them. The discovery in 1960 that the inorganic materials poly sulfur nitride is a metal was a turning point in the history of CPs. [33]. Poly sulfur nitride has an ambient temperature conductivity of the order of $10^3$ $(\Omega.\mathrm{cm})^{-1}$. These findings were crucial because they proved the existence of high-CP polymers and sparked the massive amount of research required to produce alternative polymeric conductors.

Several CPs have caught the interest of researchers due to their excellent qualities such as electrical capabilities, controlled chemicals, electrochemical qualities and ease of processing. [34]. For free-standing and flexible electrodes we used conducting polymers.

Polyacetylene (PA) is a repeat unit $(C_2H_2)_n$ organic polymer. Beginning in the 1960s, the high electrical conductivity of these polymers sparked interest in using organic chemicals in microelectronics. Shirakawa accidentally created PA, the first polymer capable of carrying electricity, in the mid-1970s [35]. The discovery of highly conducting polyacetylene encouraged an immediate surge in interest in developing new CPs. The extraordinary conductivity of polymers piqued researchers' interest in using organic compounds in microelectronics. Polyacetylene is insoluble in water, making processing the substance very impossible. While both cis and trans-polyacetylene have good thermal stability, exposure to air reduces their flexibility and conductivity significantly. Polyacetylene is insoluble in water, making processing the substance very impossible. While both cis and trans-polyacetylene have good thermal stability, exposure to air reduces their flexibility and conductivity significantly.

Poly (3, 4-ethylene dioxythiophene) offers a lot of benefits, including excellent stability, an appropriate bandgap, and small redox potential. The organosulfur compound poly 3, 4-ethylenedioxythiophene (EDOT) has the formula $(C_2H_4O_2C_4H_2S)_n$. Its melting and boiling point is 10.5°C and 225°C respectively [36].

Using a vanadium pentoxide nanofiber, the nanofiber seeding process is used to make PEDOT. A standard solution of vanadium pentoxide, sulfonic acid and ammonium persulfate is mixed with 3, 4-ethylene dioxyl thiophene to induce polymerization [37].

Polythiophenes (PTs) are sulphur heterocycles that have the formula $(C_4H_2S)_n$ and are insoluble coloured solids. Polythiophene also has conjugated double bonds in its backbone, making it an excellent intrinsic conducting polymer. It has a boiling point of 84.0°C and a melting point of >350°C. Polythiophenes is similar to polypyrrole but the main variation in structure between PTh and PPy is the presence of the heteroatom "S" in the aromatic ring instead of the "N" atom. Polythiophene is a promising material because of its inexpensive cost, strong electrical conductivity, optical characteristics, well thermal stability, smaller band gap energy and environmental stability. They are generally utilised in solar cells due to their ability to create better contact with metal electrodes and their stability under ambient settings. Heteroatoms effect on the chemical/physical property of the polymeric manufactured product has been taken into account, as well as the production procedure of the necessary monomer. Polythiophene (PTh) is insoluble in organic solvents, like many other linear polyaromatic compounds.

PANI is a semi-flexible rod polymer that belongs to the conducting polymers (CPs) family. Its chemical formula is $(C_6H_6NH)_n$. Due to unique characteristics, such as chemical stability and relatively high conductivity, PANI is one of the most important classes in the world.

F. Ferdinand Runge, Carl Fritzsche, John Lightfoot, and Henry Letheby found polyaniline in the 19th century when they were doing research in acidic conditions, using electrochemical and chemical compounds of aniline [38]. Because of its ease of synthesis, small price and customizable characteristics, PANI is a very promising intrinsically conducting polymer. PANI is also known as aniline black, and it comes in a variety of forms depending on the degree of oxidation. Because of its low solubility, it is very tough to proceed with the emeraldine form of polyaniline and produced it as a black powder. PANI is difficult to process, owing to its inflexible backbone, which is connected to its high conjugation level. The difficulties encountered in processing neat PANI have led to the creation of PANI-based composites and blends.

Poly(phenylene vinylene) or PPV is a rigid-rod polymer that conducts electricity. PPV is the only polymer of this type that can be treated into a crystalline thin film with a high degree of order, mechanically strong and environmentally stable. Its chemical formula is $(C_8H_6)_n$. PPV is a diamagnetic material with a structure midway between polyacetylene (PA) and polyphenylenes (PP) [39]. The conductivity improved but the stabilisation reduces when doped with iodine, ferric chlorides, alkali metals, or acids. Poly(phenylene vinylene) has been used to sort the first emissive layer of PLED's in 1990 [40]. In organic solar cells, PPV is also employed as an electron-donating substance also they have low absorption and photodegradation.

Among these, polypyrrole (PPy) is superb for several uses as SCs, solar cells, biosensors, electro-chromic devices and anti-corrosion coatings [41] due to their greater conductivity, charge delivering rate and extraordinary mixing rate during the charging/discharging procedure [42]. Polypyrrole (PPy) is an organic polymer formed through pyrrole oxidative polymerization. It has the formula $H(C_4H_2NH)_nH$ and is solid. It is an intrinsically conducting polymer that is used in electronics, optics, biology, and medicine. Although PPy itself is an insulator, its oxidised derivatives are excellent electrical conductors. Polypyrrole due to its extraordinary thermal stability, electrical conductivity, easy synthesis and environmental stability has attracted much attention in energy storage devices [43].

Different solvents such as water, $HNO_3$, tetrahydrofuran, benzene, and ethylene glycol with different oxidant agents like $FeCl_3$, $H_2O_2$, $(NH_4)_2S_2O_8$, $Fe(NO_3)_3$ etc can be used for the preparation of polypyrrole nanoparticles through different electrochemical procedures. The electrochemical synthesis of polymers is a difficult process that has an impact on the yield of PPy [42].

The material's conductivity is determined by the oxidation conditions and reagents used. The conductivities vary between 2 and 100 S/cm. Due to its unique qualities, including its straightforward synthesis pathway, high conductivity, strong environmental stability, relatively low density and outstanding mechanical properties, PPy has attracted a lot of interest [44].

Pure PPy with a benzoid structure is an insulator in nature, and it requires oxidant doping to function as a semiconductor. Because of its ease of preparation, remarkable redox properties, stable oxidised phase, and capacity to provide increasing conduction, it was identified to be a CP in 1968. PPy has been extensively researched among the various CPs due to its solubility in water, economically available, important electrical and optical properties [45].

Pyrrole blacks were first manufactured as powders through pyrrole by chemical polymerization. These odd polymers haven't been thoroughly defined, but they're pyrrole polymers with mainly,' carbon bonding. Weiss and colleagues described how to pyrolyze tetraiodopyrrole to generate extraordinarily conductive compounds in 1963. To analyse this system as a CP, in 1979 an excellent electrochemical method has been employed to create free-standing films having adequate mechanical qualities. After oxidising pyrrole in sulfuric acid, PPy was produced by Dall'Olio et al at room temperature having a conductivity of 8 $Scm^{-1}$ [46]. The conductivity of these films varies between 100 and 200 S/cm during electrochemically cycled between conducting and insulating states.

Electrode corrosion resulting from the absorption and deactivating of anti-ions during cyclic charge and discharge causes conductive polymers to lose their conductivity. Researchers have typically sought to develop $Co_3O_4$/Conducting polymer composites for the increment of electrochemical achievements.

We get excellent electrical conductivity and electroactivity by $Co_3O_4$/PPy composites allowing it to dramatically increase active sites lowering charge transfer resistance. With this electrode, we get capacitance retention of 77.8% at 25 $mA/cm^2$ and at 5 $mA/cm^2$ having Cs of 2212 F/g after 5000 cycles [26].

The synthesis due to the presence of $NaC_{12}H_{25}SO_4$, which acts as a surfactant resulted in conductivity of 39 S/cm for Polypyrrole. Polypyrrole-glassy carbon electrode capacitance at 100 $mAg^{-1}$ current density is around 398 F/g. verifying the remarkable electrochemical performance of PPy nanoparticles [42].

Different organic solvents can be used for pyrrole oxidation and to control the size and shape Chemical polymerization requires the use of surfactants. A surfactant can increase the conductivity, stability, solubility in organic solvents, and processibility of the conducting polymers as well as the kinetics of polymerization and their final characteristics [45].

Oxygen atoms bonded to transition metals constitute compounds known as transition metal oxides. Their catalytic activity and semiconductive characteristics make them popular. Transition metal oxides exhibit a wide range of surface structures, which affect the surface energy and chemical characteristics of these compounds. Transition metal oxides are attractive electrode materials because they can store energy both faradically and non-faradically, resulting in high specific capacitance [3]. Transition metal oxides have a larger specific capacitance than carbon materials, have higher energy density and have better chemical stability than conductive polymers. The electrode materials are at the heart of supercapacitors, and they have a direct impact on energy storage performance. In KOH aqueous electrolyte solution, transition metal oxides such as $MnO_2$, NiO, $RuO_2$, and $Co_3O_4$ have been extensively studied for their pseudo-capacitance capabilities [47]. Due to extraordinary redox responses, minor cost, eco-friendly and outstanding electrochemical properties transition metal oxide is the best material for SCs electrodes [20].

$RuO_2$ is regarded as an ideal pseudocapacitive electrode because it has higher theoretical capacitance and a quick faraday reaction. $RuO_2$ has been recognised as a leading option because of its large theoretical specific capacitance (1358 $Fg^{-1}$), high electrical conductivity (300 S $cm^{-1}$), and strong electrochemical stability [48].

It is unsuitable for use in supercapacitors due to its heavy cost and toxicity in the environment [49]. It has a large voltage window, strong conductivity, great chemical and heat stability. The greatest specific capacitance value was 720 $Fg^{-1}$ obtained using amorphous ruthenium oxide as an electrode material at a scan rate of 2 $mVs^{-1}$ in the $H_2SO_4$ electrolyte. $RuO_2$ is thus referred to as the most perfect pseudocapacitive electrode material but on the other hand, is too expensive to employ in large-scale electrode synthesis. Metal sulfide-$RuO_2$ electrodes, metal oxide-$RuO_2$ electrodes, carbon material-$RuO_2$ electrodes, and multicomponent $RuO_2$-based electrodes are all examples of $RuO_2$-based electrodes that have been developed.

Materials involving carbon may increase the surface area and the conductivity of electrodes. Several publications, however, claimed that $RuO_2$ particles restricted the porous surface of carbon materials. As a result, the surface area and the double-layer capacitance are reduced, and electrochemical properties are constrained [50, 51].

$Co_3O_4$ offer a huge surface area and extraordinary conductivity, which are fundamental qualities of a decent electrode. Nanocrystalline $Co_3O_4$ is gaining a lot of importance due to its high energy and power density. Other important features of the $Co_3O_4$ electrode are long-term performance and high effectiveness. $Co_3O_4$ relatively low cost, non-toxic nature, environmental friendliness and strong corrosion resistance make it an attractive contender for supercapacitors. $Co_3O_4$ can be synthesized by different techniques such as CVD, thermal decomposition of cobalt precursors, pulsed laser deposition, combustion methods, bio-templating, co-precipitation, microwave-assisted and sol-gel method [52] etc. However, all of these processes have their limitations, such as the use of hazardous reagents, high calcination temperatures, long reaction times, limited production gains, and the need for outer ingredients during the response, all of which constrain the purification of the products. The hydrothermal process has emerged as an efficient and suitable approach due to its simplicity, ease to scale up to industrial demand, low-temperature requirements, no need for calcination, cheap cost, and distinct morphologies of products. The word hydrothermal refers to the use of water as a solvent, whereas solvothermal refers to the use of organics as a solvent [53].

The pseudocapacitance behaviour of $Co_3O_4$ nanoparticles generated at lower temperatures is good. They can also be a comparatively cheap price in favour of a good option for SCs. $Co_3O_4$ is a transition metal oxide from the spinel group, and its reaction is as follows:

$$Co_3O_4 + OH^- \rightarrow 3\ CoOOH + e^-$$

$$CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^-$$

$Co_3O_4$ is a potential active material because of its extraordinary theoretical specific capaci tance of about 3560 F $g^{-1}$, small cost, eco-friendly, minimal toxicity, organic stability and excellent redox ability in comparison [54, 3].

Because of its easy production techniques, strong chemical stability, variable shape, and usefulness in electrocatalysis, $Co_3O_4$ appeared as distinctive among all the transition metal oxides. The cubic spinel arrangement of p-type magnetic semiconductors makes up $Co_3O_4$ materials having 2.10 eV and 1.60 eV with direct and indirect band gaps [55].

Nanowires, Nanofibers, nanoparticles, and nanosheets are among the $Co_3O_4$ nanomaterials that have been created. Indira Priyadharsini originally used the sol-gel process to make

$Co_3O_4$ nanoparticles. The electrode was made by uniformly covering a Ni foam substrate with the produced slurry. At 11 $mA/cm^2$, the electrode's specific capacitance is 761.25 F/g. The use of PVDF results in fewer active sites and a slower electron/charge transfer rate because it rises the impedance b/w the collectors and the electroactive material [56].

$Co_3O_4$ nanorods have pores, are highly oriented, and are generated by the combination of various nanocrystals, with a mean rod measurement of 150 nm. At a $5mVs^{-1}$ scan rate, the capacitance calculated is 281 $Fg^{-1}$ in 2M KOH solution, which could be boosted by increasing the surface area of the electrode (232 $m^2g^{-1}$). After 1000 charge-discharge cycles, 83.4% capacitance was preserved, indicating excellent cycling stability. Because of the larger specific surface area of well-ordered nanorods, $Co_3O_4$ nanorods had a substantially higher specific capacitance than conventional $Co_3O_4$ powders. Nanocrystalline $Co_3O_4$ also provides electrochemical stability, extraordinary conductivity, and pseudocapacitive behaviour, all of which contribute significantly to specific capacitance and hence improve electrochemical characteristics.

We can get Cs of 120 F/g at 1 A/g through a potential range of 0 to 0.6 V by the sol-gel method. By thermal decomposition, cobalt oxide nanoflakes can get Cs of 576.8 F/g after 82% capacitance retention at 1 A/g after 5000 cycles [26].

$MnO_2$ has been thoroughly investigated as the most competitive transition metal oxide due to its lack of atmosphere pollution, and great theoretical capacitance (1380 F $g^{-1}$). However, owing to its poor conductivity and sluggish ion transport rate, it is not suitable for usage in supercapacitors.

Due to minor price, natural abundance, and eco-friendly MnO, $MnO_2$, and $Mn_2O_3$ due to their dissimilar oxidation states used in aqueous and organic electrolytes for SCs. Pulsed laser deposition, hydrothermal synthesis, electrochemical synthesis, redox deposition, and sequential hydrolysis–condensation have all been used to produce manganese oxides [20].

Vanadium oxides ($V_2O_5$) are also useful in energy storage devices because of their phase transitions. $V_2O_5$ has sparked a lot of attention due to its potential application in optical switch devices and as a reversible cathode material for lithium batteries. $V_2O_5$ is also a potential electrode material for electrochemical capacitor applications because of its inexpensive cost and capability to live in a variety of oxidation positions. $V_2O_5$ was first made by quenching fine $V_2O_5$ particles in de-ionized water at 950 degrees Celsius. In an electrolyte with a pH of 2.32, the specific capacitance was 346 F $g^{-1}$. The sol-gel process was used to produce nanoporous layer-structured $V_2O_5$. 214 F $g^{-1}$ was stated to be the greatest specific capacitance. Co-precipitation and calcination were used in recent work to make nanocrystalline $V_2O_5$ powders. The $V_2O_5$ powders had a specific capacitance of 262 $Fg^{-1}$ when measured at a 5 $mVs^{-1}$ scan rate in a 2 M KCl electrolyte [57].

Hematite $Fe_2O_3$ is the most stable of all the iron oxides, consisting of hexagonal densely filled oxygen and iron atoms in a 2:3 ratio. Because of their inexpensive cost and huge specific surface area, iron oxides, particularly $Fe_2O_3$, are appealing. With a $Fe_2O_3$-carbon black composite, the highest recorded particular capacitance of $Fe_2O_3$ was 510 $Fg^{-1}$. Commercial $Fe_2O_3$ was first electrochemically tested in several electrolytes, and it was discovered that a 2 M $Na_2S_2O_3$ solution is the best electrolyte, with commercial $Fe_2O_3$ yielding capacitance of 10 F $g^{-1}$, throughout the whole range. At scan rates 5 $mVs^{-1}$, the CV curve acquired a perfect rectangular shape, implying a constant charge and discharge ratio through the voltage range [58]. When compared to commercial $Fe_2O_3$ powder, $Fe_2O_3$ nanorods have a greater surface area of 81 $m^2$ $g^{-1}$ than 19 $m^2$ $g^{-1}$.

Due to brilliant organic and thermal stability, usual abundance, budget factors and ecological friendliness NiO is best for SCs electrodes. At a 5 mV/s scan rate, NiO/carbon composite delivered a capacitance of 107 F $g^{-1}$. In 1 M $Na_2SO_4$ electrolyte, NiO afford a specific capacitance of 423 F $g^{-1}$ at 0.5 mA $cm^{-2}$ [59].

Reduced graphene oxide (rGO) is a carbon-based two-dimensional sheet [60]. rGO development has gained a lot of interest because of its unique physical, molecular features and its large surface area (2600 $m^2$/g) [61, 62].

It is a planar sheet of carbon atoms organized into hexagons as an allotrope of the element carbon. The major qualities that make graphene a potent material for the twenty-first century are its great strength, flexibility, and incredibly efficient electrical/thermal conductivity. Graphene attracted worldwide interest due to its multiple uses in energy storage devices [63], particularly in supercapacitors.

Activated carbon powders are the most commonly used materials employed in today's commercial EDLC supercapacitors due to their large specific surface area, high thermal stability [41], high conductivity, and superior corrosion protection to electrolytes. Recently due to having these properties graphene is also an emerging candidate for EDLC but they have less energy density as compared to electrochemical batteries (lithium-ion, lead acid). Pseudocapacitors have better energy density than EDLC due to their redox reactions [64]. In a 2-electrode cell, the rGO-$Co_3O_4$ composite electrode has a specific capacitance of 472 F $g^{-1}$ at a scan rate of 2mV $s^{-1}$ while rGO has 44 F $g^{-1}$. When the scan rate is increased to 100 mV $s^{-1}$, 82.6 % of the capacitance is sustained. The rGO-$Co_3O_4$ composite electrode has exceptional long-term stability and high energy density [64].

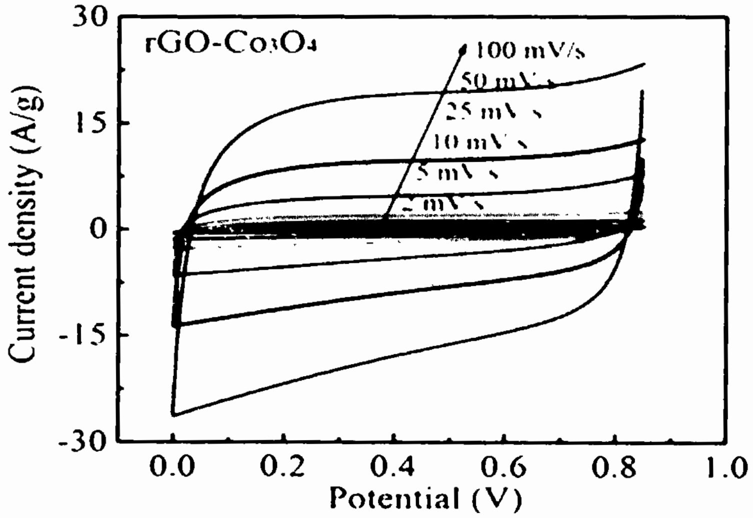

**Figure 2.1:** Cyclic Voltammetry graph of rGO-$Co_3O_4$ at different scan rate

The organic reduction of GO consumption, a very toxic reducing agent (hydrazine) is risky to human health and the environment. Besides hydrazine hydrate, ascorbic acid can also be used for this.

The oxygen-containing efficient set was removed during the rGO contraction and the sample quality deteriorated. $Co_3O_4$/PPy/rGO composites reveal extraordinary specific capacitance of 532 F $g^{-1}$ with no deprivation after 700 phases of charging and discharging.

# Chapter 03

## Synthesis and Characterization Techniques

This chapter has two phases: first describes the experimental portion of the research, specifically the materials and technique for preparing $Co_3O_4$/rGO/PPy Ternary nanostructures that used a hydrothermal mechanism. The second provides a comprehensive overview of all analysis techniques.

## 3.1 Materials

### 3.1.1 Chemicals/Major Precursors:

Iron chloride hexahydrate ($FeCl_3.6H_2O$), Pyrrole ($C_4H_5N$), Sulphuric Acid ($H_2SO_4$), Cobalt Nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), Urea ($Co(NH_2)_2$), Graphene Oxide (GO), Ammonium Persulfate $(NH_4)_2S_2O_4$, Cobalt Chloride hexahydrate ($CoCl_2.6H_2O$), Sodium hydroxide (NaOH), Hydrogen Peroxide ($H_2O_2$) used as a key precursor in the synthesis of cobalt oxide, polypyrrole, rGO, $Co_3O_4$/PPy/rGO Ternary nanocomposite for supercapacitor electrode.

## 3.2 Equipment and Instruments:

The equipment and apparatus used in the synthesis of $Co_3O_4$/PPy/rGO Ternary nanocomposites are listed below.

### 3.2.1 Equipments:

In order to make $Co_3O_4$/PPy/rGO nanostructures, the following equipment is utilized: The chemicals were placed into the solvent using a spatula. In the beakers (50ml and 100ml), homogeneous solutions were generated. The completed product was transferred from the Teflon-Lined autoclave to the flask to get the synthesized material. A glass rod was used to measure out the correct amount of solvent. Dropper were used to drop 4 or 5 drops of analytical grade ethanol into a mixture of homogeneous solutions to scatter the nanoparticles during the production process. The nanostructure materials were filtered and washed using filter sheets.

### 3.2.2 Instruments:

In the synthesis of $Co_3O_4$/PPy/rGO ternary nanocomposite, all of the tools listed below are utilized.

A digital balance was used to measure the salts and reaction reagents. The homogeneous solutions were made using a hot plate stirrer (or magnetic stirrer). The oven (drying oven) was utilized to keep the Teflon-lined autoclave at a high temperature while simultaneously drying the nanomaterials. (At high temperature, a Teflon-Lined Autoclave applies high pressure) was used to generate nanomaterials. Water was separated from nanoparticles using centrifugation.

## 3.3 Method of Preparation/ Material synthesis technique

### 3.3.1 Hydrothermal Procedure:

The hydrothermal approach relies on a change in solubility in a sealed stainless steel autoclave kept at a certain temperature and pressure. The shape, size, and crystal type of products are affected by the reaction temperature, duration, pressure, and reactant concentration [65]. The hydrothermal approach, which requires extremely high pressures and temperatures is one of the most complex, valuable, and generally accessible ways of manufacturing nanostructured materials. Single crystals are synthesised using the hydrothermal technique. Dependent on the precursors' solubility, the crystal formed under high pressure in hot water. When water is used as a solvent, the term hydrothermal is used, and when organics are utilised as a solvent, the term solvothermal is used.

The synthesis takes place in an autoclave, which receives the Nutrient solution, which contains crystal growth precursors and water. At opposing points of the growing box, a thermal gradient is adjusted such that the hotter end liquefies the nutrient but the colder end promotes crystal seed formation. Temperature, pressure, time length, and pH are the primary elements impacting the entire process and dictating the form, size, and features of the final desired product. The precursor solution would be produced first and then placed in the Teflon tube. The Teflon is then enclosed in an autoclave and placed in the oven to maintain the desired temperature.

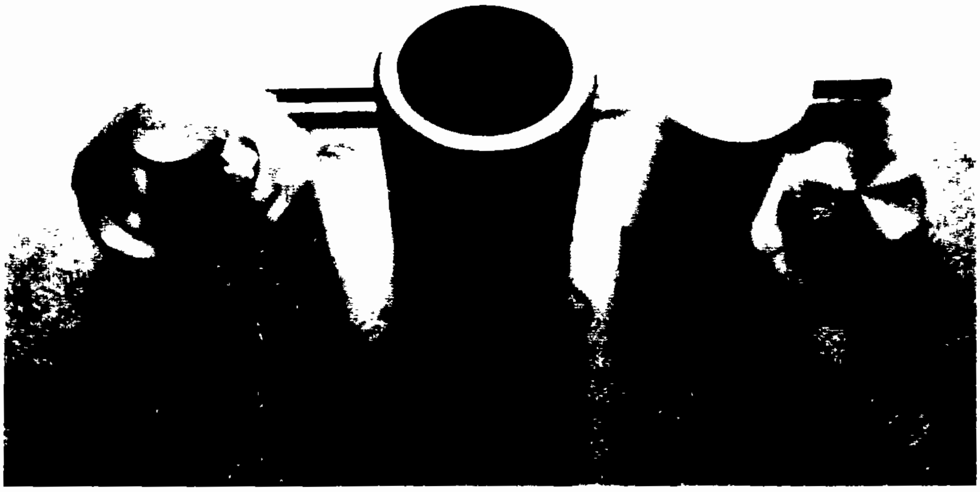

**Figure 3.1:** The Autoclave Tools

As compared to atmospheric pressure, the physical characteristics of carbon-based solvents vary dramatically under high pressure, allowing for certain unusual chemical reactions to occur. Ethanol and isopropanol can also be used as solvents. To change the reactant state organic solvents mixed with reactants and reducing agents such as ethanol can be used in this procedure. In this way morphology, size and other parameters can be affected [26].

The hydrothermal process has various benefits over other kinds of crystal formation. One is the creation of crystal-like segments that are not stable at the melting point. It is also possible to develop materials with high vapour pressure around their melting temperatures. It's also particularly well suited since massive, high-quality crystals may be formed using the hydrothermal process while maintaining composition control. The necessity for lavish autoclaves and excellent feature seeds of a reasonable size, as well as the inability to observe crystal as it produces, are potential drawbacks.

### 3.3.2 Chemical Oxidative Polymerization Method:

The process of synthesizing polymers is called polymerization. In the mechanism of polymerization, monomers, which are smaller molecules, are chemically linked to form macromolecules. Repetition units are tiny molecules that are chemically connected to create a polymer during the polymerization process, also known as polymer synthesis. The repeating components in the polypyrrole example are pyrrole monomers. The monomers employed in chemical oxidative polymerization (COP) have strong electron donor characteristics and high oxidation tendencies. Using organic/inorganic oxidising agents will cause a monomer to oxidise. A cation is created in the monomer molecule during the COP, starting the polymer growth process.

The process of synthesis is rapid and easy. The starting materials are low-cost. Different techniques exist to classify the various types of polymerization. Due to the functional groups contained in the reactants and their inherent oxidation effects, polymerization in chemical compounds can take place through several reaction processes that vary in complexity. Basic components or building blocks must have the ability to join or link with other constituents to form a polymer during the polymerization process. The energy needed by the building blocks to react and bind is frequently provided by varying the temperature and pressure. A catalyst may occasionally be employed to speed up the process. Catalysts are chemicals that initiate or expedite a chemical process while remaining unaltered inside. A repeating unit's bonds with neighbouring molecules are governed by a variety of methods. Alkenes undergo comparatively uncomplicated radical reactions to create polymers in more straightforward polymerizations; in contrast, substitution reactions at a carbonyl group need more complicated synthesis because of the way the reactants polymerize. The polymerization of alkanes is also possible, but only with the aid of strong acids. The two primary kinds of polymerization reaction processes are step growth and chain growth. The former requires careful stoichiometry control but is frequently simpler to install. The latter, however only applicable to certain monomers and more consistently provides high molecular-weight polymers.

Pairs of reactants of any length unite at each step to create a longer polymer molecule in step-growth polymerization. The gradual rise in molar mass is normal. Only at the end of the process do long chains develop. Step-growth polymers are synthesized by separate reactions between functional groups of monomer units, which often contain heteroatoms like oxygen or nitrogen. Since a tiny molecule, like water, is lost as the polymer chain is stretched, the majority of step-growth polymers are also categorised as condensation polymers. As an illustration, the growth of polyester chains occurs when alcohol and carboxylic acid groups combine to produce ester linkages while water is lost.

The addition of a monomer to a developing chain with an active centre, such as a free radical, cation, or anion, is the only chain-extension reaction step in chain-growth polymerization. Chain propagation is often accelerated by the addition of a series of monomers once a chain's development has been started by the establishment of an active centre. From the start of the process, long chains are produced.

Unsaturated monomers, particularly those with carbon-carbon double bonds, are linked together during chain-growth polymerization. A new sigma bond is formed, replacing the pi-bond. Cationic addition polymerization and anionic addition polymerization are further types of chain growth polymerization. Living polymerization is a particular instance of chain-growth polymerization. The process of polymerization is a very advanced technological process. Although the molecular weight and polymer dispersity may be increased, these techniques may add extra processing steps to separate the product from a solvent.

### 3.3.3 Modified Hummer's Method:

Hummers' technique is a chemical procedure that uses potassium permanganate to produce reduced graphene oxide from a mixture of graphene oxide, sodium nitrate, sulfuric acid and hydrazine hydrate. Engineers and lab personnel frequently utilise it as a dependable way to produce large amounts of reduced graphene oxide. Additionally, it may be changed to produce a graphene oxide material that is only one molecule thick. In 1958, Hummers invented a process for making reduced graphene oxide that was safer, quicker, and more effective [60]. Before the invention of the process, the manufacture of reduced graphene oxide required the use of powerful sulfuric, nitric acids and hydrazine hydrate which was time-consuming and dangerous. After observing the risks the aforementioned techniques caused to employees at the National Lead Company, William S. Hummers and Richard E. Offeman developed their approach as an alternative to them. This technique was comparable in that it entailed mixing graphene oxide into a concentrated acid solution. Graphene oxide, concentrated sulfuric acid, sodium nitrate, and potassium permanganate were the only elements they left out. They also avoided most of the explosive risk associated with the Staudenmeier-Hoffman-Hamdi method's usage of temperatures exceeding 98 °C.

## 3.4 Material synthesis:

### 3.4.1 Synthesis of Cobalt Oxide ($Co_3O_4$) nanoparticles:

0.03 M cobalt nitrate hexahydrate dissolved in 60 ml distilled water and 0.26 M Urea ($CO(NH_2)_2$) dissolved in it. Then Urea solution drops drop-wise into the cobalt nitrate solution. The solution is stirred by a magnetic stirrer until we get a transparent solution. Then the solution is transferred to a Teflon-lined autoclave and filled with distilled water up to 80٪ of total capacity. The autoclave was then sealed and heated at 180 ˚C for 3 h respectively. Centrifuge (4000 r/min) the solution, the precipitate obtained then washed three times with distilled water/ ethanol. After that, the precursor was dried for 8 h at 80 ˚C and then annealed at 400 ˚C for 2 h at a heating rate of 4 ˚C/min to get desired cobalt oxide nanoparticles.

### 3.4.2 Synthesis of Polypyrrole (PPy):

Polypyrrole was synthesized by mixing 0.08 M sodium dodecylbenzene sulfonate (DBSNa) surfactant dissolved in 50 ml distilled water and 0.35 M of iron chloride hexahydrate ($FeCl_3.6H_2O$) oxidant also dissolved in another 50 ml distilled water. Then both the solutions are mixed by dropping dropwise and stirred at 0-5 ˚C by a magnetic stirrer. After some time 0.15 mol (1 ml) of pyrrole monomer was added drop-wise into the mixture. Then the solution was centrifuged and washed with distilled water several times and as a result, black PPy power was obtained by drying for 8-10 h in an oven at 60 ˚C.

### 3.4.3 Synthesis of rGO:

Reduced graphene oxide synthesis was carried out by Hummer's method. Take 0.5 g of graphene oxide in 250 ml distilled water and then sonicate the solution for 2 h respectively. After that, the pH of the solution maintains at 10 by dropping the ammonia solution during continuous stirring. Then 2 ml hydrazine hydrate was added and stirred again continuously at 80 °C for 24 h and the colour of the solution changes from brown to black. It was then cooled down and passed through a separating funnel and filtered, it was then washed with distilled water several times. Finally, the precursor was dried at 80 °C for 24 h and as a result, black product of reduced graphene oxide was obtained.

### 3.4.4 Synthesis of Cobalt Oxide/ reduce graphene oxide ($Co_3O_4$/ rGO) composites:

$Co_3O_4$ /rGO nanocomposites synthesis was taken out by mixing 0.14 g of GO in 40 ml distilled water followed by 2 h of sonication. 0.11 M cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) dissolved in 20 ml distilled water and stirred it for 1 h. After that, the cobalt solution drop dropwise to the GO solution during continuous stirring. Then pH should be maintained at 7 by dropping the ammonia solution and leaving the solution for 30 min stirring. The solution is transferred to a Teflon tube and filled with upto 80% of the total capacity. Then the autoclave was kept in an oven for 7 h at 180 °C. After completing the reaction time, the autoclave was cool down to room temperature then centrifuged and washed with ethanol and distilled water three to four times to remove impurities. Finally, the precursor was dried at 80 °C for 6-8 h to get the desired $Co_3O_4$/rGO nanocomposites.

### 3.4.5 Synthesis of Cobalt Oxide/ reduce graphene oxide/Polypyrrole ($Co_3O_4$/ rGO/PPy) Ternary nanocomposites:

0.2 g rGO/$Co_3O_4$ composite as prepared above was mixed in 80 ml distilled water and stirred for 1 h. After adding 2.1 ml pyrrole to rGO/$Co_3O_4$ solution, sonicate the solution for 1 h and we get rGO/$Co_3O_4$/pyrrole solution. A separate solution of iron chloride and hydrochloric acid is added to the above solution and the solution is kept in an ice bath at 0-5 °C for 24 h during continuous stirring. After 24 h the polymerization is complete and then centrifuge the solution several times and then put in the oven at 70 °C for 8 h respectively. Then the sample is ground and as a result of this, we get PCG nanocomposites respectively.

## 3.5 Characterization Techniques:

The grain size, surface morphology, elemental structure, elemental composition and electrochemical performance of nanoparticles, as well as their effects, are studied using characterisation techniques. These approaches are used to investigate structural, morphological, elemental composition and their electrochemical performance. The following are the characterizations that are employed in different nanomaterials analyses.

- X-ray Diffraction (XRD)
- Scanning Electron Microscope (SEM)
- Energy Dispersive X-ray Spectroscopy (EDX)
- Cyclic Voltammetry (CV)
- Electrochemical Impedance Spectroscopy (EIS)

### 3.5.1 X-Ray Diffraction (XRD):

The method of X-ray diffraction is widely used in materials research to get Information on unit cell sizes, lattice characteristics, and crystalline domain size for crystalline segment identification. The basis of X-ray diffraction is the constructive interference of a single X-ray beam scattering at particular directions from all arrangements of lattice spacing in crystallites.

An X-ray tube, sample chamber and x-ray sensor seem to be the three core components of XRD. XRD emit X-rays by heating a filament to produce electrons. The electrons are then moving with a high voltage towards a target anode, which is usually Cu, Mo or Co. Two separate mechanisms produce X-rays when electrons collide with the target material, resulting in the release of constant radiation (Bremsstrahlung) and characteristic X-ray radiation.

When electrons have enough energy to knock off inner shell electrons from anode atoms and electrons from higher energy levels fill in the voids, the characteristic X-ray photons are released (X-ray spectra are produced).

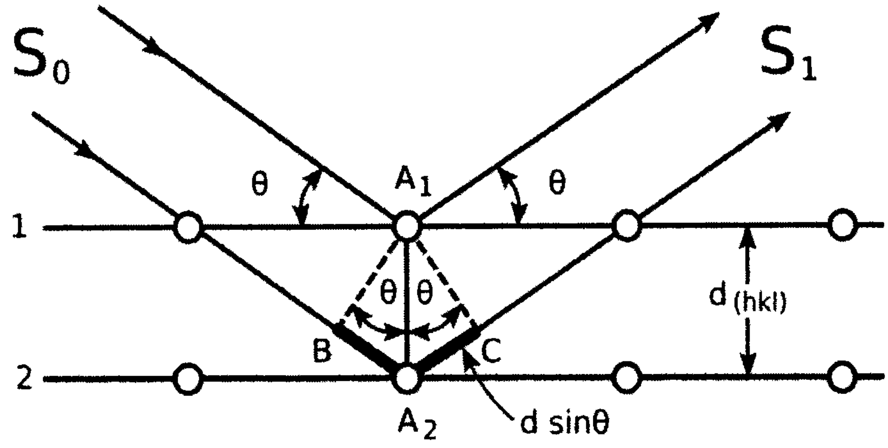

**Figure 3.2:** Bragg's diffraction

The most common single-crystal diffraction target material is copper, Cu Kα radiation has a wavelength of (Cu Kα) = 1.5418 and is the most typical target material. These X-ray beams are filtered for diffraction, resulting in monochromatic X-rays that are collimated and directed onto the sample. The intensity of the reflected X-rays is recorded while the sample and detector are rotated.

Constructive interference occurs when the geometry of the incident X-rays impact on the sample meets the Bragg Equation, resulting in a peak in intensity.

$$2d\sin\theta = n\,\lambda \qquad \text{(Bragg's Law)}$$

Where "d", "θ" and "λ" is the interplanar distance, diffracted angle and x-ray wavelength. "n" is the number of order n=0,1,2,3........

A sensor registers and proceeds the X-Ray radiation to convert it to a device such as a printer or CPU. The sample rotates at an angle to the collimated X-ray beam direction, to collect diffracted X-rays and the sensor is attached to an arm that spins at a 2θ angle. A goniometer is a tool to keep the sample spinning while maintaining the angle. For common precipitate patterns, which are well-known data is taken at 2θ ranging from 5° to 80°. In a crystalline sample, the above equation connects the relationship b/w the wavelength and diffraction angle, as well as the lattice spacing d. Bragg's relation is graphically illustrated in figure 3.2.

The Scherrer equation may then be used to compute the particle size:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where "D" is the crystalline domains' average size. "K" is a dimensionless figure factor having a value of approximately 0.9 for spherical particles. "λ", "β" and "θ" is the X-ray wavelength, full width at half maximum (FWHM) of the reflection and diffraction angle respectively.

## 3.5.2 Scanning Electron Microscopy (SEM):

One of the most extensively utilised methods for the characterisation of nanomaterials and nanostructures is SEM. SEM generates an image by using electrons rather than light. These beams of electrons interact with the sample's atoms to generate signals that provide data about the surface topography, chemical arrangement, and crystalline structure of the sample. The Scanning Electron Microscope also offers a significantly greater resolution, allowing for much higher magnification of closely spaced specimens.

At least one detector (typically a secondary electron detector) is included in every Scanning Electron Microscope but most have back-scattered electron detector and energy dispersive spectrum detector respectively.

The specimens were tested by placing them on the stage. The basic principle is that an electron beam is produced by a suitable source, such as a tungsten filament or a field emission cannon. When tungsten wire was subjected to an electric field, it activated to release electrons. Both the metal disc (anode) and the cathode are activated simultaneously, allowing the anode to accept electrons from the cathode.

A high voltage is used to accelerate the electron beam, which is then passed via a series of apertures and electromagnetic lenses which concentrate it downward toward the sample in a vertical route through the vacuum-sealed microscope. The role of condenser lens is to adjust the width of electron beam and to control the amount of electrons travelling down the column. Objective lens is used to focus the beam into a spot on the sample. Rastering or deflection coils helps to deflects electron beam respectively. When the beam strikes the sample, electrons and X-rays are expelled that can be detected by the sensors/detectors.

Everhart Thornley or Secondary electron detector detects secondary electron and convert this signal into SEM image.

Additional detectors like back-scattered electron detectors are also present that detects the incident electrons that hit sample, and reflect back. They have high energy and originate from deep within the sample and interacts strongly with sample.

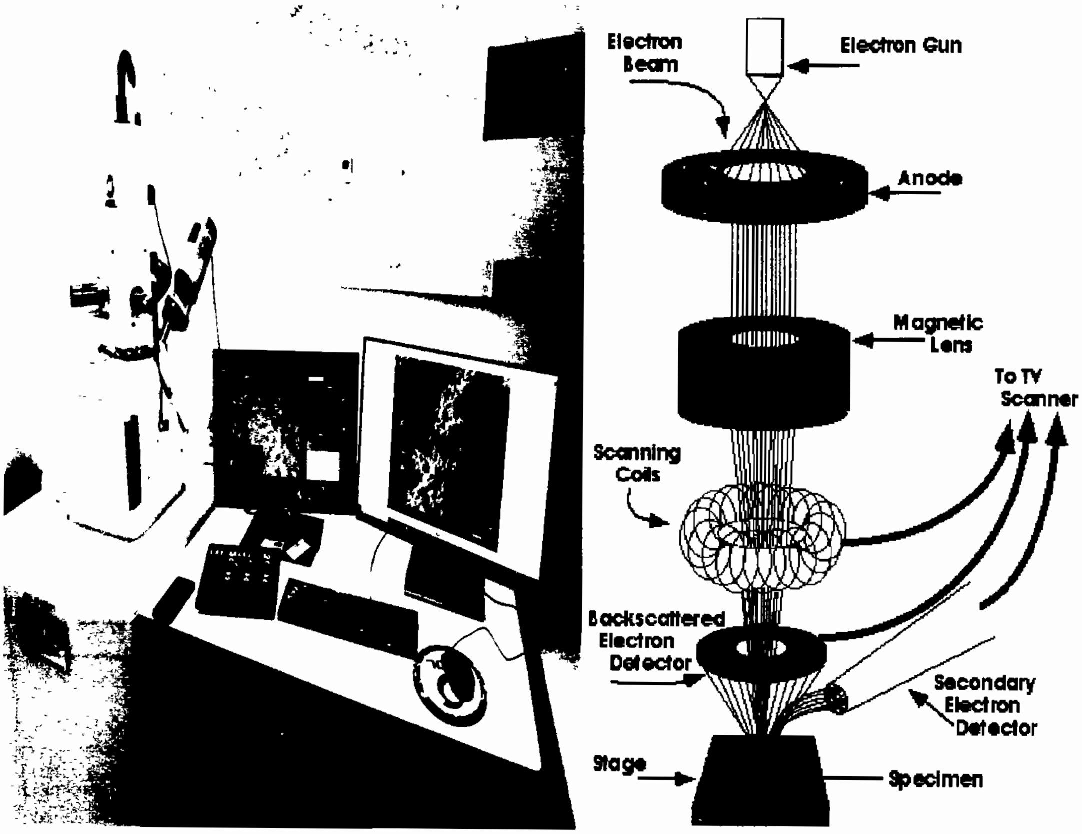

**Figure 3.3:** Experimental Setup for Scanning Electron Microscope

### 3.5.3 Energy Dispersive X-ray (EDX):

Energy Dispersive X-ray Spectroscopy, a well-known non-destructive X-ray technology. EDS is a widely used technology for detecting and analyzing the elements (elemental compositions) contained in material as tiny as a few cubic micrometres.

The elemental analysis or chemical characterisation of material is done with EDS. X-rays produce by falling electron beams into the sample that is under-investigated. As a result of this, the electrons of atoms get energy through electrons that fall on them. Then atom's electrons excite and go to a high energy level and as a result of this, a hole is produced at this place from where it goes to an excited state. Then electrons from higher energy shells lose their energy and fill this hole and in this way, excitation/de-excitation of electrons occurs and we can get about element composition. An energy-dispersive spectrometer can detect the elemental composition of a material by measuring the amount and energy of X-rays emitted by a specimen. The energy obtained from voltage measurement by each incident X-ray is delivered to a computer for display.

### 3.5.4 Cyclic Voltammetry (CV):

Cyclical Voltammetry (CV) is a very important approach for assessing the electrochemical achievements of materials used in electrochemical energy storage devices such as supercapacitors. Cyclic voltammetry is an electrochemical process used for measuring the current response of a redox-active solution w.r.t cycled potential sweep. Sweeping the potential back and forth between the defined bounds is how the current is measured. The redox peak is predicted by a cyclic voltammogram's graphical analysis, which predicts the electrode's capacitive behaviour.

As a consequence, the material's oxidation and reduction potentials may be calculated. By carefully examining the CV curve, several important inferences concerning the material and its qualities (capacitance), as well as the system behaviour, may be derived. In CV testing, one or more potential cycles might be employed. Only the outer surface of nanoparticles can be used for charge storage.

Similar to other kinds of voltammetry, cyclic voltammetry uses a three-electrode setup with a working electrode, a reference electrode, and a counter electrode submerged in an electrolyte.

The working electrode (WE) material has a significant impact on the voltammetric procedure's performance. The reaction of interest takes place on the working electrode, it should have a good signal-to-noise ratio and be repeatable. As a result, it is essentially determined by two factors; the target analyte's redox behaviour and the background current across the measurement's potential area. The potential window, electrical conductivity, surface repeatability, mechanical qualities, cost, availability, and toxicity are all factors to consider. Working electrodes for electroanalysis can be made of a variety of materials, the most common of which are mercury, carbon or noble metals (particularly platinum and gold).

The reference electrode (RE) has a constant potential, it may be utilised as a reference standard for determining the potential of other electrodes in the cell. Silver-silver chloride or calomel electrodes are common reference electrodes.

The counter electrode (CE) is also known as an auxiliary electrode since it acts as a source or sinks for electrons, allowing current to flow from an external circuit via the cell. Between the working electrode and the reference electrode, the potential is measured, while the current is measured between the working electrode and the counter electrode.

The sample's scanning rate (mV/s) is the rate of voltage change over time throughout each of these phases. The scan rate might be anywhere from a few $mVs^{-1}$ to hundreds of $mVs^{-1}$. As a result, in establishing the voltammetry nature of the substance to be assessed, the scanning rate is critical. Depending on the rate of scanning, peak currents in oxidation and reduction, as well as peak potentials, should change. Furthermore, the electrode material has strong rate capability as well as better pseudocapacitive behaviour also the scan rate rises and the peak current (faradaic current) increases [66].

A quicker scan rate leads to a greater quantity of redox responses because the electroactive type is present at the conductor's (working electrode) surface. Moreover, due to lack of time or the products of a chemical process whose compounds are not electroactive, a slower scan rate increases the danger of losing the peak.

The ratio of anodic to cathodic peak currents establishes if the process is reversible, irreversible, or quasireversible. If the above ratio is 1, the system is reversible meaning the anodic and cathodic peak currents have the same value. The process is quasi-reversible if the ratio is less than or greater than 1, but irreversible when the oxidised or reduced product is irreversible. The current peaks are virtually acquired because the CV is taken in a state where the solution is kept undisturbed; otherwise, the limiting current may replace the peak current.

It also gives an estimate of the specific capacitance of the material, which can be calculated using the following equation:

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

Where "m" and "V" is the mass of the electroactive material, scan rate (mV/s) and ∫idV represent the region below the curve in the scheme among V and I [67]. As a result, the chemical and electrochemical characteristics of the substance are investigated using CV.

### 3.5.5 Electrochemical Impedance Spectroscopy:

Electrochemical impedance spectroscopy is a very important method to investigate the properties of an electrochemical system through the lens of impedance which can be thought of as the AC analogy of resistance in a DC circuit. It allows us both to study the bulk and surface properties of our system through analogies to circuit elements. We can say that electrochemical impedance spectroscopy is a technique that measures the impedance of an electrochemical system at a range of different frequencies. To highlight a number of the supercapacitor's parameters and access their behaviour in a certain frequency range EIS method is used. EIS is based on the alternating current (AC) electrode process.

In electrostatic EIS, the input signal is voltage and the output signal is current while in galvanostatics EIS, the input signal is current and the output signal is voltage respectively. The electrochemical impedance spectroscopy gives us two types of information about the sample in the form of a Nyquist plot and a Bode Plot respectively. The Nyquist plot is a relationship between real impedance and imaginary impedance and it consists of two parts, high frequency and low-frequency part.

As frequency causes impedance, so it is necessary to explore the various frequency ranges to get an impedance spectrum. EIS experiment is carried out via different signal factors [68]. It is possible to comprehend the patterns of EIS statistics by contrasting them with a customized Randles circuit [69].

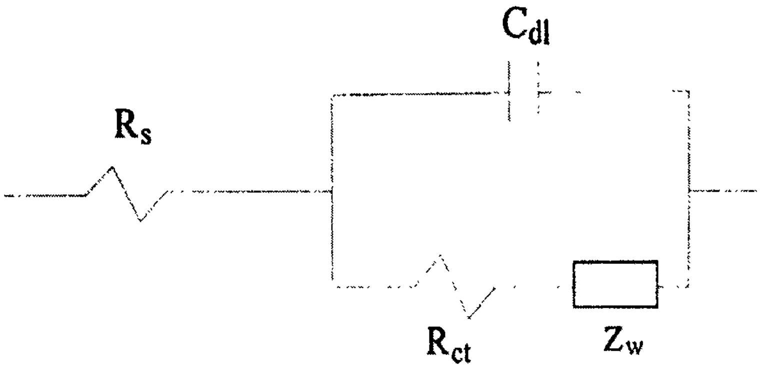

**Figure 3.4:** Randles circuit

EIS is a great resource for examining the properties of conducting polymers. It is useful for corrosive research and for calculating the flat-band voltage with the Schottky equation [70]. The interface capacitance of semiconductors and an electrolyte is correlated to a voltage by the Motte-Schottky equation.

The resistance of charge transfer (Rct), which is responsible for the graph's semicircular form in the high-frequency band, occurs at the electrode/electrolyte interaction. Straight-line (constant slope) plot occurs in low-frequency region in the EIS spectra [71].

# Chapter 04

## Result and Discussions

### 4.1 X-Ray Diffraction Analysis:

The x-ray diffraction (XRD) technique was carried out using CuKα radiations (λ=0.15418nm) to examine the crystal structure of the nanomaterial. The XRD pattern of Cobalt oxide ($Co_3O_4$), Polypyrrole (PPy), reduced graphene oxide (rGO) and PPy/$Co_3O_4$/rGO ternary nanocomposites are shown in Fig. 4.1 (a-d) respectively.

Figure 4.1a shows the XRD patterns of cobalt oxide nanoparticles, Cobalt oxide nanoparticles show peaks at 31.57°, 36.67°, 38.53°, 44.51°, 55.82°, 59.26°, 65.12°, and 77.21° corresponding to (220), (311), (222), (400), (422), (511), (440), and (533) planes of the crystalline cubic $Co_3O_4$ confirmed with JCPDS # 042-1467. There were no noticeable diffraction peaks of any impurity phases, suggesting that this hydrothermal process was effective in producing pure $Co_3O_4$. By using Scherrer's formula, we get $Co_3O_4$ crystallite size based on diffraction peak "311" found to be 63nm.

Figure 4.1b shows the amorphous nature of polypyrrole and indicated a broad hump around 25.3°. The absence of a sharp peak or a broad peak indicated that no crystalline structure had developed in the material [72].

Figure 4.1c shows that reduced Graphene oxide exhibits diffraction peaks at 26.5° and 54.6° corresponding to (002) and (004) planes in rGO. The diffraction peak at 26.5° is not as sharp as the other peak which is at 54.6°. The diffraction peak at 26.5° shows a broad humped while the peak at 54.6° shows the Crystallinity of the material. The overall result confirms the semi-crystalline nature of the material respectively.

All the peaks of cobalt oxides, rGo and the amorphous nature of Polypyrrole are well observed in figure 4.1d confirming the presence of PPy-$Co_3O_4$-rGO ternary nanocomposites respectively.

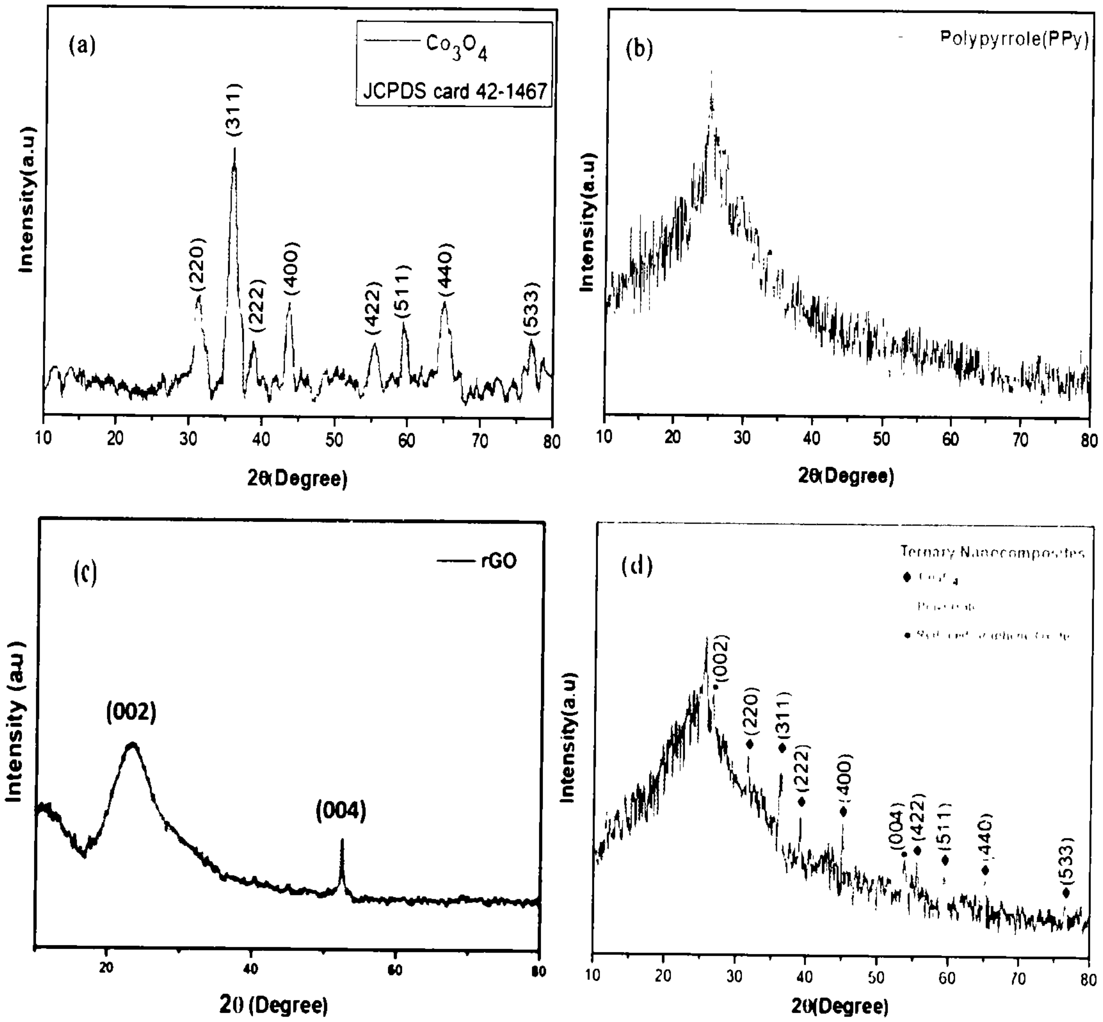

**Figure 4.1:** XRD patterns of (a) Cobalt oxide nanoparticles (b) PPy (c) rGO (d) $Co_3O_4$-PPy- rGO ternary nanocomposites.

## 4.2 Scanning Electron Microscopy Analysis (SEM):

The surface morphology and particle size of the structure of Cobalt oxide ($Co_3O_4$), Polypyrrole (PPy), reduced graphene oxide (rGO) and their ternary PPy/$Co_3O_4$/rGO nanocomposites are observed by scanning electron microscopy. With scanning electron microscope we get high precision, better resolution (up to 100 nm) and also can get magnified images.

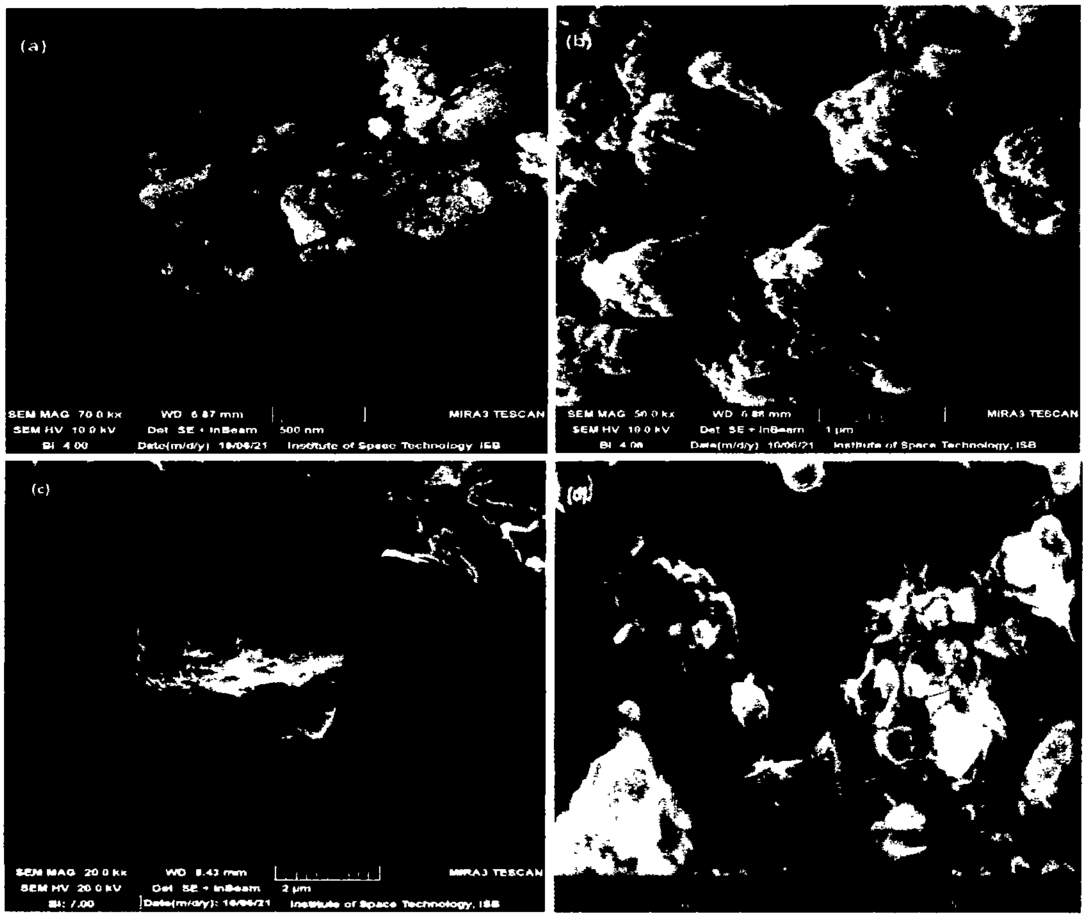

**Figure 4.2**:SEM images of (a) Cobalt oxide nanoparticles (b) PPy (c) rGO (d) $Co_3O_4$-PPy- rGO ternary nanocomposite.

Figure 4.2(a-d) represents the typical SEM images of Cobalt oxide ($Co_3O_4$), Polypyrrole (PPy), reduced graphene oxide (rGO) and their ternary PPy/$Co_3O_4$/rGO nanocomposites respectively.

It can be observed from figure 4.2a that the synthesized sample consists of a large quantity of $Co_3O_4$ nanoparticles. This image is at high resolution and the morphology in this image is closer to cubic-like nanoparticles that can be confirmed with the xrd pattern of the $Co_3O_4$ nanoparticles. Figure 4.2b shows that the morphology of the synthesized sample is likely globular and with xrd we can confirm the amorphous nature of polypyrrole. Figure 4.2c shows the sheet-like morphology of reduced graphene oxide. Figure 4.2d shows the presence of cobalt oxide, polypyrrole, reduced graphene sheet and with xrd diffraction peaks data we can confirms its presence respectively.

## 4.3 Energy Dispersive X-Rays Analysis:

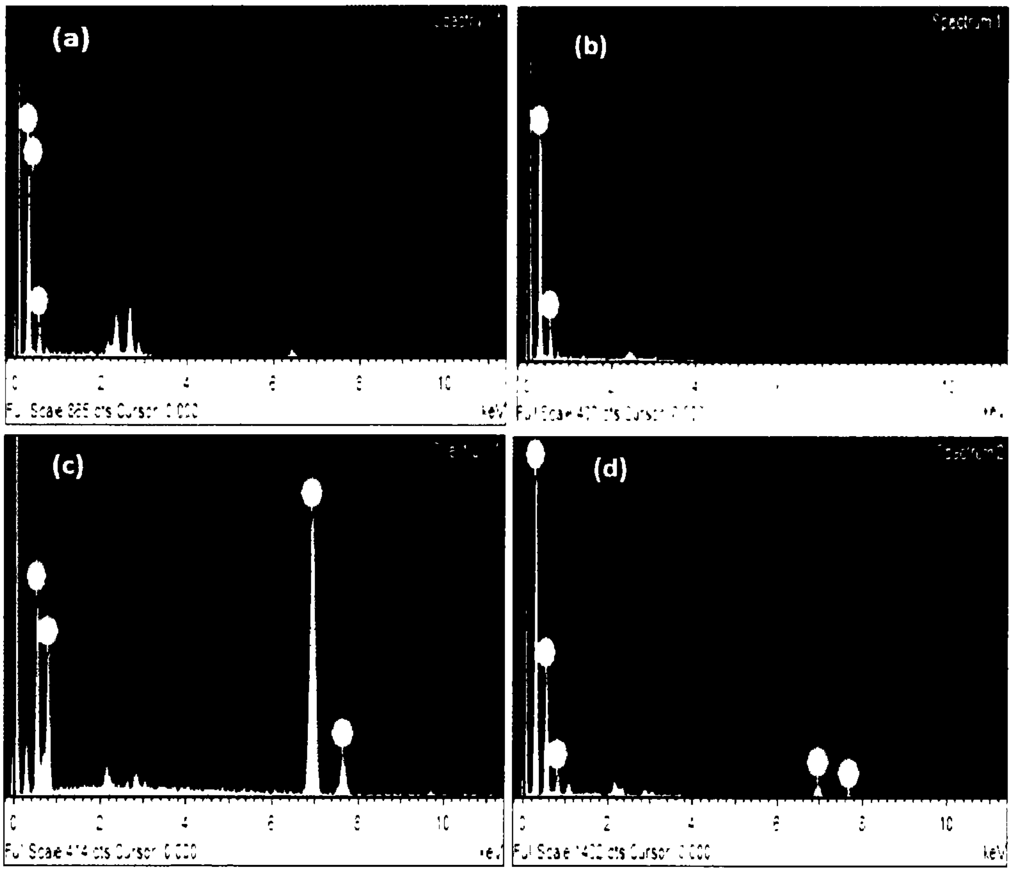

**Figure 4.3:**EDX spectra of (a) Polypyrrole (b) rGO (c) Cobalt oxide nanoparticles (d) $Co_3O_4$-PPy-rGO ternary nanocomposite

The elemental composition of Cobalt oxide ($Co_3O_4$), Polypyrrole (PPy), reduced graphene oxide (rGO) and their ternary PPy/$Co_3O_4$/rGO nanocomposites are observed by energy dispersive X-rays spectroscopy (EDX). The EDX spectrum is used to examine the prepared sample's elemental content. Figure 4.3a shows the EDX/EDS spectrum of polypyrrole, which confirms the presence of carbon and nitrogen that the pyrrole has in its natures respectively. Figure 4.3b shows the EDX/EDS of reduced graphene oxide that contains carbon and oxygen. Figure 4.3c shows the EDX/EDS of cobalt oxide nanoparticles, but here we can see three peaks of cobalt and one of oxygen. These three peaks occur due to the exciting and de-excite of electrons in their outermost shell and figure 4.3d illustrate the EDX/EDS of $Co_3O_4$/rGO/PPy composites respectively.

## 4.4 Cyclic Voltammetry:

Cyclic Voltammetry (CV) is a very important approach for assessing the electrochemical achievements of materials for electrochemical energy-storing devices such as supercapacitors. It is employed to interpret an electrode's current and voltage responses and also for measuring the current response of a redox-active solution concerning cycled potential sweep. It also provides an analysis of an electron transfer process at an electrode. The electrochemical performance of Cobalt oxide ($Co_3O_4$), Polypyrrole (PPy), reduced graphene oxide (rGO) and their ternary PPy/$Co_3O_4$/rGO nanocomposites are observed by Cyclic Voltammetry.

The electrochemical characteristics were investigated using cyclic voltammetry for polypyrrole (PPy), cobalt oxide ($Co_3O_4$), reduced graphene oxide (rGO) and their ternary PPy/$Co_3O_4$/rGO nanocomposite in an electrolyte of 1M sodium hydroxide through a potential from -0.2 to 0.7V. The reference and counter electrodes used are AgCl/Ag and platinum respectively.

Figure 4.4a represents the relationship between potential and current response for Polypyrrole (PPy), cobalt oxide ($Co_3O_4$), reduced graphene oxide (rGO) and ternary PPy/$Co_3O_4$/rGO nanocomposites at a scan rate of 5 mV/s respectively.

The CV curve displays the unique shapes of all the samples that were distinguishable from the ideal rectangular form of the EDLCs by having a pair of redox peaks except reduced graphene oxide because reduced graphene oxide has no redox peaks. Its cyclic voltammetry curve is rectangular in shape respectively.

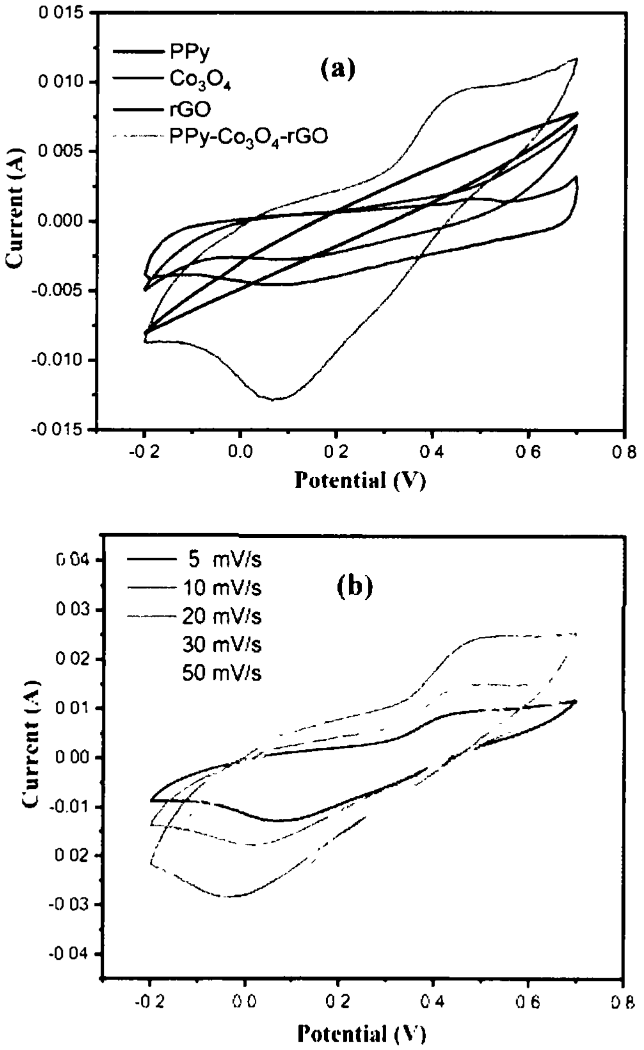

**Figure 4.4:**Cyclic Voltammetry of (a) Polypyrrole, cobalt oxide, reduced graphene oxide and $Co_3O_4$/PPy/rGO ternary nanocomposites at 5 mV/s scan rate in 1M NaOH electrolyte (b) Cyclic Voltammetry of ternary nanocomposites at different scan rates

As shown in figure 4.4a, the polypyrrole and cobalt oxide curves are not like reduced graphene oxide because in reduced graphene oxide the faradic reactions do not occur and due to this, we get the rectangular curve. While in polypyrrole/cobalt oxide faradic reactions occur and due to this, we get deviation from the curve that can be seen. We can also see this oxidation/reduction peak in ternary nanocomposite respectively.

In Figure 4.2b, we can see the different curves of the ternary nanocomposites at different scan rates, we observe that the ternary composite has good oxidation/reduction and also the area of the curve increases as the scan rate increases.

## 4.5 Electrochemical Impedance Spectroscopy (EIS):

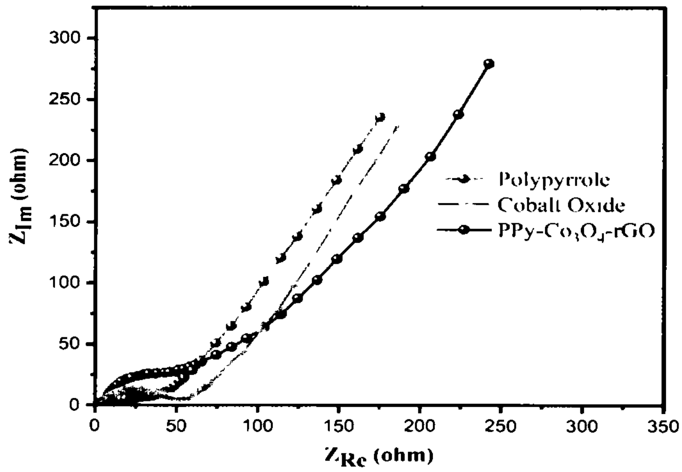

**Figure 4.5**:Electrochemical impedance spectroscopy of Polypyrrole, cobalt oxide and $Co_3O_4$/PPy/rGO ternary nanocomposites

Figure 4.5 show the Nyquist plot of polypyrrole, cobalt oxide and ternary nanocomposites of $Co_3O_4$/PPy/rGO at a frequency range from 1000 kHz to 0.1 Hz.

As frequency causes impedance, so it is necessary to explore the various frequency ranges to get the impedance spectrum. EIS experiment is carried out via different signal factors [68].

Nyquist plots were used to analyze the real and imaginary impedance of $Co_3O_4$, PPy and Ternary PPy/$Co_3O_4$/rGO nanocomposite. Real impedance is consistent with the actual resistance of the material, while imaginary impedance describes the capacitance of the materials respectively.

Although Polypyrrole (PPy) is a conducting polymer having high impedance, cobalt oxide has less impedance as compared to polypyrrole due to its high conductivity and its good redox ability. Among all of these reduced graphene oxide have higher charge mobility and have a large active surface area that why when it is added to ternary nanocomposites nanocomposite, the capacitance of composites increases respectively.

## Conclusion:

The objective of this research was to develop an electrode material with improved electrochemical characteristics for supercapacitive properties such as its capacitance, cyclic stability and impedance analysis for use in supercapacitors. By using different methods like polymerization, hydrothermal method and Hummer's method. We synthesized polypyrrole, cobalt oxide, reduced graphene oxide and their ternary $Co_3O_4$/PPy/rGO nanocomposites by a two-step method to explore their supercapacitive capabilities for use in real-life applications. SEM, EDX and XRD were used to confirm the surface morphology, elemental composition and crystal structure of $Co_3O_4$, PPy, rGO and their ternary nanocomposite of $Co_3O_4$/PPy/rGO respectively. To investigate the electrochemical properties of the synthesized nanoparticle and their nanocomposite, CV and EIS was carried out in a 1 M NaOH solution. By using EIS, we calculated the resistance and frequency-dependent impedance of our materials. In the complex PCG (PPy/$Co_3O_4$/rGO) structure, $Co_3O_4$ nanoparticles hinder restacking of rGO sheets, which consequently helps in the favorable mobility of the ions. Due to the high electrical conductivity of the rGO, the $Co_3O_4$/PPy/rGO Nyquist plot displays low impedance values respectively. By using CV, we found that $Co_3O_4$/PPy/rGO ternary nanocomposites having a high specific capacitance of 413 F/g with high cyclic stability at different scan rate respectively. Due to its high specific capacitance, cyclic stability, low impedance and cheap synthesis of the prepared nanocomposite, it is a favourable choice for supercapacitor applications.

# Reference:

[1] Dong Xiang, Longwei Yin, Chenxiang Wang, Luyuan Zhang. High electrochemical performance of $RuO_2$-$Fe_2O_3$ nanoparticles embedded ordered mesoporous carbon as a supercapacitor electrode material. Energy, 2016. 106,103-111.

[2] Maryam Khalaj, Arman Sedghi, Hoda Nourmohammadi Miankushki, Sanaz Zarabi Golkhatmi. Synthesis of novel graphene/$Co_3O_4$/polypyrrole ternary nanocomposites as electrochemically enhanced supercapacitor electrodes. Energy, 2019. 188, 116088.

[3] Xiyang Yan, Yansu Wang, Zhiling Ma. Synthesis, Characterization and Electrochemical Performance of Cobalt Oxides for Supercapacitor. International Journal of electrochemical science, 2018. 13, 1074–1083.

[4] Zheng Chen, Yaochun Qin, Ding Weng, Qiangfeng Xiao, Yiting Peng, Xiaolei Wang, Hexing Li, Fei Wei, Yunfeng Lu. Design and Synthesis of Hierarchical Nanowire Composites for Electrochemical Energy Storage. Adv Funct Mater, 2009. 19, 3420–3426. Manthiram, A. Vadivel Murugan, A. Sarkar and T. Muraliganth. Nanostructured electrode materials for electrochemical energy storage and conversion. Energy & Environ. Sci, 2008. 1,621–638.

[5] S. Mekhilef, R. Saidur, A. Safari. Comparative study of different fuel cell technologies. Renewable and Sustainable Energy Reviews, 2012. 16, 981– 989.

[6] Rizwan Raza, Nadeem Akram, Muhammad Sufyan Javed, Asia Rafique, Kaleem Ullah, Amjad Ali, M.Saleem, Riaz Ahmed. Fuel cell technology for sustainable development in Pakistan – An over-view. Renewable and Sustainable Energy Reviews, 2016. 53, 450–461.

[7] Gregor Hoogers. Fuel Cell Technology Handbook, Boca Raton, FL; CRC Press, 2003. Vol 1.

[8] H. Bakhshi Yamchia, H. Shahsavaria, N.Taghizadegan Kalantaria, A. Safaria, M.Farrokhifarb. A cost-efficient application of different battery energy storage technologies in microgrids considering load uncertainty. Journal of Energy Storage, 2019. 22, 17–26.

[9] Ghassan Zubi, Rodolfo Dufo-López a, Monica Carvalho, Guzay Pasaogluc. The lithium-ion battery: State of the art and future perspectives. Renewable and Sustainable Energy Reviews, 2018. 89, 292–308.

[10] Languang Lu, Xuebing Han, Jianqiu Li, Jianfeng Hua, Minggao Ouyang. A review on

the key issues for lithium-ion battery management in electric Vehicles. Journal of Power Sources, 2013. 226, 272-288.

[11] Kai Liu, Yayuan Liu, Dingchang Lin, Allen Pei, Yi Cui. Materials for lithium-ion battery safety. Science Advances, 2018. 4, 9820.

[12] J. Garche, C. Dyer, P. Moseley, Z. Ogumi, D. Rand, B. Scrosati. Encyclopedia of Electrochemical Power Sources. Elsevier B.V, Amsterdam, 2009. 1, 587–598.

[13] Max Lu, Francois Beguin, Elzbieta Frackowaik. Supercapacitors: Materials, systems and applications. John Wiley & Sons, 2013.

[14] Ranjit S. Kate, Suraj A. Khalate, Ramesh J. Deokate. Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for supercapacitors: A review. Journal of Alloys and Compounds, 2018. 734, 89-111.

[15] Fan Shi, Lu Li, Xiu-li Wang, Chang-dong Gu and Jiang-ping Tu. Metal oxide/hydroxide based materials for supercapacitors. Royal Society of chemistry advances, 2014. 4(79), 41910-41921.

Okonkwo, P. C, Collins, E, & Okonkwo, E. Application of biopolymer composites in super capacitor. In Biopolymer composites in electronics, Elsevier, 2017. 487-503.

[16] Alon Oz, Shany Hershkovitz and Yoed Tsur. Electrochemical impedance spectroscopy of supercapacitors: A novel analysis approach using evolutionary programming. AIP Conference Proceedings, American Institute of Physics. 2014. 1627, 76-80.

[17] B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer Academic/Plenum, New York, 1999. 1ed.

[18] Cheng Zhong, Yida Deng, Wenbin Hu, Jinli Qiao, Lei Zhangd, Jiujun Zhang. A review of electrolyte materials and compositions for electrochemical supercapacitors. Chem. Soc. Rev, 2015. 44(21), 7484-7539.

[19] Amine Lahyani, Pascal Venet, Abdessattar Guermazi, Alaa Troudi. Battery/Supercapacitors Combination in Uninterruptible Power Supply (UPS). IEEE Transactions on Power Electronics, April. 2013, Vol. 28(4), 1509–1522.

[20] Santosh J. Uke, Vijay P. Akhare, Devidas R. Bambole, Anjali B. Bodade and Gajanan N. Chaudhari. Recent Advancements in the Cobalt Oxides, Manganese Oxides, and Their Composite As an electrode Material for Supercapacitor: A Review. Frontiers in Materials.

August 2017. Volume 4. Article 21.

[21] A. Gonzalez, E. Goikolea, J. A. Barrena, R. Mysyk, Review on supercapacitors: Technologies and materials. Renewable and Sustainable, Energy Reviews, 2016. 58, 1189–1206.

[22] John R. Miller and Andrew F. Burke. Electrochemical Capacitors: Challenges and Opportunities for Real-World Applications. The Electrochemical Society Interface. Spring 2008; Vol. 17, 53-57.

Li Li Zhang and X. S. Zhao. Carbon-based materials as supercapacitor electrodes. Chem. Soc. Rev, 2009. 38(9), 2520–2531.

[23] P.L.Taberna, P.Simon and J.F.Fauvarque. Electrochemical Characteristics and Impedance Spectroscopy Studies of Carbon-Carbon Supercapacitors. Journal of the Electrochemical Society, 2003. 150(3). A292-A300.

[24] Martin Winter, Ralph J. Brodd. What Are Batteries, Fuel Cells, and Supercapacitors? Chem. Rev. 2004, 104, 4245-4269.

[25] Zainul Abdin, Kaveh Rajab Khalilpour. Single and Polystorage Technologies for Renewable- Based Hybrid Energy Systems. In Polygeneration with Polystorage for chemical and energy hubs. Academic Press. 2019, (pp 77-131).

[26] Xuelei Wang, Anyu Hu, Chao Meng, Chun Wu, Shaobin Yang, and Xiaodong Hong. Recent Advance in $Co_3O_4$ and $Co_3O_4$-Containing Electrode Materials for High-Performance Supercapacitors. Molecules, 2020. 25, 269.

[27] Nilesh R. Chodankar, Hong Duc Pham, Ashok Kumar Nanjundan, Joseph F. S. Fernando, Kolleboyina Jayaramulu, Dmitri Golberg, Young-Kyu Han, and Deepak P. Dubal. True Meaning of Pseudocapacitors and Their Performance Metrics: Asymmetric versus Hybrid Supercapacitors. Small, 2020, 2002806.

[28] Min-Young Cho, Mok-Hwa Kim, Hyun-Kyung Kim, Kwang-Bum Kim, Jung Rag Yoon, Kwang Chul Roh. Electrochemical performance of hybrid supercapacitor fabricated using multi-structured activated carbon. Electrochemistry Communications, 2014, 47, 5-8.

[29] Mathieu Toupin, Thierry Brousse, Daniel Be Langer. Charge Storage Mechanism of $MnO_2$ Electrode Used in Aqueous Electrochemical Capacitor. Chem. Mater, 2004. 16(16), 3184-3190.

[30] Denisa Hulicova, Masaya Kodama, and Hiroaki Hatori. Electrochemical Performance

of Nitrogen-Enriched Carbons in Aqueous and Non-Aqueous Supercapacitors. Chem. Mater. 2006, 18, 2318-2326.

[31] L. Demarconnay, E. Raymundo-Piñero, F. Béguin. A symmetric carbon/carbon supercapacitor operating at 1.6 V by using a neutral aqueous solution. Electrochemistry Communications. 2010. 12(10). 1275-1278.

[32] Shuichi Ishimoto, Yuichiro Asakawa, Masanori Shinya, and Katsuhiko Naoi. Degradation Responses of Activated-Carbon-Based EDLCs for Higher Voltage Operation and Their Factors. Journal of the Electrochemical Society, 2009. 156(7), A563-A571.

[33] J.L. Bredas and G.B. Street. "Polarons, Bipolarons and Solitons in Conducting Polymers," American Chemical Society, Accounts of chemical Research. 1985, 18(10), 309-315.

[34] Xiaofeng Lua, Wanjin Zhanga, Ce Wanga, Ten-Chin Wenb, Yen Weic. One-dimensional conducting polymer nanocomposites: Synthesis, properties and applications. Progress in Polymer Science. 2010. vol. 36(5), pp. 671-712.

[35] Alan J. Heeger, Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials (Nobel Lecture), Angewandte Chemie International Edition, 2001. Ed 40(14), 2591-2611.

[36] Stephan Kirchmeyer and Knud Reuter, Scientific importance, properties and growing applications of Poly (3, 4-ethylenedioxythiophene), Journal of Materials Chemistry, 2005. 15(21), 2077–2088.

[37] Xinyu Zhang, Alan G. MacDiarmid and Sanjeev K. Manohar. Chemical synthesis of PEDOT nanofibers. Royal Society of Chemistry, Chemical communications, 2005. 42, pp. 5328-5330.

[38] H. Letheby. On the Production of a Blue Substance by the Electrolysis of Sulphate of Aniline, J. Chem. Soc, 1862. 15, 161-163.

[39] J.H. Burroughes, D.D.C Bradley, A.R Brown, R.N Marks, K. Mackay, R.H Friend, P.L Burns & A.B Holmes. "Light-Emitting Diodes Based on Conjugated Polymers," Nature, 1990. 347, 539-541.

[40] N.S. Sariciftci, D. Braun, C. Zhang, V.I. Srdanov, A.J. Heeger, G. Stucky and F. Wudl, "Semiconductor polymer-buckminsterfullerene heterojunctions: diodes, photodiodes and photovoltaic cells." Appl. Phys. Letters, 1993. 62(6), 585-587.

[41] Hai Dinh Pham, Viet Hung Pham, Eun-Suok Oh, Jin Suk Chung, and Sunwook Kim. Synthesis of polypyrrole-reduced graphene oxide composites by in-situ photopolymerization and its application as a supercapacitor electrode. Korean J. Chem. Eng. 2012, 29(1), 125-129.

[42] Rama Devi, Khilawan Patel, Vinayak Sahu, Komal Kashyap, Kavita Tapadia, Tungabidya Maharana. Fabrication and Characterization of Polypyrrole Nanoparticles For Supercapacitor Electrode Materials. Mater. Sci. Eng. 2020. 798. 012034.

[43] Abdirahman Yussuf, Mohammad Al-Saleh, Salah Al-Enezi, and Gils Abraham. Synthesis and Characterization of Conductive Polypyrrole: The Influence of the Oxidants and Monomer on the Electrical, Thermal, and Morphological Properties. International Journal of Polymer Science, 2018. Article ID 4191747, Pages 8.

[44] Sobhan Bahraeian, Khatereh Abron, Fatemeh Pourjafarian, Rohah.A.Majid, Study on Synthesis of Polypyrrole via Chemical Polymerization Method. Advanced Materials Research, 2013. 795,707-710.

[45] Ravindra Kumar, Satyendra Singh, B.C.Yadav. "Conducting Polymers: Synthesis, Properties and Applications." International Advanced Research Journal in Science, Engineering and Technology, 2015. 2(11), 110-124.

[46] R. McNeill, R. Siudak, J.H. Wardlaw and D.S. Weiss, "Electronic Conduction in Polymers: The Chemical Structure of Polypyrrole," Aust. J. Chem, 1963. 16(6), pp. 1056-1075.

[47] Mingjia Zhi, Chengcheng Xiang, Jiangtian Li, Ming Li and Nianqiang Wu. Nanostructured carbon–metal oxide composite electrodes for supercapacitors: a review. Nanoscale, the Royal Society of Chemistry, 2013. 5, 72-88.

[48] Guihua Yu, Xing Xie, Lijia Pan, Zhenan Bao, Yi Cui. Hybrid nanostructured materials for high-performance electrochemical capacitors. Nano Energy. 2013. 2, 213–234.

[49] Hongyan Xu, Libo Gao, Qiang Zhang, Junyang Li, Jiangtao Diwu, Xiujian Chou, Jun Tang, and Chenyang Xue. Preparation Method of $Co_3O_4$ Nanoparticles Using Degreasing Cotton and Their Electrochemical Performances in Supercapacitors. Journal of Nanomaterials, 2014. Article ID 723057, 9 pages.

[50] Zhong-Shuai Wu, Da-Wei Wang, Wencai Ren, Jinping Zhao, Guangmin Zhou, Feng Li, and Hui-Ming Cheng. Anchoring Hydrous $RuO_2$ on Graphene Sheets for High-

Performance Electrochemical Capacitors. Adv. Funct. Mater. 2010, 20, 3595-3602.

[51] Sohyun Jeon, Ji Hwan Jeong, Hyomin Yoo, Hak Ki Yu, Bo-Hye Kim, and Myung Hwa Kim. $RuO_2$ Nanorods on Electrospun Carbon Nanofibers for Supercapacitors. ACS Appl. Nano Mater. 2020. 3, 3847-3858.

[52] S.Vijayakumar, A.Kiruthika Ponnalagi, S.Nagamuthu, G.Muralidharan. Microwave assisted synthesis of $Co_3O_4$ nanoparticles for high-performance supercapacitors. Electrochimica Acta. 2013. 106. 500– 505.

[53] Keqing Zhou, Jiajia Liu, Panyue Wen, Yuan Hu, Zhou Gui. Morphology-controlled synthesis of $Co_3O_4$ by one step template-free hydrothermal method. Elsevier, Materials Research Bulletin. 2015. 67. 87-93.

[54] Ming-Jay Deng, Fu-LuHuang, I-Wen Sun, Wen-Ta Tsai and Jeng-Kuei Chang. An entirely electrochemical preparation of a nano-structured cobalt oxide electrode with superior redox activity. Nanotechnology 2009. 20. 175602 (5pp).

[55] Muhammad Shahid Mehmood, Alagarsamy Pandikumar, Amir Moradi Golsheikh, Huang Nay Ming, Lim Hong Ngee. Enhanced electrocatalytic performance of cobalt oxide nanocubes incorporated reduced graphene oxide modified platinum electrode for methanol oxidation. RSC Adv. 2014. 4 (107) 62793–62801.

[56] Cao Guan, Ximeng Liu, Weina Ren, Xin Li, Chuanwei Cheng, and John Wang. Rational Design of Metal-organic Framework Derived Hollow $NiCo_2O_4$ Arrays for Flexible Supercapacitor and Electrocatalysis. Adv. Energy Mater. 2017, 7, 1602391.

[57] C. G. Granqvist. Spectrally Selective Coatings for Energy Efficiency and Solar Applications. Physica Scripta, 1985. 32,401-407.

LA. Serbinov, S.M. Babulanam, GA. Niklasson, C.G Grangvist. Threshold behaviour for the electrical conductivity of $V_2O_5$ films reduced by heating in vacuo, J. Mater. Sci. 1988, 23, 2076-2078.

[58] Ravinder N. Reddy, Ramana G. Reddy. Sol-gel $MnO_2$ as an electrode material for electrochemical capacitors. J. Power Sources, 2003. 124, 330-337.

[59] Balasubramaniam Gnana Sundara Raj, Baskaran Natesan, Abdullah M. Asiri, Jerry J.Wu, Sambandam Anandan. Pseudocapacitive properties of nickel oxide nanoparticles synthesized via ultrasonication approach. Ionics 2020. 26: 953–960.

[60] Ji Chen, Bowen Yao, Chun Li, Gaoquan Shi. An improved Hummers method for eco-

friendly synthesis of graphene oxide. Carbon, 2013. 64, 225-229.

[61] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov. Electric Field Effect in Atomically Thin Carbon Films. Science, 2004.306, 666-669.

[62] Kasinath Ojha, Oruganti Anjaneyulu and Ashok K. Ganguli. Graphene-based hybrid materials: synthetic approaches and properties. Current Science, 2014. 107, 3, 397-418.

[63] Wenguang Tu, Yong Zhou, and Zhigang Zou. Versatile Graphene-Promoting Photocatalytic Performance of Semiconductors: Basic Principles, Synthesis, Solar Energy Conversion, and Environmental Applications. Adv.Funct.Mater, 2013. 23(40), 4996-5008.

[64] Chengcheng Xiang, Ming Li, Mingjia Zhi, Ayyakkannu Manivannan, Nianqiang Wu. A reduced graphene oxide/$Co_3O_4$ composite for supercapacitor electrode. Journal of Power Sources, 2013. 226, 65-70.

[65] Qiu, K.; Lu, Y.; Cheng, J.; Yan, H.; Hou, X.; Zhang, D.; Lu, M.; Liu, X.; Luo, Y. Ultrathin mesoporous $Co_3O_4$ nanosheets on Ni foam for high-performance supercapacitors. Electrochim Acta, 2015. 157, 62-68.

[66] Taehyun Kim, Ananthakumar Ramadoss, Balasubramaniam Saravanakumar, Ganesh Kumar Veerasubramani, Sang Jae Kim. Synthesis and characterization of $NiCo_2O_4$ nanoplates as efficient electrode materials for electrochemical supercapacitors. Applied Surface Science, 2016. 370, 452-458.

[67] Kassim anuar, Sagadavan murali, Adzmi fariz, H.N.M. Mahmud ekramul. Conducting Polymer/Clay Composites: Preparation and Characterization. Materials Science, 2004. 10(3), 255-258.

[68] Lin, J. W. P., & Dudek, L. P. Synthesis and properties of poly (2, 5-thienylene). Journal of Polymer Science: Polymer Chemistry Edition, 1980. 18(9), 2869-2873.

[69] Street, G. B., & Clarke, T. C. Conducting polymers: a review of recent work. IBM Journal of Research and Development, 1981. 25(1), 51-57.

[70] Schopf, G., & Kossmehl, G. Polythiophenes-electrically conductive polymers. Berlin, Heidelberg: Springer Berlin Heidelberg, 1997. 93-112.

[71] Roncali, J. Conjugated poly (thiophenes): synthesis, functionalization, and applications. Chemical Reviews, 1992. 92(4), 711-738.

[72] Chu Kuen Ong, Sudip Ray, Ralph P. Cooney, Neil R. Edmonds, Allan J. Easteal. Preparation and Characterization of Composites of Polyethylene with Polypyrrole-Coated Wollastonite. Journal of Applied Polymer Science, 2008. 110(1), 632–640.

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