Effect of PANI over Electrochemical Properties of V_2O_5-PANI Nanocomposites for Energy Storage Nanodevices

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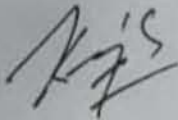
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CERTIFICATE

This is to certify that the thesis entitled "**Effect of PANI over Electrochemical Properties of V$_2$O$_5$-PANI Nanocomposites for Energy Storage Nanodevices**" by Ahmad Hassan Khan submitted to Quaid-I-Azam University, Islamabad, for the degree of Master of Philosophy (M.Phil.) in Physics is a record of bonafide research carried out by him in the Laboratory of Nanoscience and Technology (LNT), Department of Physics under my supervision. I believe this thesis fulfills part of the requirement for the award of Master of Philosophy. The result embodied in the thesis has not been submitted for the award of any other degree.
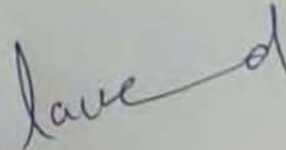
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Dedicated

To

My Parents

&

Siblings

Declaration

I, Ahmad Hassan Khan, Reg. No. **02182113028**, at this moment, declare that the project "**Effect of PANI over Electrochemical Properties of V$_2$O$_5$-PANI Nanocomposites for Energy Storage Nanodevices",** submitted by me under the guidance and supervision of Prof. Javed Iqbal Saggu, Professor at Quaid-i-Azam university Islamabad is my work and has not been submitted to any other university, institute or published earlier. The plagiarism test has been carried out using Turnitin software and lies in the permissible range. However, if this work is found to be plagiarised at any stage, I will be held responsible for it as per rules and regulations.

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A long and eventful journey is almost coming to an end. The period became a golden memory to cherish for a lifetime with all their affection, care, and immense help, which provided enough ignition to steer ahead and finish the massive-looking task. First and foremost, I want to offer this endeavour to ALLAH Almighty for the wisdom he bestowed upon me, the strength, peace of mind, and good health to finish this work. Thousands of blessings on the Holy Prophet (S.A.W.W), who is an ideal source of guidance for

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Abstract

The primary concern in addressing the need for supercapacitors with high energy density is the advancement of electrode materials that possess a broad potential range and exhibit a high specific capacitance for energy storage devices. Metal oxides due to high specific capacitances are worthy for electrode material yielding high energy and power delivering capacities. Among them, the Vanadium pentoxide (V_2O_5) has gained a persistent interest as a supercapacitor electrode due to excellent electrochemical property, cost effectiveness, layered structure, and many oxidation states (2^+ to 5^+). The addition of conducting polymers with V_2O_5 host matrix is expected to significantly tune the electrodes properties of supercapacitors. The desired V_2O_5 and its composites (V_2O_5-PANI) have been prepared with simple and versatile chemical methods to improve the electrical conductivity, electrode permeability and surface area of the electrode by moderating the agglomeration rate. The structural studies have clearly revealed that the V_2O_5-PANI nanocomposites are successfully prepared with single phase component structures having plenty of structural defects. The vibrational analysis for the existence of functional groups has further confirmed the successful formation of nanocomposites. The band gap energy of V_2O_5-PANI nanocomposites is significantly narrowed with addition of PANI which is potential for rapid charge and discharge of energy storage devices due to the more easily movement of electrons with better electron mobility and enhanced electrical conductivity. The electrochemical studies of the prepared nanocomposites depict that the capacitance is significantly enhanced with addition of different ratios of conducting nature of PANI polymer. It is interestingly observed that $(V_2O_5)_{0.50}(PANI)_{0.50}$ has shown highest capacitance of 745 F/g with low ohmic resistance of 0.24 Ω. This high capacitance with low Ohmic resistance of the prepared nanocomposites is highly suitable for energy storage devices with low voltage drop, low energy loss in form of heat with high efficiency and less thermal stress with large lifetime of the capacitor.

Chapter No. 01   Introduction

1.1 Material Science

Material Science is concerned with examining the characteristics of different materials and analyzing how materials can be used to formulate products that meet specific needs. Material Science assembles Physics, Chemistry and Engineering fields to understand the composition, properties, and production methods. Material Science examines the arrangement and action of different materials and their relationship and possible applications in engineering and other fields. It multifaceted Physics, Mathematics, Chemistry, and Engineering to dwell on the problems of modern technology. It includes studying manufacturing processes, for example, welding and casting, and the effect of different techniques on materials. Materials Science is essential for advancing new technologies and materials, ranging from creating cutting-edge semiconductor devices to producing advanced materials used in aerospace and biomedical applications. Materials Science is essential for advancing new technologies and materials, ranging from creating cutting-edge semiconductor devices to producing advanced materials used in aerospace.

In order to flourish Material Science, we need to understand materials' composition, features, and behaviors with their capacity to devise novel materials. This material science brief helps us study its past, domain, and potential advancement. Figure 1.1 shows the life cycle of the materials.
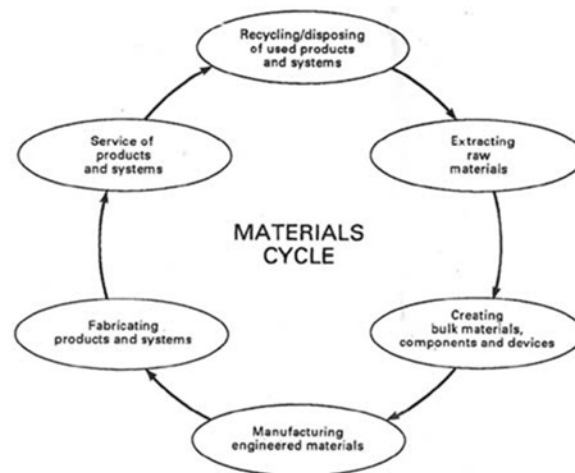

Figure 1.1: Life Cycle of materials

The materials cycle describes the transformation of raw materials into finished goods. Some materials are obtained directly from nature, however most materials used today have been modified

into purpose-built products. Materials design and manufacture have always been critical to the advancement of civilization from the dawn of time.

1.2 Nanoscience

The word "Nano" is a Greek letter which means very small. One nanometer is equal to 10^{-9} meter. Nanoscience is the study of material with a diameter between 1 and 100 nm range and its use in daily life [1]. The material at the nano level shows different properties than their bulk form because materials at the nano level have very small sizes and larger surface-to-volume ratios. At the nano level, materials also change their physical and chemical properties. In physics, material smaller than 10^{-9} meters shows quantum behaviour, and the classical law of physics does not apply to them. Nanoscience is also important to biology and biochemistry as DNA subcellular structures are nanostructures[2].

1.3 Nanotechnology

Nanotechnology is one of the most exciting 21st-century technologies. The potential to observe, evaluate, control, and build substances at the nanoscale provides the application of nanoscience theory. The National Nanotechnology Initiative (NNI) in the United States defines nanotechnology as "A discipline of nanoscale (1-100 nm) science, engineering, and technology which allows innovative applications in a wide range of fields, including chemistry, physics, and biology as well as medicine, engineering, and electronics." This definition states that there are two prerequisites for nanotechnology. Utilizing structures by changing their size and shape at the nanoscale is the main goal of nanotechnology. The second challenge is novelty: since small items must be handled at the nanoscale, nanotechnology must take advantage of specific properties. Because more than comprehensive knowledge in just one field will be required, a combination of physics, chemistry, material science, solid state, and biological understanding is required. Practically all branches of research and technology are progressively utilizing nanotechnology. The difference between nanoscience and nanotechnology is that the former is a technology used to control matter at the atomic level to fabricate novel nanomaterials with different properties[3]. At the same time, the latter provides knowledge about atom agreements and their fundamental properties at the nanoscale.

Figure 1.2: The role of Nanotechnology in Material Science [4].

1.4 Nanomaterials

Nanomaterials are basic of nanoscience and nanotechnology. Materials having length, height, and width at a nanoscale range of 1-100nm are called Nanomaterials. The quantum confinement effect, which has extremely interesting properties, emerges at this range. Nanomaterials can be created specifically for a given purpose or form spontaneously as byproducts of combustion processes. These materials may have different chemical and physical characteristics from their analogues in bulk form. This site has distinct optical, magnetic, electrical, and other characteristics. These new characteristics have a considerable favorable impact on electronics, medicine, and other industries. Nanomaterials research uses developments in materials metrology and synthesis that have been made for microfabrication research to approach nanotechnology from a material science perspective. Nanoscale materials frequently have special optical, electrical, thermos-physical and mechanical capabilities[5].

1.4.1 Classification of Nanomaterials

Based on dimensions, the nanomaterials are classified into four categories.

1.4.1.1 Zero-Dimensional Nanomaterials

Materials with zero dimensions are those whose all dimensions are at nanoscale (i.e., no dimension is larger than 100 nm). They have received much attention because of the excellent and distinctive chemical and physical characteristics that make them ideal for use as electrode materials [6]. Zero-dimensional nanomaterials include carbon ones, as depicted in Fig. 1.3 shows zero-dimensional nanoclusters.
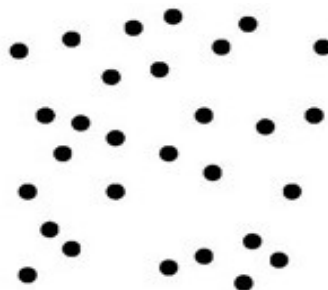
Figure 1.3: Zero-dimensional nanoclusters

1.4.1.2 One-Dimensional Nanomaterials

One-Dimensional nanostructures are very thin materials with two dimensions only present at the nanoscale[7]. Due to their unique structure and outstanding chemical and physical capabilities, extensive study has been done on them to design electrode materials for supercapacitors. Notably, extended axis of one-dimensional nanostructures allows for effective electron and ion transport channels[8]. Figure 1.4 shows one-dimensional nanomaterials.

Figure 1.4: One-dimensional nanofiber, rod and tube

1.4.1.3 Two-Dimensional Nanomaterials

A comprehensive and refined class of atomically thick nanoparticles comprising one to several layers of atoms is known as two-dimensional nanomaterials (2D nanomaterials).Two-dimensional nanomaterials lateral size can be as long as micrometers, and even longer ones can be created via novel synthesis techniques. These nanomaterials are distinguished by their high entropy, efficient area of surface, durability, plasmonic, electron confinement, and optical characteristics [7]. These nanomaterials can be tailored to become insulators or superconductors. They are extensively used in supercapacitor applications and catalysis. Since the surface areas of these electrode materials have an enormous effect on capacitance, so these materials are expected to lead to a paradigm shift in the study of electrochemical capacitors[9]. Figure 1.5 illustrates the two-dimensional nanomaterials.

Figure 1.5: Two-dimensional nanomaterials

1.4.1.4 Three-Dimensional Nanomaterials

Material that can move freely in three dimensions is called three-dimensional nanomaterials. These nanomaterials have a larger surface area, mechanical stability, and porous structure. It provides an easy pathway to electrolyte access in Supercapacitor electrodes. These nanomaterials are synthesized by novelizing material into nanostructures and using metal foam as templates. Bulk powder and nanowires are examples of 3D materials.

1.5 Nanoscale Physics

Physics at the nanoscale describes the physical phenomenon and changes that occur when macroscopically sized materials are converted to the nanoscale level. It describes the basic cross-disciplinary effect in materials. The particle at the nanoscale changes due to the following factors.

1)   Quantum Confinement
2)   Surface to Volume Ratio

1.5.1 Quantum Confinement

The study of the bound electron's energy is known as the quantum confinement effect. The effect of quantum confinement is seen when a particle's size is equivalent to an electron's wavelength. The electron's energy level becomes discrete under quantum confinement instead of continuous in the bulk material. This phenomenon is caused by quantum dots in nanocrystals. This quantum dot effect affects nanomaterials' electrical, optical, and mechanical characteristics. Nanomaterials contain greater energy electrons than bulk materials because of their special characteristics. Bound electrons have more energy than electrons in bulk substances, according to the size of the QDs.

1.5.2 Surface-to-Volume Ratio

The surface to volume ratio is very important in the electrochemical properties of any material; these properties are truly linked with the size of the constituent by which any material is made. If we talk about a sphere of any known radius. If we cut this sphere into nano-size spheres, these small spheres have a large surface area. So, we conclude that as we decrease the size of the particle, its surface-to-volume ratio increases.

Surface area is linked with the reactivity of material; a larger surface area means more reactive material because growth and catalytic chemical properties are linked with the surface area. So, nanomaterials have high reactivity compared to the same material in bulk size. A very interesting property in the nanoscale is that some unreactive materials become reactive by changing their size to nanoscale. We can conclude that increasing surface to volume ratio enhances chemical properties.

1.6 Energy Storage

Energy is an important element in worldwide development. The non-renewable energy sources cause pollution and global warming, and they are cost-effective. For this purpose, renewable energy storage is a good step toward a clean environment and for cheap source of energy. Energy storage is linked to ancient times. Ancient Humans used fire with wood and charcoal [10]. In this current age, supercapacitors are the energy storage source that fulfils our desires. Electronics

that can be worn, such as flexible display screens, sensors and health monitors, have received much interest, which is getting advanced daily. Due to their recent advancement, flexible and wearable supercapacitors (SCs) have gained much attention as energy devices. Batteries are also a source of energy storage.

1.6.1 Batteries

A battery is a compact energy storage system essential to operating various everyday equipment and appliances. It uses regulated electrochemical processes to transform chemical energy stored into electrical energy. Typically, a battery comprises one or more distinct cells, each consisting of an anode and a cathode, an electrolyte that helps ions travel and a separator that prohibits direct contact between the electrodes while permitting ion flow. Batteries exist in various dimensions and configurations, from tiny button cells used in watches and calculators to massive batteries used in electric cars and renewable energy storage systems. To attain the necessary properties, each type of battery uses a particular chemistry and set of components. Lithium-ion and lead-acid are a few examples of common battery chemistries.

For instance, lithium-ion batteries are frequently employed in portable gadgets because of their high energy density and rechargeability. During charging and discharging cycles, they depend on the passage of lithium ions between the anode and cathode. On the other hand, lead-acid batteries are frequently used in automotive applications and uninterruptible power supply systems because of their robustness and capacity to deliver large power bursts.

1.6.2 Capacitors

The circuit component known as a capacitor, as opposed to a battery, is used to temporarily store electrical energy by distributing charged particles to create a potential difference. A capacitor can charge and dissipate all its energy faster than a battery. It is typically made up of two conducting plates arranged close to each other and buffered by a dielectric medium. When a potential difference (P.D) is applied to its plates, charge transfer occurs and accumulates until the applied potential reaches the PD condition between the plates. The capacitance of the capacitor is calculated by equation (1.1).

$$C = \frac{Q}{V} \hspace{4cm} (1.1)$$

Where "C" is capacitance, "Q" is charge stored, and "V" is applied potential difference. The capacitance of a capacitor depends on the charge stored on the plate of the capacitor and the potential difference applied to its plate. Its capacitance ranges from pica farad to microfarad. A capacitor's energy and power density are calculated from the equation, respectively.

$$E = 1/2CV^2 \tag{1.2}$$

$$P=IV \tag{1.3}$$

In equations (1.2) "E" is energy density, "C" is capacitance, "V" is applied voltage, and in equation (1.3) "P" is power density, "I" is current, and "V" is applied potential.
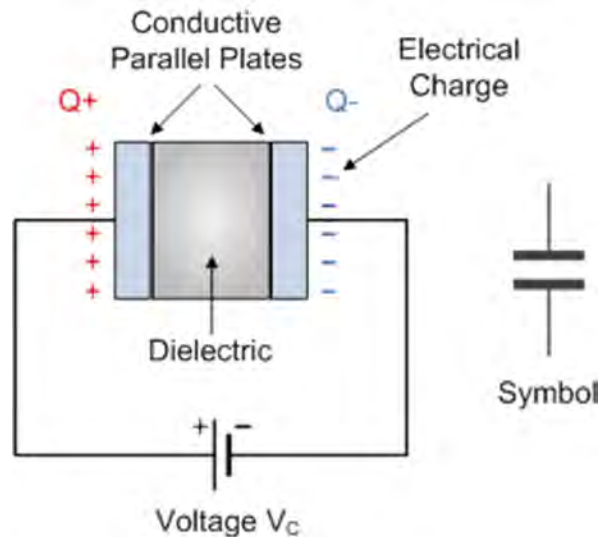

Figure 1.6: Schematic diagram of capacitor [11]

1.6.3 Supercapacitors

Energy is crucial for human development. The consumption and production of energy based on burning fossil fuels would significantly harm the environment and the world's economy. As a result, the need for high-efficiency, environmentally friendly renewable energy storage systems have increased. Electrochemical energy must be a part of the clean energy portfolio. The electrochemical energy conversion concept underlies the operation of unconventional energy sources, including batteries, supercapacitors, and fuel cells. Among these, supercapacitors is the best energy storage device. Its remarkable performance, simplicity, and durability have drawn much attention. Its method of storing charge, in which ions accumulate at the electrode surface while charging and are ejected during discharging, is mostly responsible for this. This distinguishes it from batteries with low power density and poor stability because of repeated redox reactions. A porous electrode has replaced the supercapacitor's conductors, providing effective surface areas for storage of ions. The operation of a supercapacitor involves two conductors divided by a dielectric medium, similar to that of a standard capacitor, where the separation of charges at the conductor is

8

used to measure capacitance. The nanometer-scale separation between two opposing charges is another feature that causes a larger capacitance than a typical capacitor. Supercapacitors are receiving more attention than traditional capacitors and batteries because of their high capacitance, power density, and cyclic stability.

1.6.3.1 Types of Supercapacitors

1.6.3.1.1 Electrode Double Layer Capacitor

It is a type of supercapacitor in which electrolyte ions stick to the electrode surfaces due to the electrostatic force of attraction [12]. Electric charges build up at the electrode/electrolyte interface during charging forming an electric double-layer [13]. There are no Faradaic reactions because the charge is stored here by developing an electric double layer. Voltage inputs lead to development of an electronic layer of charges on the electrode material, and to further balance out these charges, ions with the opposite charge from the electrolyte are stored on the material's layer. The inner Helmholtz plane, a group of solvent molecules, lies between these two charge levels. EDLC delivers a rapid charge/discharge cycle due to the non-Faradaic charge storage mechanism. EDLC has a longer cycle life than pseudocapacitors. The electrode configuration in EDLC does not change because there are no chemical reactions, and as a result, a high specific capacity and strong cyclic stability have been reported.
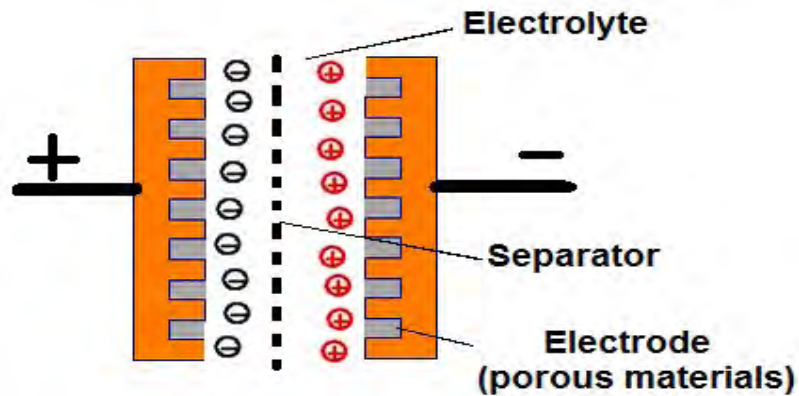

Figure 1.8: Schematic diagram of EDLC [14]

1.6.3.1.2 Pseudocapacitors

Pseudocapacitors use Faradaic processes to carry out charge transfer reactions to store energy [15]. Redox reactions (reduction/oxidation) occur at the capacitor electrodes, and for the supercapacitor to have a long cycle life, these reactions must be reversible. In pseudocapacitors, electrodes do continual chemical changes due to fast charge/discharge. In the pseudocapacitors, a rapid and reversible Faradaic redox process happens. Since charge transfer occurs in pseudocapacitors, the adsorption of ions does not change the chemical nature of the electrode material [16]. In this instance, the charge is transmitted via a redox reaction, adsorption, and intercalation on the electrode material's surface. Along with EDLC, pseudo-capacitance has been seen in supercapacitor devices. Pseudocapacitors are usually made of conducting polymers and metal oxides [17]. Due to the prolonged reversible oxidation/reduction cycles these materials have very high energy densities and high capacitance. As we know, porous materials have good electrolyte ion transport across them; it is highly recommended for materials with good porous nature (ideally mesoporous structure) to be used as an electrode in pseudocapacitors. Compared to electric double-layer capacitors, pseudocapacitors perform far better but have lower power density than EDLC.Figure 1.9 depict basic diagram of Pseudocapacitors.
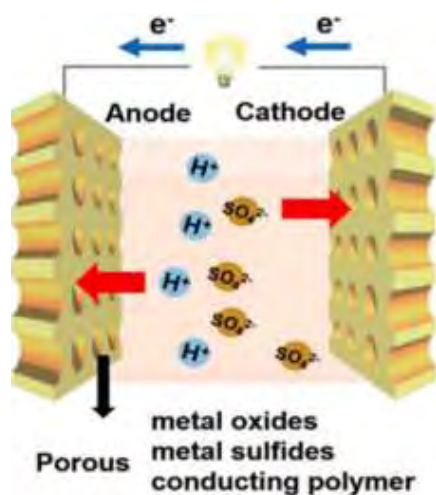
Figure 1.9: Schematic diagram of Pseudocapacitor

1.6.3.1.3 Hybrid Supercapacitor

Hybrid supercapacitors have two or more electrode materials. These electrodes store energy through both Faradic and non-Faradaic processes. As a result, it has characteristics of both EDLCs and pseudo capacitors. In these capacitors, asymmetric electrode materials are used. These supercapacitors offer a larger potential window and more specific capacitance than symmetric capacitors. A hybrid capacitor's primary goal is to increase energy density. Three electrode types, such as a composite electrode, a battery-type electrode, and an asymmetric electrode, are

frequently used in hybrid capacitors. Composite electrodes are made by combining pseudocapacitive electrode material with carbon-based compounds. One electrode of battery battery-type electrodes is constructed of carbon, whereas the other is a battery-type electrode. In these supercapacitors, both electrodes will naturally be capacitive, but one will show EDLC fashion while the other will show a pseudocapacitive manner. The benefits of these supercapacitors are their large potential windows, and large charge storage capacity. Additionally, their rate of self-discharge is minimal. These supercapacitors have attracted interest in several areas lately due to their extraordinary ability for charge storage. Hybrid capacitors exhibit distinct features when compared to redox and electric double-layer capacitors. There is much promise in these new capacitor generations. Hybrid supercapacitors store more charge due to both redox and non-redox process. The electrical equipment of the next generation will be able to get electricity from these capacitors quite effectively.
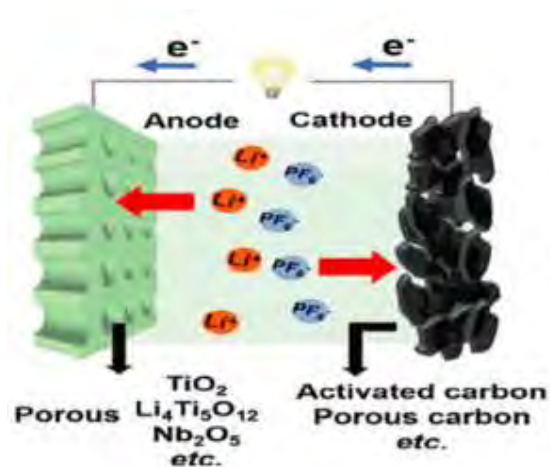

Figure 1.10: Hybrid Supercapacitor

1.7 Components in Supercapacitor

A supercapacitor has four distinct components that contribute to its overall structure. The components involved in an electrochemical system are the electrode, electrolyte membrane, electrolyte, and current collector. Figure 1.11 shows component of Supercapacitor.
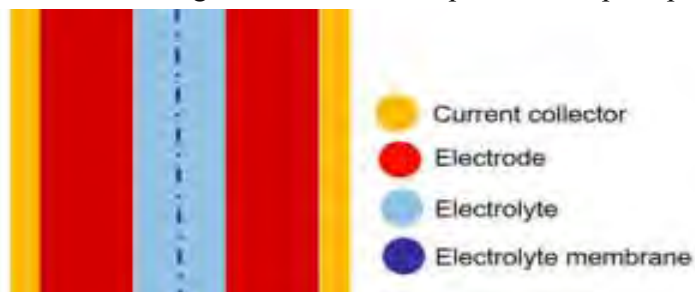
Figure 1.11: The basic structure of the Supercapacitor

1.7.1 Electrolyte

The electrolyte used by a supercapacitor has a significant impact on its performance. A wide voltage range, electrochemical stability, high ion concentration and conductivity, low viscosity, and low toxicity are all desirable characteristics of an electrolyte. The ability of the electrolyte to function within a steady potential range governs the choice of electrolyte. Acids and alkaline solutions are examples of aqueous electrolytes that have low resistance and can be used to make supercapacitors.
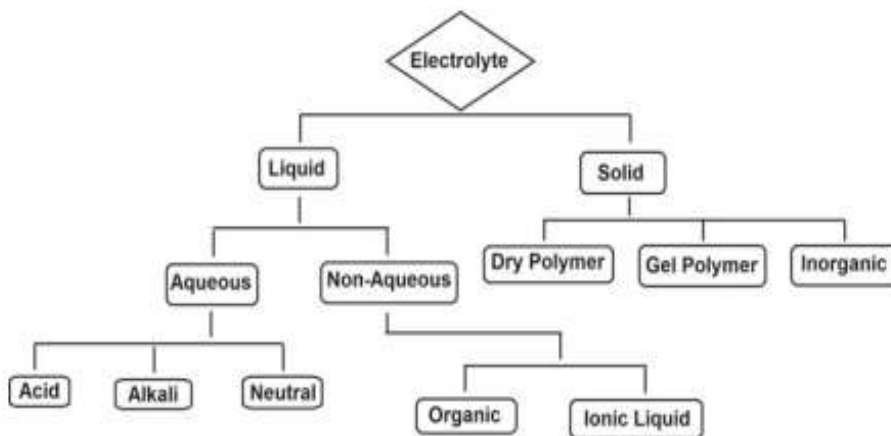
Figure 1.12: Different types of electrolytes for supercapacitor

1.7.1.1 Aqueous Electrolytes

These electrolytes use water as a solvent for salts in supercapacitors. Compared to ionic conductivity, electrochemical behaviour, affordability, and the convenience of handling them outdoors, aqueous electrolytes provide several benefits. Since water has a 1.23 thermodynamic potential window, it can electrolyze into hydrogen and oxygen gases at low potentials[18]. This gas

creation raises the possibility of device damage exceeding acceptable levels. Ionic equilibrium and hydrogen bonding in water molecules lead to water breakdown into hydrogen and oxygen atoms. In an ionic environment, water is easily electrolyzed into hydrogen and oxygen atoms—additionally, the hydrogen bonds in water decrease as the O-H bonds do. O-H bonds are stronger in isolated water molecules with weak hydrogen bonds. Notably, isolated gaseous water has a stronger O-H bond than methanol, and ethanol [19] aqueous electrolytes have a small potential window yet strong conductivity and capacitance. A neutral aqueous electrolyte, such as Na_2SO_4 or KCl, can raise the potential window for aqueous electrolytes from 1.0 to 1.5 V to 2.0 V [20]. The use of aqueous electrolytes is restricted due to their small potential window. Furthermore, the working of an electrolyte is influenced by several factors, such as ionic size, abrasive mobility, and ion conductivity. They exhibit lower cost and a more streamlined production process than organic electrolytes.

1.7.1.2 Ionic Liquid Electrolytes

Ionic liquid electrolytes are those types of salt that are liquid at room temperature. IL electrolytes do not require additional solvents. These electrolytes have greater chemical stability because of ionic bonds. These electrolytes have superior electrochemical stability, high working windows, and thermal stability because these electrolytes act as organic salt at room temperature in liquid form. The main benefit of IL electrolytes is a broader potential window, roughly up to 3.5 V. It is high compared to organic and aqueous electrolytes and allows for great power and energy density. ILs have an ionic conductivity of just 14 mS/cm, significantly less than organic electrolytes. Ionic electrolytes are dense than aqueous electrolytes, ranging from 41 to 219 cp [21].

1.7.1.3 Solid Electrolyte

Flexible electronic devices, printed electronics, wearable devices, and tiny devices have become increasingly necessary. Researchers are concentrating on creating solid-state electrolytes for supercapacitor applications to meet these requirements [22]. Solid electrolytes are solid ionic conductors and are a fundamental part of a solid-state battery [23]. Solid electrolytes make the fabrication and packaging processes easier. Polymers, both synthetic and natural, as well as inorganic materials like ceramic, are frequently used as solid electrolytes [24]. These electrolytes provide high chemical stability and have lower electrical conductivities. These electrolytes can also vary in volume, which gives device designers more freedom. They are also quite strong mechanically [25].

1.7.1.4 Organic Electrolyte

Organic electrolytes perform better in the potential window and operating temperature ranges than other electrolytes. In organic electrolytes, inorganic salts are mixed with organic solvents. Organic electrolyte-based electrochemical supercapacitors have a potential window ranging from 2.5 to 2.8 V, which equates to high energy and power densities. The limited electrical conductivity in the electrolyte is induced by the extremely dense nature of organic solvents, which results in voltage drop. The viscosity of the salt might be very low or very high, which interferes with optimal conductivity. These electrolytes have larger corrosion resistance than other electrolytes. However, there are disadvantages to using organic electrolytes, including their high cost, toxicity, and the necessity for rigorous purification to maximize efficiency. It is significant to note that building a supercapacitor made of organic electrolytes cannot be done outside since the environment will react with it and damage the electrochemical performance. Organic electrolytes' low ionic conductivity is a serious problem since they raise equivalent series resistance (ESR). Due to using a particular type of organic electrolyte and trace amounts of water, electrochemical supercapacitors using organic electrolytes are susceptible to self-discharging.

1.7.3 Electrolytic Membrane

A supercapacitor's electrolyte separator membrane serves two main purposes. First, one is allowing the flow of electrolyte ions and preventing circuit breakdown between electrodes. A membrane with strong ionic conductivity is likely favoured for supercapacitor applications. This can be achieved by using inexpensive materials as electrolyte membranes, such as Xerox paper or Whitman TM filter paper. These membranes are inexpensive and cost-efficient. Nanostructured electrolyte membrane technology has advanced recently. The Nafion membrane illustrates one such membrane; due to its nanoscale characteristics, it displays strong ionic conductivities [26]. Commercial supercapacitors frequently employ Nafion membranes. However, the price of Nafion makes the creation of innovative electrolyte membranes employing inexpensive polymers necessary [27]. The supercapacitor should have a porous structure to make it easier for ions to go from the electrolyte to the electrodes. Figure 1.13 shows structure of porous membrane.
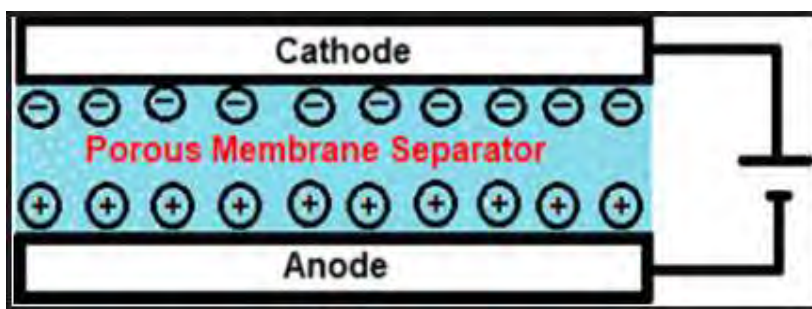

Figure 1.13: Shows Porous Membrane Separator

1.7.3 Current Collector

Current collector's major function, as stated by its name, is to facilitate the transfer of electrons from the electrode to the external circuit. Metal plates composed of aluminium and copper are commonly used current collector. In some cases, an alloy, such as a steel plate, is employed as a current collector. In conventional practice, it is recommended for supercapacitors to be equipped with a pair of current collectors that wrap around the cathode and anode.
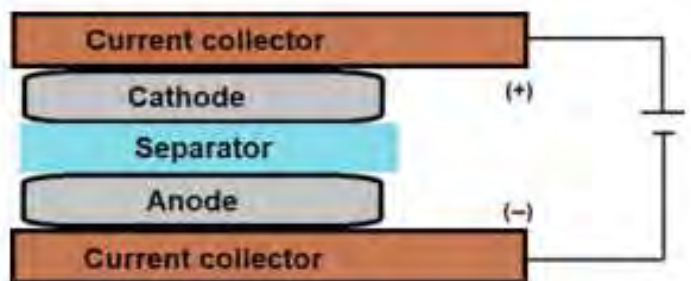

Figure 1.14: Schematic Diagram of the current collector

1.7.3.1 Nickel

The most preferred current collector type for supercapacitor devices is nickel-based. It offers low resistance with the electrode material, good mechanical strength, outstanding electrical conductivity, and affordable cost [28]. Foam and foil are both common uses for nickel. Nickel foam with concave high surface area has extraordinary capacitive properties compared to nickel foam with a smooth surface [29] Nickel foam current collectors exhibit a faster redox response than nickel foil ones, according to cyclic voltammetry studies [30]. The nickel foam can accommodate large amounts of electroactive materials because of the porous nature of nickel foam and low contact resistance between nickel foam and the current collector. The porous design of nickel foam provides significant electrolyte ion movement over the electrode interfaces and electro-active material [31].

1.7.3.2 Aluminium

Aluminium as a current collector is inexpensive, has excellent electrical conductivity, is lightweight, strong mechanically, and acts as a weak interface resistive current collector. The main disadvantage of using aluminum foil is that electrode material pops off the foil under bad operating circumstances. So, Aluminum current collectors are coated with graphene and lasers to prevent corrosion of the aluminium surface and electrode delamination from the current collector [32]. The current collector for supercapacitor applications uses aluminium foam as the current collector.

Supercapacitors with long cycle life and good electrical conductivity use aluminium foam as the current collector [33].

1.7.3.3 Stainless Steel

It is frequently used in batteries and supercapacitors as a current collector [34]. It is very cheap and chemically stable. Its useful characteristics include high mechanical strength, durability, conductivity, and chemical stability. It is easily accessible and has a low cost. The electrolyte utilized in the system affects its chemical and electrochemical stability is its major drawback.

1.7.3.4 Copper

Copper as a current collector has high thermal and electrical conductivity, durability, and a unique reddish-orange colour. 3D porous copper is a unique current collector that provides outstanding electrical conductivity—the pores in the copper foam range in size from micrometers to millimeters [35]. The copper current collector has excellent electrical conductivity and porosity to produce high-performance supercapacitors. By increasing the copper current collector's surface area using ultrasound, a mesoporous and microporous framework is created on its surface [36]. Energy storage applications also use different current collector materials such as titanium, platinum, tantalum, and carbon fibre. The specific electrolytes used in supercapacitor applications also impact the choice of current collector material. To achieve maximum efficiency in supercapacitors, it is imperative to use an electrolyte substance that does not corrode the current collector.

1.7.4 Electrode

The electrode is the active part of the supercapacitor because the electrode-active materials utilized determine the charge storage inside the supercapacitor. Electrodes should have strong electrical conductivity, enormous surface area, and a porous structure.Electric double-layer capacitors have small electrodes, whereas redox capacitors are built of electronically conducting polymers that are far more flexible in nature. To achieve the highest performance, the electrode must be carefully chosen.
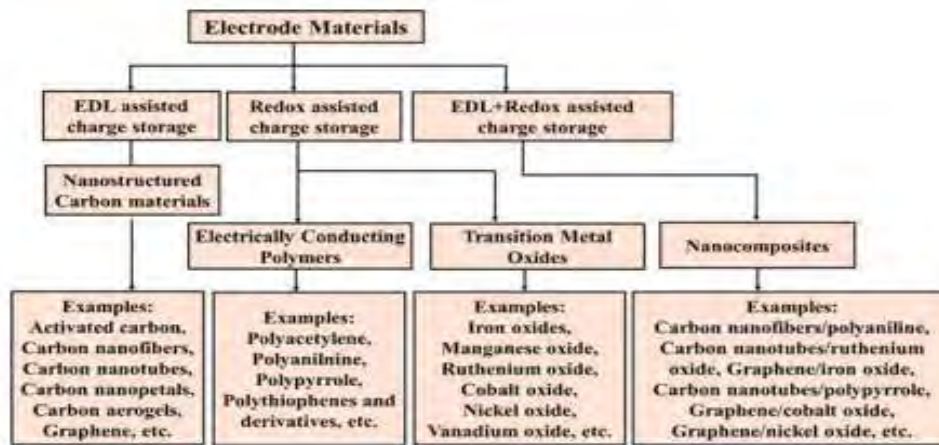
Figure:1.14 Schematic diagram of various Electrode Materials used in Supercapacitors [37]

1.8 Uses of Supercapacitors

1.8.1 Portable and Electronic Flexible Devices

Portable gadgets like cell phones, smartwatches, computers, cameras, and other devices have become essential in today's environment. These technologies have revolutionized our daily lives, which perform several new tasks. Advanced energy storage technologies are still needed to power these clever gadgets effectively. Supercapacitors, batteries, and fuel cells have become essential to energy storage. Hybrids of batteries and supercapacitors have proven to be the best option for powering current and future mobile electronic gadgets [38]. With the help of this hybrid design, lightweight battery technology may be incorporated into small, portable devices like watches, sensors, mobile phones, and headphones, effectively supplying the required power.

1.8.2 Power Supply

Systems with uninterrupted power supplies (UPS) also use supercapacitors. These systems offer surge protection, portable charging options, and emergency power devices. The UPS intends to provide fragile appliances with instant backup power while a generator starts [39].

1.8.3 Hybrid Electric Vehicle

Supercapacitors garnered significant interest starting in 1990 when they were integrated into hybrid electric cars alongside batteries and fuel cells. This integration facilitated the provision of power required for acceleration and enabled the recovery of braking energy. Supercapacitor-battery hybrids have emerged as dependable energy providers for various electric vehicles, including automobiles, watercraft, and public vehicles. The significance of alternative energy systems lies in their differentiation from traditional fuel-based systems due to their low emissions and little environmental impact.

1.8.4 Wind and Solar Powering

Supercapacitors are crucial components of current and future storage of energy devices, owing to the irregular characteristics of wind and solar technologies. It is essential to implement a storage mechanism to harness the energy produced by solar cells during daylight hours for overnight usage. In a manner akin to this, the energy generated by wind turbines in periods of high wind velocity requires storage to facilitate utilization during periods of low wind velocity. The supercapacitor systems provide power in the absence of wind and light energy. They are ideal solutions for energy storage systems.

1.8.5 Implantable Healthcare

Supercapacitors are frequently used in various healthcare systems that require power in microwatts to milli-watts. These supercapacitors are employed in medical devices, including cardiac insulin pumps and other healthcare applications.

Figure 1.15: Application of supercapacitors in the medical field

1.8.5 Defense and Aerospace

The utilization of supercapacitors in military and aerospace disciplines is highly advantageous due to their capacity to promptly deliver power, prolonged operational lifespan, and ability to operate effectively under low-temperature conditions. Consequently, supercapacitors are highly useful for various applications, including power backup in electronic systems, emergency handheld radios requiring backup power and memory retention, GPS-guided missiles and projectiles. Additionally, they have been extensively employed in many aerospace contexts that need a high-power density, such as in space shuttles and satellites.

1.9 Transition Metal Oxides

Transition metal oxides are a fascinating class of solids with a wide range of structures and characteristics. Their bonding might be almost ionic, highly covalent, or metallic in nature [40]. TMOs are the oxides of d-block elements that have partially filled d-orbital. They have drawn the scientific community's interest due to their extraordinary features, such as magnetic, optical, and electrical [41]. In light of their excellent mechanical, electronic, and redox capabilities, they are widely used in energy storage applications [42].Transition metal oxide-based electrodes are greatly favoured because electrolyte transport towards the interior pores is high ratio, resulting in improved performance and their many valence state shifts cause redox capacitance. Yet, performance is somewhat modest when compared to noble transition metal oxides. The greatest technique for attaining the optimum supercapacitor performance is nanostructuring of the electrode architecture.

1.9.1 Vanadium Pentoxide

Among transition metal oxides ,Vanadium pentoxide, often known as V_2O_5, has enormous promise as an electrode material for supercapacitors. This material has many positive traits, including large specific capacitance, superior cycling stability, and affordability. It is suitable for energy storage because of the intercalation sites in its layered structure that allow ions from the electrolyte to be accommodated. Studies have shown that V_2O_5 can beat several carbon-based materials with large specific capacitance of 400 F/g in aqueous solutions. It also demonstrates good cycling stability, which enables it to maintain performance across several charge and discharge cycles. V_2O_5 is excellent an electrode material for supercapacitors, and ongoing research intends to improve its functionality and broaden its useful uses in energy storage systems.
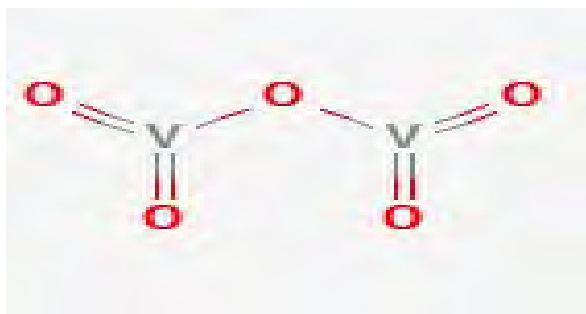

Figure 1.16: Atomic arrangement of V_2O_5 [43]

1.10 Conducting Polymers

Conducting polymers (CPs) have gained the attention of researchers over the last three decades due to their mechanical and thermal stability, low corrosion resistance, and excellent

electrical conductivity capabilities. Conducting polymers Popular applications include batteries, display devices, supercapacitors ,sensors, and electronic circuits [44].

1.10.1 Polyaniline

A conductive polymer known as polyaniline has attracted interest as an electrode material for supercapacitor application because of its positive traits, including high electrical conductivity, stability, and affordability. In supercapacitors, polyaniline can behave as a pseudocapacitive material, allowing quick and reversible charge storage through redox processes. Because polyaniline has a high specific capacitance as an electrode material, it can store many charges per unit mass. It also has stable chemical characteristics and good mechanical qualities. Its usage in supercapacitors is not without difficulties, however, as it has a somewhat lower energy density than other electrode materials and requires careful management of the polymerization process to maintain uniform characteristics and performance. Although polyaniline has the potential as an electrode material for supercapacitors applications, more investigation and development are needed to improve the material's functionality and resolve any issues. Figure 1.17 shows chemical illustration of polyaniline.
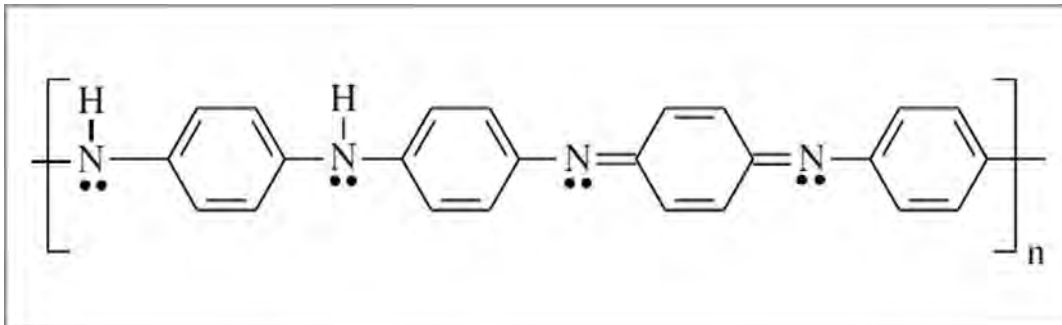

Figure 1.17: Atomic structure of Polyaniline [45]

Chapter No. 02   Synthesis Methods

Introduction

Nanoparticles are vital for several applications, such as semiconductors, energy storage, catalysis, and medicine. They have a size range from 1 to 1000 nm. Particles act differently at the micro-scale than they do in the bulk. For example, the surface area of tiny particles increases significantly. This results in reduced melting points, increased electrical and thermal conductivity, strong magnetic interaction, and special optical features [46]. For these advantages the following techniques are used.

2.1 Top-Down-Approach

This technique breaks down large particles into smaller ones like micro and nano. These approaches are easy to use but worthless for producing extremely small and irregularly shaped particles. The obscurity of obtaining uniform size and form using this method is a significant disadvantage of this technique [47].

2.1.1 Thermal Evaporation

In this technique, heat is given, and as a result, the endothermic reaction causes molecules' chemical bonds to break. Among the several methods for creating inorganic nanoparticles, it is the most frequently employed to create stable monodisperse with the ability to assemble themselves. Through thermal evaporation, thin films are created on various substrates. Figure 2.1 shows thermal evaporation technique.
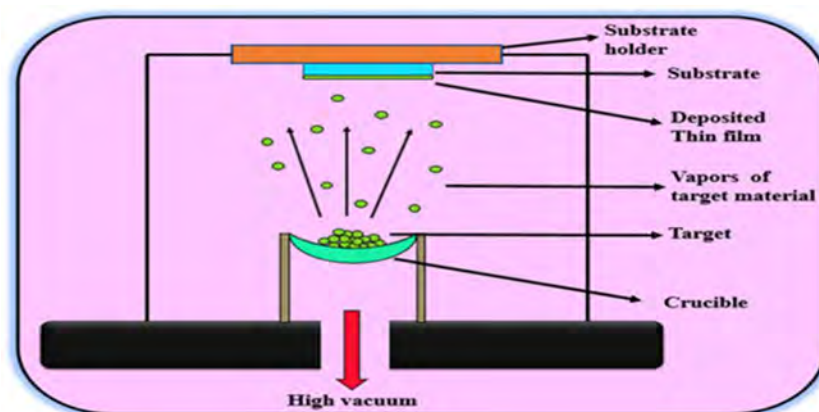

Figure 2.1: Schematic diagram of thermal evaporation

2.2.2 Ball Milling Method

Ball milling is the easiest and most practical technique used in the Top-down Approach. It grinds materials to create particles. This technique is used to synthesize plenty of NPs and metal alloys. At high temperatures, phase changes occur due to pressure and temperature produced by wall interaction and ball collision with the vessel wall. A milling vial contains a particular amount of powder material, which is then snubbed by the friction and collision of the balls with the vials. Many materials are used to reduce size. Powder reduction, crystalline size, surface modification, and mechanical dislocation are all significantly affected by ball milling [48].
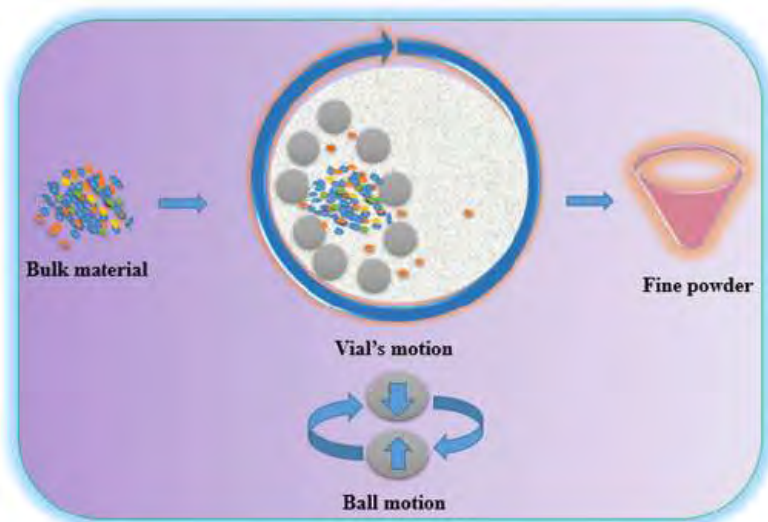

Figure 2.2: Illustrates method of Ball Milling [49]

2.1.3 Sputtering

When high-energy electrons have collisions with ionized gas, commonly referred to as plasma, the resulting plasma ions contribute to the phenomenon known as sputtering. It is a widely recognized method employed in the Top-down Approach due to its utilization of a non-thermal vaporization process. The mentioned approach may be performed under a pressure of 0.67 Pa and is facilitated using a vacuum pump. The present technique involves the deposition of nanoparticles onto the base material by emitting particles resulting from the bombardment of very energetic ions. This technique is employed for thin layer formation and the application of surface coatings. Glow discharge sources operate by applying an electric voltage across electrodes within a gaseous environment at low pressure.
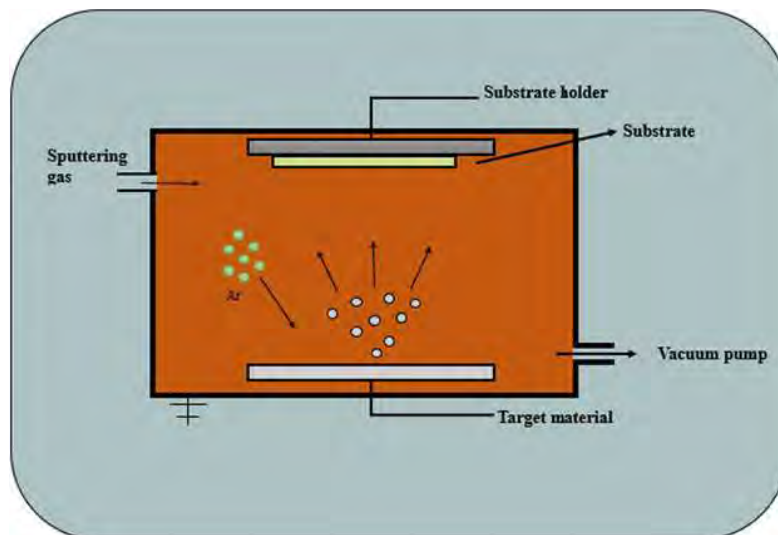
Figure 2.3: shows the Sputtering Technique [50]

2.1.4 Laser Ablation

Laser ablation is the technique of eliminating a portion of the surface's material with a powerful laser. It is primarily applied in various industrial contexts, including machining, drilling, and the application of special coatings (such as pulsed laser deposition). It helps to provide a controllable amount of energy to a specific target region. It is commonly used to synthesize carbon nanomaterials, including CNT and fullerene [51].Figure 2.4 shows working scheme of laser ablation.

Figure 2.4: Working principle of Laser Ablation

2.2 Bottom-up Approach

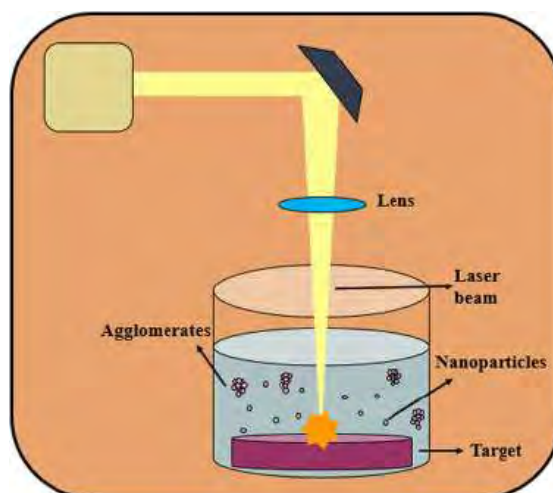It is contrast of the top-down approach to synthesize nanostructures. Atoms, molecules, or clusters are put together to form nanoparticles one at a time. The preparation of uniformly sized and evenly distributed nanoscale particles is the main application of this method. Large and complex molecules are created by combining the smaller molecules. This method establishes the formation of crystals and cells in nature. It is further separated into two methods: the liquid phase method and the gaseous phase method. Organic contaminants in the gaseous phase are lower than in the liquid phase technique. The gaseous phase can create ultrafine particles with a size of less than 1 um.

2.2.1 Sol-Gel Method

The sol-gel technique, also known as solution gelling, is a multi-step process for creating thin films that use various physical and chemical techniques, including hydrolysis, Condensation, drying, densification, polymerization, and gelation [52]. The ability to acquire control over diverse components at the atomic level by combining precursors in a solution at low temperatures is a key advantage of the sol-gel process. Moreover, the surface characteristics, structure, order, and homogeneity of the resultant product can be changed by modifying the sol-gel process. parameters. [53].Figure 2.5 shows schematic diagram of sol-gel technique.
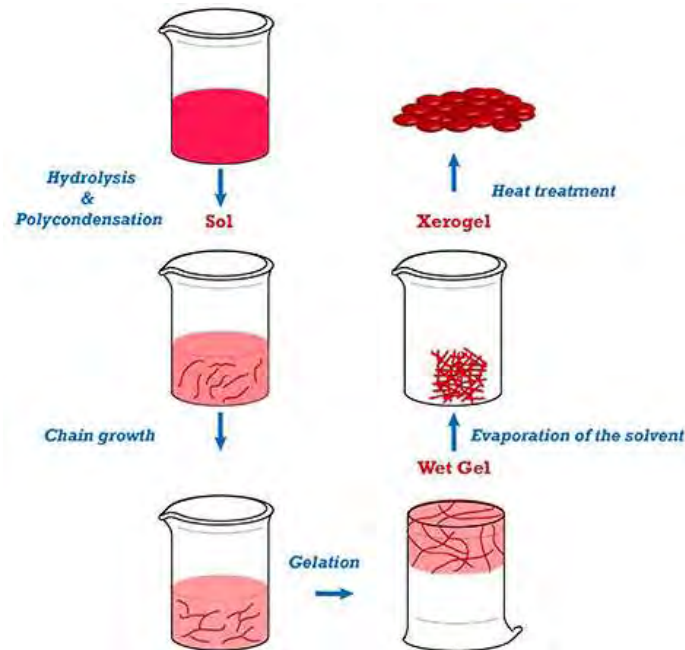

Figure 2.5: Sol-Gel technique

2.2.1 Hydrothermal Synthesis

A common method for making nanomaterials is called hydrothermal synthesis, which uses high pressure and temperature conditions in solution. Precursors in the solution react in the process, resulting in the nucleation and growth of nanomaterials. This approach is widely utilized in all materials science and nanotechnology areas since it allows easy command over the resultant nanomaterials' size and composition. Figure 2.6 shows working process of hydrothermal synthesis.
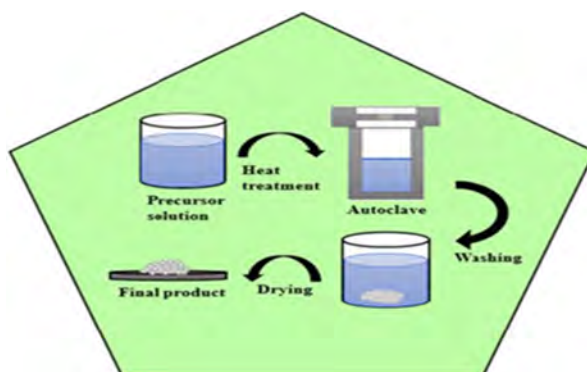

Figure 2.6: The steps of Hydrothermal Method

2.2.2 Co-precipitation

Co-precipitation is an efficient method for creating nanoparticles. In order to create nanoparticles, it includes the sequential precipitation of two or more soluble salts from a solution. This approach yields highly uniform nanoparticles with a confined size distribution that are easy and inexpensive to produce. The size and shape of the nanoparticles can be adjusted by changing reaction variables like temperature and pressure. The produced nanoparticles can be used in various industries, including electronics, medicine, and energy storage.

2.3 Synthesis of polyaniline

2.3.1 Materials

Distilled Aniline, Ammonium persulfate, HCL solution, and Distilled water.

2.3.2 Synthesis Process

PANI is synthesized by oxidation of distilled aniline. First, we make 100ml HCl solution by mixing 0.83 ml of HCl in distilled water and stirring it for 20 minutes to mix it completely. After making a homogenous HCl solution, we put 3.5g of APS in the 100 ml HCL solution and stirred it

for two hours to get a homogenous APS solution. Next, we make an Aniline solution by mixing 1.25 ml of aniline in 100 ml of distilled water to an Aniline solution. We put aniline solution in ice to keep its temperature below 5˚c and stirred it for six hours. During the string of the Aniline solution, we put the APS solution dropwise in the Aniline solution. After some time, the oxidation of aniline started, and after pouring the APS solution completely, the solution was left for 12h in an open atmosphere. After 12h, we get black, greenish PANI solution, and we filter and deionize this solution to remove HCl to get PANI powder, which is dried in a furnace to get a fine form.

2.4 Synthesis of V_2O_5

2.4.1 Material
V_2O_5 bulk powder, Deionized water, and NaCl

2.4.2 Synthesis Process
First, put 1g of V_2O_5 In 60 ml deionized water and stir this solution for a half hour at 30˚ c . After stirring, put 2M NaCl in the solution slowly and stir the solution for 72 hours. Then, the solution is centrifuged with ethanol, and after washing, the solution is dried in vacuum oven for 12 hours to get V_2O_5 nanostructures. The V_2O_5 powder is further calcined in the Furnace for 7 hours at 700˚C temperature to remove impurities.

2.5 Synthesis of V_2O_5 -PANI Nanocomposite

V_2O_5 and PANI nanocomposite are synthesized through the situ method. The nanocomposite was synthesized by mixing 0.75 g of PANI and 0.25 g of V_2O_5, 0.50 g of each, 0.25 g of PANI, and 0.75 g of V_2O_5. The nanocomposite is prepared in motor pastor by mixing both materials for 1 hour, and a few drops of acetone are added during mixing. After mixing, the nanocomposite is heated at 60˚C for 12 hours. This process is repeated for all composites. These prepared nanocomposites further for structural and electrochemical characterization.

2.6 Nickel Foam Preparation

Nickel Foam is activated by washing with 2M HCl, acetone, and distilled water to remove any impurities from the surface. After washing, activated Nickel foam is ready to use as the working electrode. Electrode material paste is prepared by mixing 10% PVDF,10% activated carbon, and 80% electrode material in NM. This paste was coated on nickel foam, and then dried in a vacuum oven for 12 hours at 60˚C temperature. After drying, nickel foam is ready to use for characterization.

Chapter No. 3   Characterization Techniques

Introduction

Characterization Techniques are very helpful in studying the structure and properties of the material used for a supercapacitor application. Characterization of materials is very important for studying the capability and properties of materials used in supercapacitors. Various techniques have been used to analyze material, including X-ray Diffraction for structural analysis, UV-visible spectroscopy for finding optical properties , Raman Spectroscopy for vibrational analysis, and crystal orientation of materials.

3.1 X-ray Diffraction (XRD)

3.1.1 Introduction

This tool characterizes material properties like crystalline size and crystal structure, etc. In 1912, German Max Von Laue first examined this technique and won the Noble Prize for this Technique. This is a non-destructive technique. This technique works by using X-ray radiation on the sample used for examination. The rays are diffracted XRD in a pattern determined by the size and position of a crystal constituent. This technique determines a material's atomic and molecular structure without changing its physical and chemical nature [54]. The procedure involves irradiating a specimen of the substance using incident X-rays, followed by the measurement of the intensities and scattering angles of the resultant scattered X-rays. The relationship between the intensity of scattered X-rays and the angle at which they are dispersed is used to determine the material's structure. By studying the position and intensities of the peaks in the scattered intensity, useful data about the material's structure are determined. X-rays having wavelengths between 1KeV to 120KeV are preferred for diffraction. XRD is used to examine materials like polymers, ceramics, and metals in thin films and powder [55].

3.1.2 Working Principle

X-rays are created by heating a filament, which causes electrons to eject from the cathode tube. Then, these electrons accelerate toward a metal target, often made of copper. The copper target causes the electrons to lose energy through X-rays, having coherent wavelengths. The generated X-rays are then pointed at the desired target. The intensity of the diffracted X-rays is measured while the sample rotates around the X-ray tube and detector. A diffractogram pattern, which is used to measure the size of the crystal, atomic layer thickness, crystal deformation, and identifying minerals, is created by the interaction of x-rays with the sample. About 98.8% energy

of electrons is used to heat target materials, and only 0.2% is used in X-ray production. Figure 3.1 shows working principle of XRD.
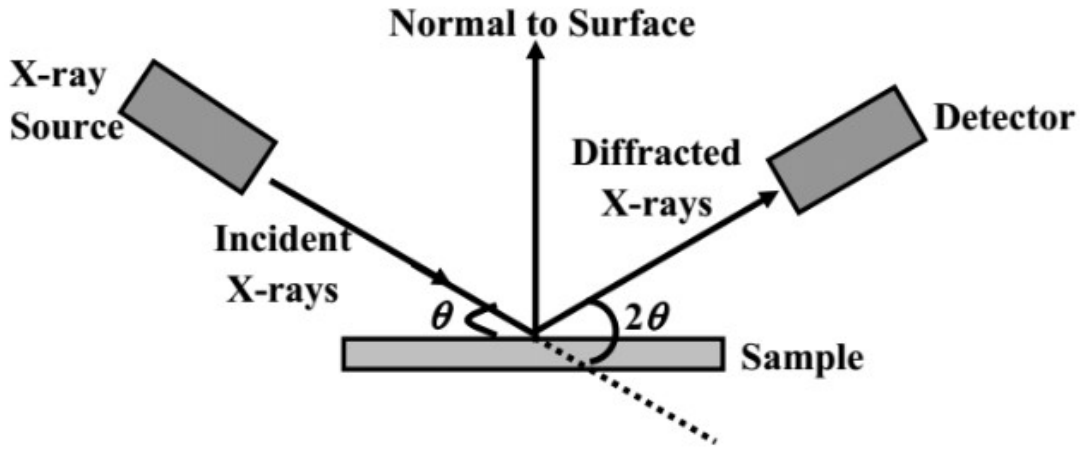

Figure 3.1: Working principle of XRD [56]

3.1.4 Braggs Law

Lawrence Brag and his father, William Henry Bragg, gave this law in 1913. This law states, "The x-ray's angle of incidence will reflect with the same angle of scattering when it hits a crystal surface"[57]. When X-rays hit an atom in lattice planes, every atom in the plane acts as a scattering point and emits X-rays constructively or destructively according to Bragg's law to get the desired diffracted beam [58]. When two parallel waves of the same wavelength are in phase at some angle "θ", the wave reflected from the lower plane covers more distance than the wave reflected from the upper plane. Constructive interference occurs, if the path difference between waves is an integral multiple of the incident wavelength. This constructive interference is given by equation (3.1).

$$2d \sin \theta = n \lambda \tag{3.1}$$

Where "d" is interplanar spacing, "n" is an integral number, "θ" is the angle of incidence, and "λ" is the incident wavelength. Destructive interference occurs if two waves are out of phase and their path difference is half the incident wavelength. Path difference is subtracted in destructive interference, while the path difference is added in constructive interference. Figure 3.2 shows the Braggs law illustration.
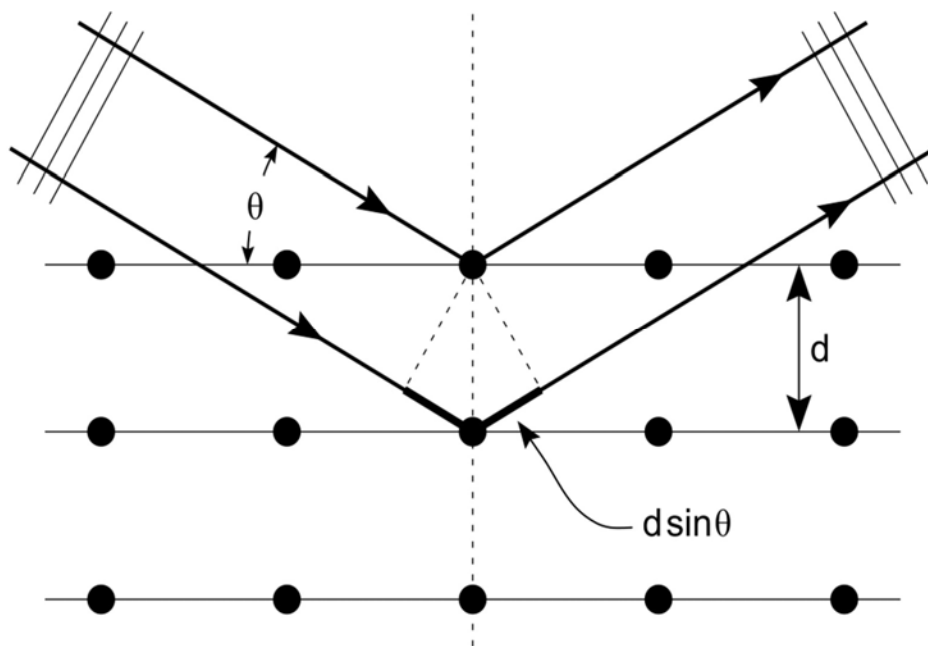
Figure 3.1: Illustration of Braggs Diffraction [59]

3.2 Fourier Transform Infrared Radiation (FTIR)

FTIR is used to get information from molecular vibrations related to functional groups. It is a non-destructive technique. When radiation hits the sample, the material absorbs specific wavelength radiation to cause a change in molecule dipole moment. Material having a larger dipole moment gives a more intense absorption band in FTIR spectra. The intensity of the absorption peak is affected by dipole moment, and changes in energy levels radiations that fall on material cause stretching and bending of molecules of materials. As a result, the vibrational energy level of material molecules goes to an excited state.

3.2.1 Working Principle

In this technique, infrared radiation passes through the Michelson interferometer. The beam splitter divides the beam into two portions and transmits one portion of beam to a fixed mirror and the other to a movable mirror. After reflection, both beams reconnect at the beam splitter. These two reflected beams interfere constructively or destructively due to optical path differences. When reflected are in phase with zero path difference, the beam interferes constructively. If the reflected beam is out of phase and has a path difference of $1/2\lambda$ path difference, then the beam interferes destructively. The relation of mirror displacement with optical path difference is given by equation (3.2).

$$OPD= 2\Delta n \qquad\qquad (3.2)$$

The signal we get after interference is plotted between light intensity and optical path difference is called interferogram. Different light interference patterns will be created depending on the moving mirror position. The light intensity for each wavenumber can be estimated using a Fourier transform, which can be done quickly by a counterfire and is the best analytical tool as compared to other IR techniques in terms of sensitivity and accuracy 3.3 Basic principle of FTIR.
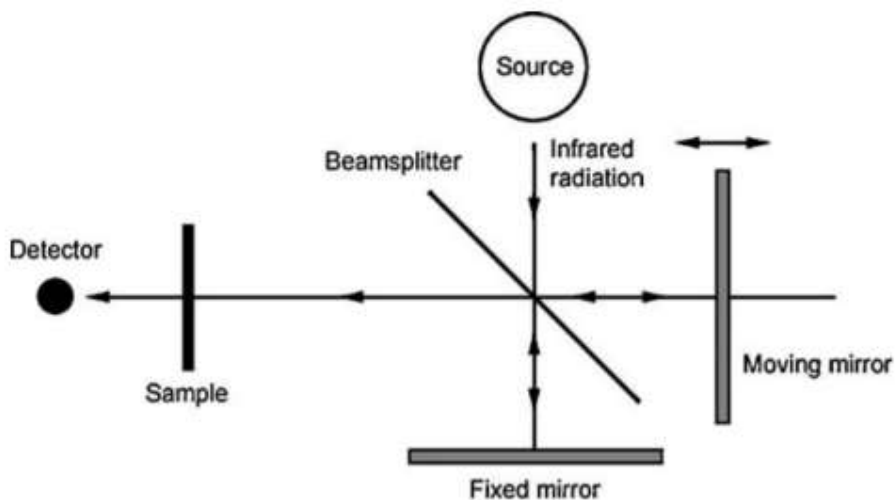

Figure 3.2: FTIR basic working setup [60]

3.3 UV-visible spectroscopy

3.3.1 Introduction
One of the most fundamental methods for characterizing samples is UV-visible, which refers to light absorption in the ultraviolet and visible ranges. It is a quick and affordable method. Its primary job is to study the chemical concentration in a material quantitatively. It is a non-destructive technique. A monochromatic beam with a wavelength ranges from 200 nm to 800 nm is employed in this spectroscopy.

3.3.2 Working Principle of UV–visible Spectroscopy
A rotating disc splits a visible light source, often a tungsten or xenon filament lamp, into the visible and ultraviolet spectrums. In both the sample cell and the reference cell, monochromatic electromagnetic waves are collected at the detector, where the recorder provides the graph between absorbance and wavelength that is depicted. UV spectroscopy works on the principle of Beer-Lambert Law, defined as the logarithmic ratio of radiation directly proportional to the concentration of species in the solution. Equation 4.3 demonstrates the Beer-Lambert Law.

$$A= - \log T= - \log\left(\frac{I}{Io}\right) \qquad\qquad 4.3$$

$$A=\mathcal{E}bc$$

In the equation, Io and I are transmitted and incident beam, respectively; $\mathcal{E}$ is molar absorptivity, b is path length, and c is the concentration of species.

According to Beer-Lambert Law, light absorption increases by increasing species' concentration. Two lamps are used in the technique: a Hydrogen lamp for the UV spectrum and a tungsten lamp for the visible range. Figure 4.4 shows the setup of UV – UV-visible spectroscopy.
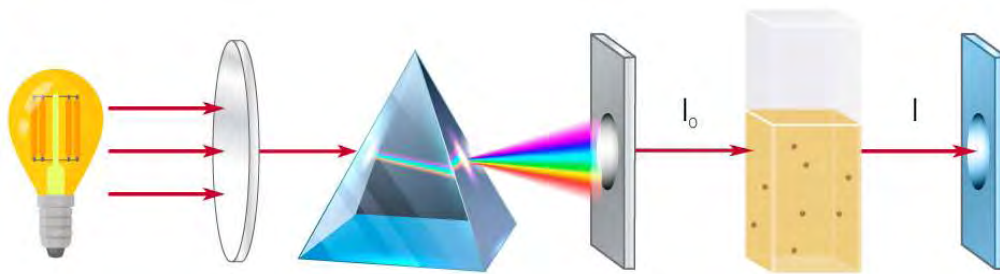

Figure 3.3: The working principle of UV-visible spectroscopy

3.4 Cyclic Voltammetry

CV is a prominent tool used to examine redox process of materials. It is used to study electron transfer chemical reactions. Cyclic voltammetry consists of working, reference, and counter electrodes. A Potentiostat is used to control potential. When a potential is applied to a working electrode, current begins to flow. Current is recorded between the Counter and working electrode [61].

3.5 Electrochemical Impedance Spectroscopy (EIS)

EIS is a widely used analytical tool to evaluate the complex impedance of supercapacitors in the frequency range of 1MHz to 1MHz.EIS is measured by placing Supercapacitor in a three-electrode system cell over a small AC voltage perturbation. The Nyquist plot is used to measure impedance, in which real and imaginary impedance is presented. This impedance provides information about cell resistance and capacitance. EIS analyzed the behaviour of electrodes and electrolytes by providing information about ionic resistance, double-layer capacitance, poor charge retention, and charge transfer resistance.

EIS data are useful for designing and operating supercapacitors by giving information about factors that affect supercapacitor performance, such as cell geometry, electrode material and electrolyte composition.

3.6 Galvanostatic Charge Discharge (GCD)

GCD is accurate tool used to elaborate supercapacitor parameters such as specific capacitance, cycle stability, power density, and energy density. GCDs measure voltage by applying positive current. Two steps comprise the total GCD measuring process: first, the Supercapacitor charged using a steady current, then discharged over a predetermined period or voltage range.

4.1. Structural Analysis

The crystalline structure and phase purity of V_2O_5, PANI, and V_2O_5-PANI nanocomposite have been examined by X-ray diffraction spectroscopy ranging from 10^0-90^0 with Cu-K_α wavelength. The XRD pattern demonstrates V_2O_5 crystalline nature, with these peaks corresponding to the orthorhombic phase of the V_2O_5 nanostructures. The existence of a single-phase V_2O_5 sample is confirmed by all V_2O_5 diffraction peaks. No additional extra peak was found showing the purity of V_2O_5. The diffractogram shows a characteristic peak at $2\theta=20^0$ with a corresponding reflection plane of (001). All the other diffraction peaks in the V_2O_5 diffractogram appear at 2θ values of 15^0, 20^0, 21^0, 26^0, 31^0, 41^0, 47^0, 51^0, 63^0 and can be indexed to reflections plane of (200), (001), (101), (201), (301), (002), (600), (020), (003) respectively. The characteristic peak at 20^0 and all other emerging peaks of V_2O_5 are well indexed with standard JCPD card number(00-041-1426). The XRD pattern of V_2O_5 is shown in Figure 4.1
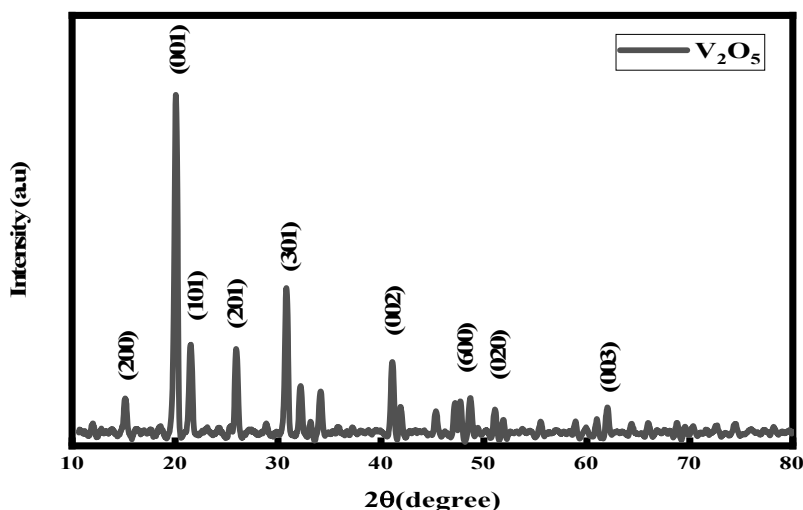

Figure 4.1: X-ray diffraction pattern of pristine V_2O_5

The XRD pattern of PANI shows a broad   peak showing the amorphous structure of a material. XRD of PANI has only a broad peak at $2\theta=25^0$. The strong peak pattern represents the presence of the benzenoid and quinoid groups in PANI. The XRD pattern of PANI is shown in Figure 4.2.
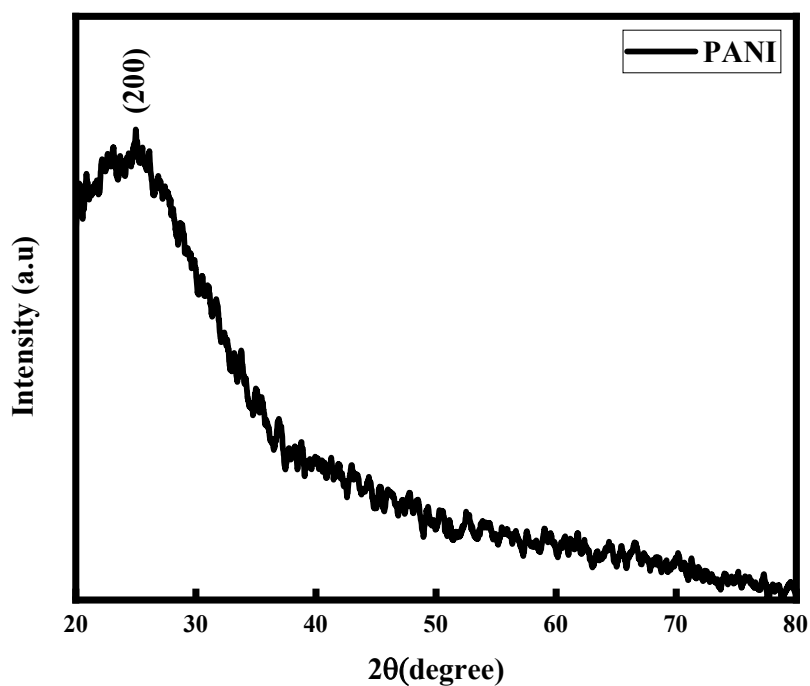
Figure 4.2: X-ray diffraction pattern of PANI

The XRD of pristine V_2O_5 and its nanocomposites is shown in Figure 4.3. The XRD patterns depicted that the intensity of the peaks of nanocomposites increases as the PANI substitution ratio in the nanocomposites increased. This shows that PANI is successfully incorporated into nanocomposites. The XRD pattern of nanocomposites does not show any PANI peaks because of amorphous nature of PANI . The XRD pattern of nanocomposites shows a increase in crystallinity by adding PANI. The nanocomposite $(V_2O_5)_{0.50}(PANI)_{0.50}$ depicts high intensity in XRD pattern because of more content of PANI as compared to other nanocomposite. The reason behind increase in intensity of peaks in nanocomposites is the excellent interaction between V_2O_5 nanostructures and PANI at nanoscale. The nanocomposites show shift in peaks toward lower angle showing tensile strain in nanocomposites.
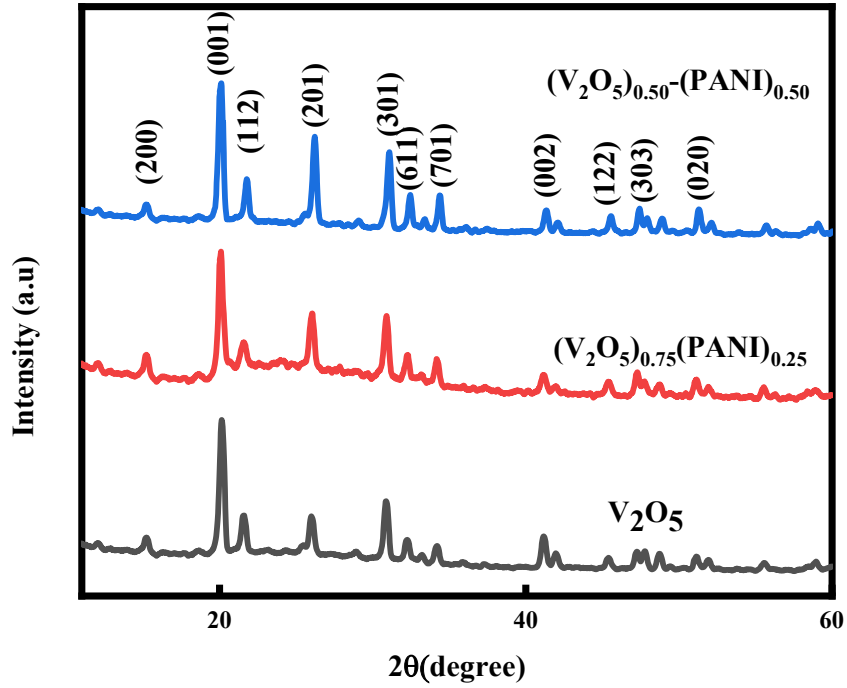
Figure 4.3. Combined X-ray diffraction pattern of nanocomposites $(V_2O_5)_x$-$(PANI)_{1-x}$

4.1.1 Crystallite Size

The Debye Scherrer equation was used to compute the average crystallite size of the samples. The average crystallite size of the samples was estimated from strong peak at (001) with corresponding angle at 20°. Table 4.1 shows the average crystallite size of pristine V_2O_5 and nanocomposites $(V_2O_5)_x(PANI)_{1-x}$. As the concentration of PANI in V_2O_5 increases, the crystallite size of nanocomposites decreases. It demonstrates that adding PANI to V_2O_5 increases crystallite size. The increase in crystallite size is attributed to presence of defects in V_2O_5. The equation 4.1 shows Debye Scherrer equation.

$$D = \frac{0.94\lambda}{\beta cos\theta} \qquad \textbf{4.1}$$

Where in equation 4.1 "λ" is wavelength , "β" is FWHM and "θ" is Braggs diffraction.

Table 4. 1. Different parameter values were obtained from XRD.

Nanocomposite	Position (2θ)	FWHM (2θ)	Lattice spacing (d_{hkl})	Unit cell volume (10^6 pm^3) Å^3	Crystallite size (nm)	Density (g/cm^3)
V_2O_5	20.14	0.14	4.39	179.5	33	3.36
$(V_2O_5)_{0.75}(PANI)_{0.25}$	20.08	0.11	4.37	179.5	38	3.36
$(V_2O_5)_{0.50}(PANI)_{0.50}$	20.03	0.09	4.35	179.5	41	3.36
$(V_2O_5)_{0.25}(PANI)_{0.75}$	26.10	0.12	3.41	179.5	47	3.37
PANI	25.0	0.94	3.9	35.54	29	1.32

4.2 Functional and Molecular Analysis

FTIR is a non-destructive technique to find a compound's functional group and molecular structure. Figure 4.4 shows FTIR spectra of pristine PANI, pristine V_2O_5, and nanocomposite $(PANI)_{0.50}(V_2O_5)_{0.50}$. The figure shows V_2O_5 has a strong absorption band at 997 cm^{-1}, representing the strong stretching vibration of V=O, the absorption band at 516 cm-1 and 800 cm^{-1} shows symmetric and asymmetric stretching vibration of V-O-V, respectively. PANI spectra show characteristics peak at absorption bands of 1563 cm-1 and 1483 cm-1, representing the C=C stretching mode of quinoid and benzenoid rings, respectively. The absorption bands at 1298 cm^{-1}, 1133 cm^{-1}, and 1080 cm^{-1} show the C-N stretch of the secondary aromatic amine of PANI chains, C-N stretching modes, and C-H in-plane bending mode, respectively. The nanocomposite $(PANI)_{0.50}(V_2O_5)_{0.50}$ shows characteristics stretching band of V=O at the peak of 1002 cm^{-1}, and the peak of 1133 cm^{-1} shows that V=O stretching overlaps with C-H in-plane bending vibration.
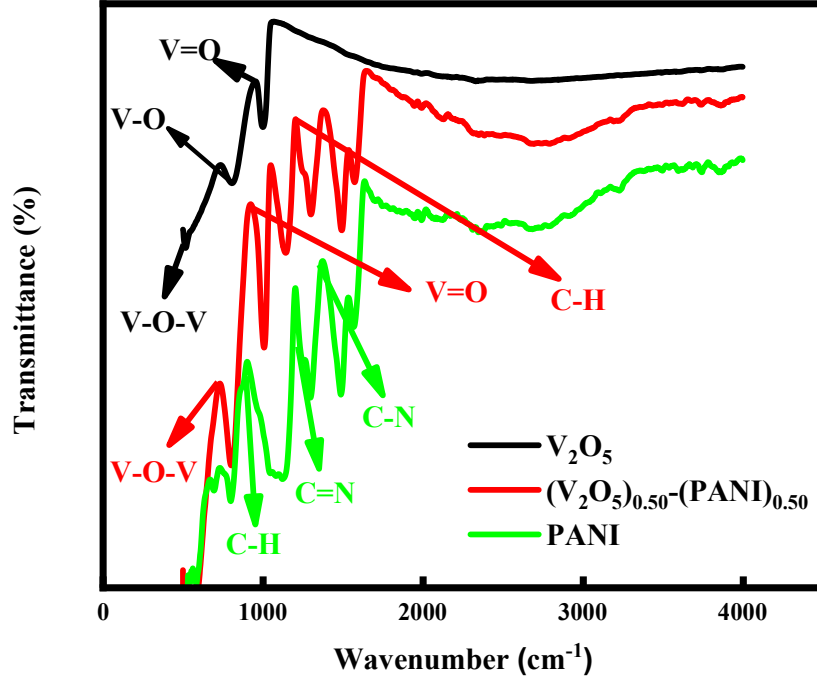
Figure 4.4.: Represent FTIR analysis of V_2O_5, PANI and their nanocomposites

4.3 Optical Tailoring

Optical properties are material responses against electromagnetic radiation, especially to visible light. The optical properties of V_2O_5, PANI, and nanocomposites have been examined through UV-visible spectroscopy in a wavelength range of 200-800 nm at room temperature. Figure 4.5 shows the UV-spectra of pristine V_2O_5, pristine PANI and $(V_2O_5)_x$-$(PANI)_{1-x}$ (x=0.25 ,0.50 ,0.75). The Tauc plot of pristine V_2O_5 ,pristine PANI and nanocomposites has been obtained with the help of the following relation.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (4.2)$$

In this equation "α" is the absorption coefficient, "$h\nu$" represents the photon energy, and exponent "2" indicates the nature of transition, which is associated with the direct bandgap of the materials and "A" represents the absorption coefficient corresponding to the bandgap energy. The yauc plot is used to find energy band gap of samples. The absorption peak of pristine V_2O_5 , PANI and nanocomposites $(V_2O_5)_x(PANI)_{1-x}$ (X=0.75,0.50,0.25) is shown in figure 4.5.The pristine V_2O_5 and PANI and nanocomposites $(V_2O_5)_x(PANI)_{1-x}$ (X=0.75,0.50,0.25) show absorption peak of 259 nm, 261 nm, 252 nm, 240 nm and 245 nm respectively. The absorption peaks slightly shift toward shorter wavelength which represent blue shift in absorption spectrum.
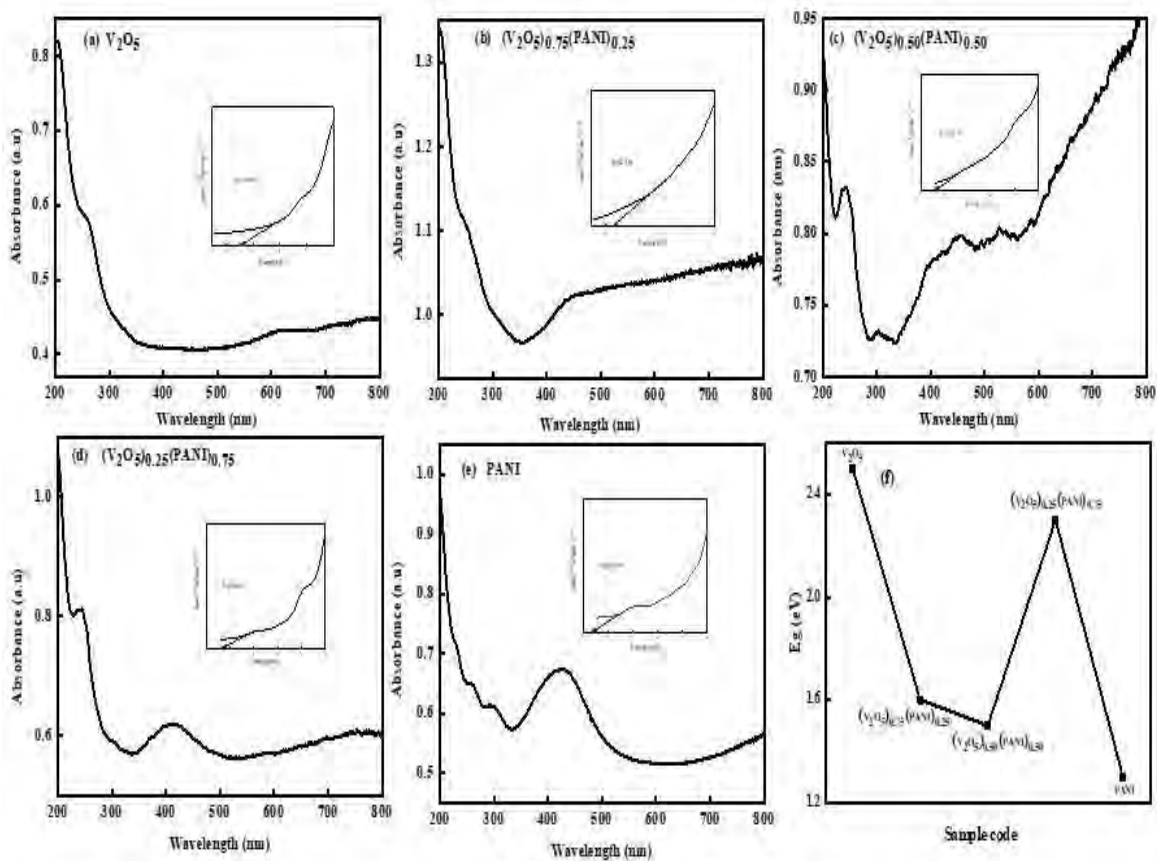
37

Figure 4.5: UV plots of a) V_2O_5 b) $(V_2O_5)_{0.75}(PANI)_{0.25}$ c) $(V_2O_5)_{0.50}(PANI)_{0.50}$ d) $(V_2O_5)_{0.25}$ $(PANI)_{0.75}$ e) V_2O_5 f) Ragone plot of E_g as a function of sample code

The Tauc plot of nanocomposites is shown in figure 4.6. The Tauc plot results show that the band gap energy values of V_2O_5, PANI and nanocomposites $(V_2O_5)_x(PANI)_{1-x}$ (X=0.75,0.50,0.25) are 2.5 eV, 1.3 eV, 2.3 eV, 1.5 eV, and 1.6 eV respectively. These results revealed that by increasing PANI concentration in nanocomposites has notably tuned the optical band gap of V_2O_5 toward visible region. The observed variation of the band gap can be traced to the addition of PANI. The detectable reduction in band gap energies might potentially be attributed to many mechanisms, such as the advent of localized states between the conduction and valence bands of V_2O_5. These localized states are related to variables such as the presence of oxygen vacancies, variartion in the electronic band structure, and the introduction of defects generated by stress.
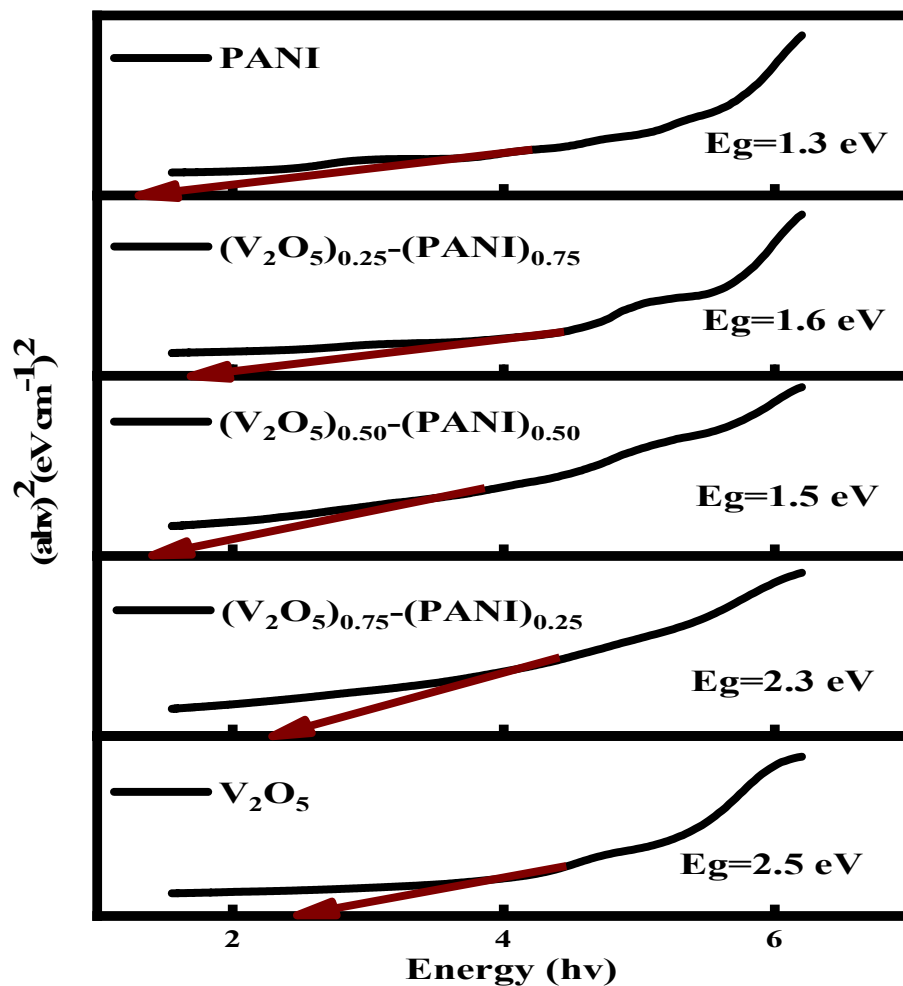
38

Figure 4.6: Tauc's plots of pristine V_2O_5, PANI and nanocomposites $(V_2O_5)_x(PANI)_{1-x}$ (X=0.75,0.50,0.25)

4.4. Electrochemical Properties

The sample CV, GCD, and EIS techniques have been used to examine the electrochemical characteristics of the electrode material. Different sample ratios are used to carry out this analysis. Three electrode configurations have been used in three arrangements to test the electrochemical characteristics with a 2M NaOH aqueous solution as the electrolyte.

4.4.1 Cyclic Voltammetry (CV)

Cyclic voltammetry is a electrochemical tool used to find the specific capacitance of material by applying a changed potential between the electrodes of a supercapacitor. The cyclic voltammetry measurements are carried at scan rates of 5mv/s, 20mv/s,50mv/s,80mv/s, and 100mv/s with a

potential window from 0V to 0.7V in 2M NaOH aqueous solution as electrolyte. CV calculations were done on pristine V_2O_5, PANI, and their nanocomposite $(V_2O_5)_x(PANI)_{1-x}$ (x= 0.75, 0.50, 0.25) at different scan rates as shown in figure 4.7. We used nickel foam as the working electrode, platinum wire as the reference electrode, and Ag-AgCl as the counter electrode in this measurement. The specific capacitance(Cs) of materials is calculated by equation.

$$Cs = A/mK\Delta V \qquad (4.3)$$

Where "A" is the area , "m" represents the mass of the deposited sample, "k" is the scan rate, and "ΔV" is a applied potential window.

Cyclic Voltammogram curves of nanocomposites show improved specific capacitance and higher stability than pristine V_2O_5 and PANI. The nanocomposite $(V_2O_5)_{0.50}(PANI)_{0.50}$ has the highest Cs of 745 F/g as compared to pristine V_2O_5, having a Cs of 334 F/g, and pristine PANI, having a Cs of 120 F/g and remaining nanocomposites having different ratio of material has also high specific capacitance as compared to V_2O_5 and PANI.

The increase in Cs of nanocomposite is coupling advantage of V_2O_5 and PANI. V_2O_5 has high energy density and Cs because of fast oxidation and reduction and a large potential window, which help to store more charges at the electrode/electrolyte interface. On the other hand, PANI has very fruitful properties such as good environmental stability, porous structure, larger surface area, and wide working potential window. The PANI chain also helps to increase the interaction between electrolytes and nanocomposites electrode/electrolyte interface. PANI has a fast reversible reaction due to π conjugated polymer chain and has a high surface area, which helps to increase charge storage to get maximum specific capacitance. After coupling these prestigious properties of both materials to form nanocomposites to get higher specific capacitance. Table 4.2 shows the specific capacitance of different nanocomposites.

Table 4.2. Specific capacitance values of pure V_2O_5 and its nanocomposites at different scan rates.

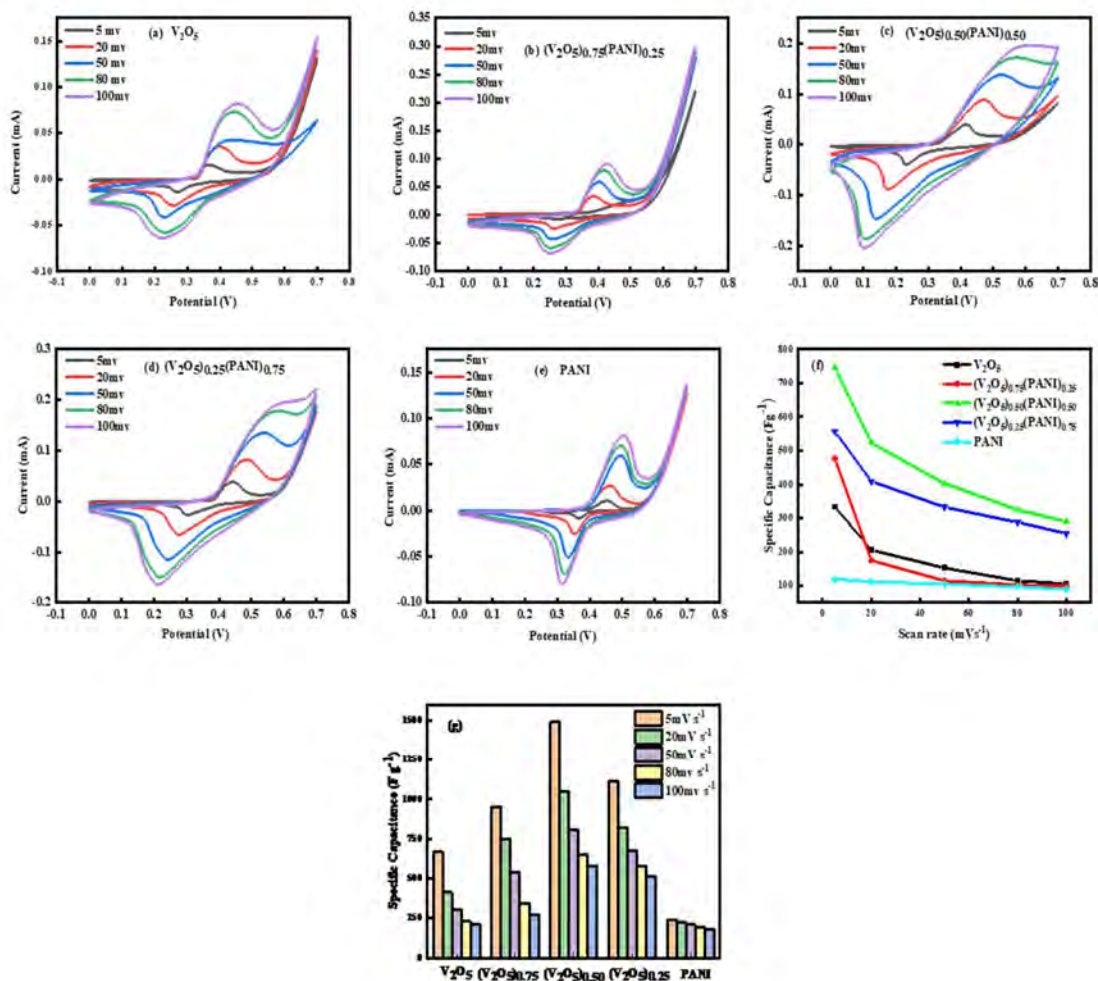| Scan rate (K)	Specific capacitance (Cs) F g^{-1}				
mV s^{-1}	V_2O_5	$(V_2O_5)_{0.75}(PANI)_{0.25}$	$(V_2O_5)_{0.50}(PANI)_{0.50}$	$(V_2O_5)_{0.25}(PANI)_{0.25}$	PANI
100	106	136	290	255	90
80	115	173	325	288	97
50	153	268	403	337	105
20	206	375	523	409	112
5	334	476	745	557	120

Figure 4.7: Cyclic Voltammogram of a) V_2O_5 b) $(V_2O_5)_{0.75}(PANI)_{0.25}$ c) $(V_2O_5)_{0.50}(PANI)_{0.50}$ d) $(V_2O_5)_{0.25}(PANI)_{0.75}$ e) PANI f) specific capacitance Vs Scan rate g) Bar graph of C_{sp} at a different scan rate

We conclude that specific capacitance of nanocomposite falls with an increase in scan rate due to a reduction in the size of the diffusion layer. At higher scan rate ,ions did not have enough time to diffuse absorb at electrode surface effectively, this lead to reduce surface area for ion adsorption and lower specific capacitance. The Cyclic Voltammograms also shows pseudocapacitive behaviour because of oxidation and reduction at the electrode interface.. The voltammogram of pristine V_2O_5 and $(V_2O_5)_x(PANI)_{1-x}$ at different scan rates is shown in Figure 4.7.

4.4.2 Galvanostatic Charge Discharge (GCD)

GCD is a unique method to examine supercapacitors under constant currents. To analyze the charge-discharge process, charge /discharge measurements of nanocomposites are done at different current densities of 1 A/g, 2 A/g,3 A/g,4 A/g,5 A/g, which we reported from our cyclic voltammetry results in 2M aqueous solution of NaOH as electrolyte using three-electrode configuration. This technique uses the following equation to find specific capacitance, Power, and energy density.

$$Cs = I \times \frac{\Delta t}{V} \qquad\qquad (4.4)$$

$$Eg = \frac{1}{2}Cp \ (\Delta V)^2 \qquad\qquad (4.5)$$

$$Pg = \frac{Eg}{\Delta t} \qquad\qquad (4.6)$$

Specific capacitance values from this technique show that specific capacitance increases with a decrease in current density. At higher current density , the ions do not have enough time to use the maximum of the material effectively, so only the surface layer of the composite contributes to charge-discharge processes. As a result, we get low specific capacitance at higher current density. Furthermore, a rise in the IR drop has been seen with increased current density. The nanocomposite $(PANI)_{0.50}(V_2O_5)_{0.50}$ has the highest Cs of 834 F/g as compared to neat V_2O_5 and neat PANI having a Cs of 366 F/g and 290 F/g current density of 1 A/g respectively. Other nanocomposite having concentration of $(V_2O_5)_{0.25}$-$(PANI)_{0.75}$ and $(V_2O_5)_{0.75}$-$(PANI)_{0.25}$ shows high Cs of 628 F/g and 406 F/g respectively at a current density of 1 A/g .

Table 4.3. Specific capacitance values obtained from Galvanostatic charge discharge (GCD).

Current density A/g	Specific capacitance (Cs) F/g				
	V_2O_5	$(V_2O_5)_{0.75}(PANI)_{0.25}$	$(V_2O_5)_{0.50}(PANI)_{0.50}$	$(V_2O_5)_{0.25}(PANI)_{0.75}$	PANI
1A/g	366	406	834	628	290
2A/g	324	368	768	580	248
3A/g	282	330	660	546	240
4A/g	224	304	600	469	192
5A/g	200	280	570	430	170
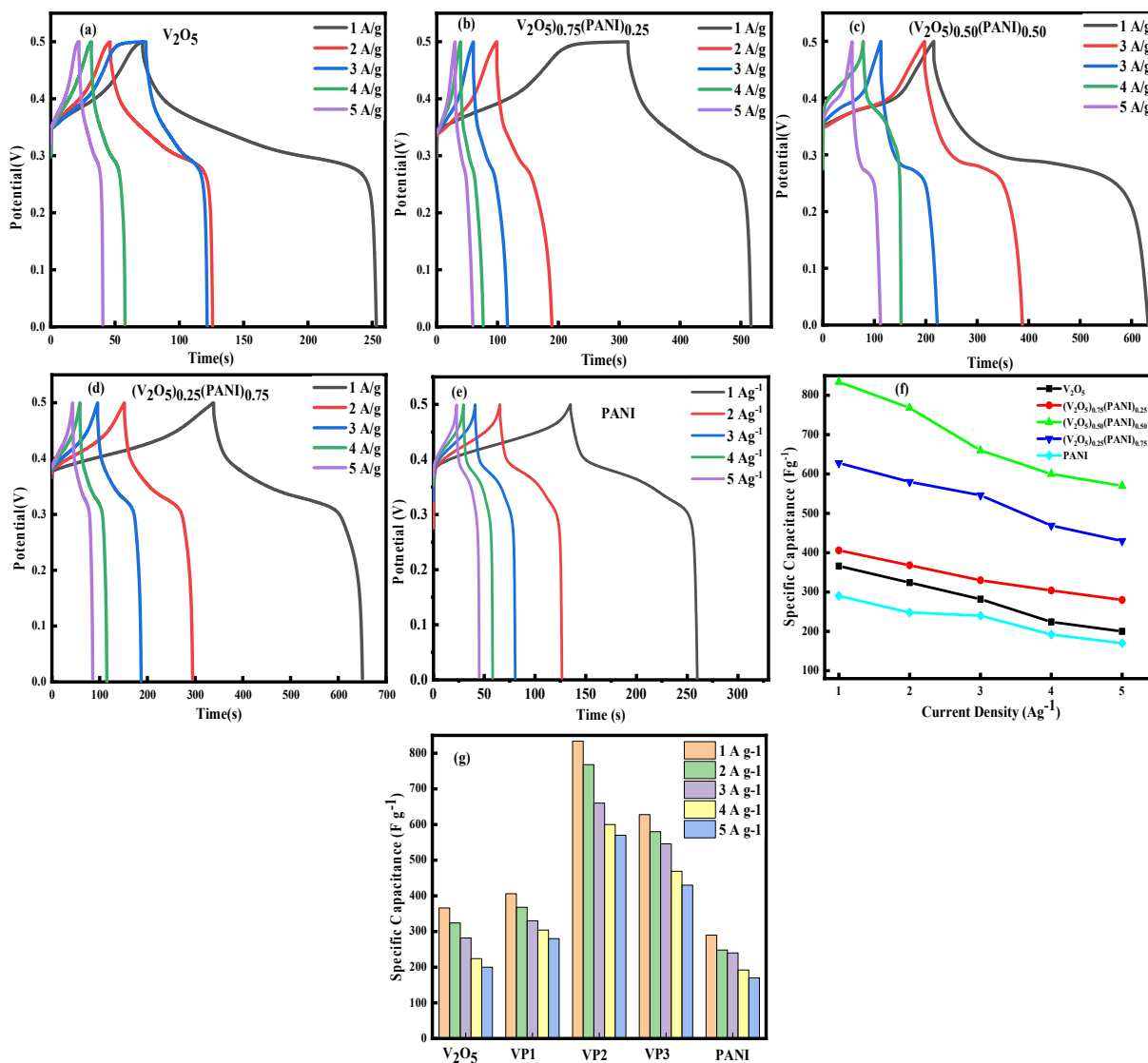
Figure 4.8: Charge discharge curve of a) V_2O_5 b) $(V_2O_5)_{0.75}PANI)_{0.25}$ c) $(V_2O_5)_{0.50}(PANI)_{0.50}$ d) $(V_2O_5)_{0.25}(PANI)_{0.75}$ e) PANI f) Specific capacitance Vs Current density g)Graphical comparison of C_{sp} at different Current density.

Power density of 917 Wh/kg and energy density of 29 W/kg of nanocomposite $(V_2O_5)_{0.50}(PANI)_{0.50}$ shows a high-performance supercapacitor. These results show that by increasing the concentration of polyaniline, we get high specific capacitance in a supercapacitor because PANI has a porous structure and large surface area, so more electrons are stored on the electrode surface, resulting in higher specific capacitance. Figure 4.8 shows specific capacitance calculated from Galvanostatic charge-discharge.

4.4.3 Electrochemical Impedance Spectroscopy (EIS)

EIS is widely used to find the impedance of electrode materials with a.c perturbation voltage. EIS measurements were made utilizing a three-electrode system with a 2M NaOH aqueous solution as the electrolyte in the frequency range of (1.0-100,000) Hz. The Nyquist plot is used to find the impedance spectra of the material. The impedance spectra values are 0.33 Ω, 0.21 Ω 0.31 Ω, 0.24 Ω, and 0.29 Ω, of neat V_2O_5, PANI, and their nanocomposites $(V_2O_5)_x$-$(PANI)_{1-x}$ (x= 0.75, 0.50, 0.25) respectively and shown in figure 4.9. The impedance spectra value shows that nanocomposite $(PANI)_{0.50}(V_2O_5)_{0.50}$ has the least ESR value of 0.24 Ω, showing better electronic conductivity and less cell resistance and is also consistent with CV and GCD findings. This nanocomposite also shows a semicircle, which indicates charge transfer resistance at the electrode/electrolyte interface and shows pseudocapacitive behaviour. The size of the semicircle gives information about the speed of the electrochemical reaction. The ESR value of other nanocomposites also shows less resistance by increasing the concentration of PANI. These results show that these nanocomposites are ideal for energy storage nanodevices.
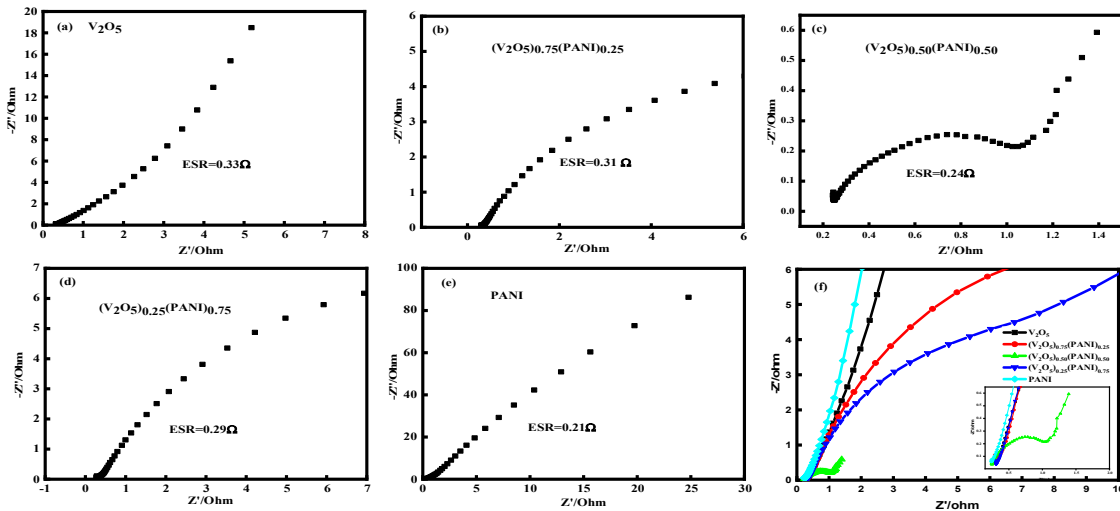

Figure 4.9: Electrochemical Impedance Spectroscopy of a) V_2O_5 b) $(V_2O_5)_{0.75}(PANI)_{0.25}$ c) $(V_2O_5)_{0.50}(PANI)_{0.50}$ d) $(V_2O_5)_{0.25}(PANI)_{0.75}$ e)PANI f) Ragone plot of ESR value of composites

4.5 Cycle Retention

The Important factor of electrode material for its use energy storage device is its cyclic retention. In order to check cyclic retentivity of electrode material ,we put the device through continuous charge-discharge experiments for up to 1000 cycles in a 2 molar of NaOH electrolyte at current density of 3 A/g.The pristine V2O5 and PANI show cyclic retention of 50% and 80% respectively after 1000 cycle. The drop in cyclic retentivity of V2O5 is due to electrode degradation, poor mechanical stability, and internal resistance due to electrolyte decomposition.

The nanocomposite $(V_2O_5)_{0.50}(PANI)_{0.50}$ shows improved cycle retentivity of 70% after 1000 cycle. The addition of PANI in V2O5 improve the cycle retentivity of nanocomposite by 20%.The PANI prevent nanocomposite from volume distortion ,provide thermal stability and increase ion diffusion. This result demonstrates $(V_2O_5)_{0.50}(PANI)_{0.50}$ nanocomposite potential for its use in energy storage devices. Figure 4.10 Shows cycle retention of pristine V_2O_5 ,PANI and $(V_2O_5)_{0.50}(PANI)_{0.50}$.
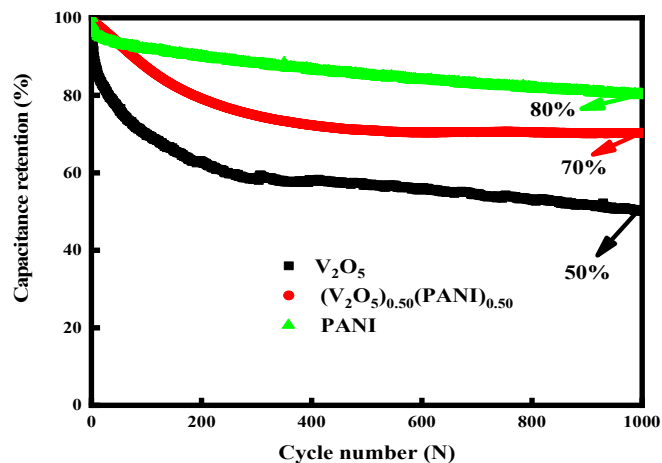

Figure 4.10: Cyclic Retentivity of V_2O_5 and nanocomposites

Conclusions

In conclusion, this research has successfully established the synergistic effects of PANI-V_2O_5 nanocomposites in the context of supercapacitor electrodes. The electrodes exhibited a broad range of charge storage potential, spanning 0.0-0.7 V. This characteristic significantly enhances energy density, power density. Simultaneously, notable advancements have been made in enhancing surface area, electrical conductivity, specific capacitance, and cyclic retentivity by synthesizing a nanocomposite at the different ratio. The confirmation of the presence of specific faults in crystalline V_2O_5-PANI nanocomposites was achieved by structural analysis. The existence of a functional group in nanocomposites has been defined using vibrational analysis. The computation of the energy band gap demonstrated a negative correlation between the concentration of PANI and the magnitude of the band gap. The incorporation of polyaniline (PANI) into energy storage devices has been found to improve their optical characteristics significantly. The comprehensive electrochemical investigation of V_2O_5-PANI nanocomposites has revealed that $(V_2O_5)_{0.50}(PANI)_{0.50}$ nanocomposite displays the higher Cs of 745 F/g at a scan rate of 5 mV/s and a low equivalent series resistance (ESR) of 0.24 Ω. The observed improvement in Cs can be attributed to many factors, including significant oxidation of structural voids in vanadium, improved electronic conductivity, and improved surface area available for ions storage at the working electrodes. The energy density and power density, calculated from galvanostatic charge-discharge measurements of this nanocomposite, stand at 29 Wh/kg and 917 W/kg, respectively. Remarkably, the cyclic stability of the nanocomposite $(V_2O_5)_{0.50}(PANI)_{0.50}$ is found to be 70%, outperforming pristine V_2O_5 .The nanocomposites that have been developed are excellent electrode materials for use in energy storage nanodevices.

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