Synthesis of Nanostructured Metal Oxides and Sulfides for High Performance Energy Devices

A Dissertation Submitted to the Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, in the Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy in Physical Chemistry

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Nasreen Bibi
Abstract

In the last few decades, energy crises enforced scientists and researchers to search for the new nanostructured materials that may have a potential for energy harvesting and storage devices. Energy storage have earned a key position in energy devices due to its viability as compared to energy harvesting devices. Metal oxide and sulfides nanostructured materials have an enormous potential for energy devices owing to their high electrochemical performance and excellent stability. In the current study, hydrothermal method has been employed for the synthesis of Ce$_2$Zr$_2$O$_7$, CeO$_2$, Y$_2$Zr$_2$O$_7$, PbS, CeS$_2$, MnS and nanocomposite of Ce$_2$Zr$_2$O$_7$/PbS, CeO$_2$/CeS$_2$ and Y$_2$Zr$_2$O$_7$/MnS materials. The synthesized nanostructured materials have been characterized to find their applications in supercapacitor devices. Structural and morphological studies have confirmed the purity and the clear morphology of the materials. Electrochemical study using three-electrode system demonstrates that metal sulfide has higher specific capacitance than metal oxide but metal oxide reveals superiority in the cyclic stability. Therefore, due to synergistic effect, the nanocomposite of metal oxide and sulfide gain the conductivity of the sulfide and the stability of the oxide. As a result, the nanocomposites depict the better electrochemical performance in a sense of capacitance retention and cyclic stability with good rate capability.

Specific capacitance (C$_{sp}$), energy density (E) and power density (P) of the nanostructured electrode using Ni foam as a substrate have been measured with three-electrode system by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) techniques. The C$_{sp}$ and E of Ce$_2$Zr$_2$O$_7$/PbS, CeO$_2$/CeS$_2$, Y$_2$Zr$_2$O$_7$/MnS are 219, 420, 221 F/g and 6.7, 21.2, 10 Wh/kg at a constant applied current density of 1 A/g, respectively. The C$_{sp}$ of Ce$_2$Zr$_2$O$_7$/PbS, CeO$_2$/CeS$_2$, Y$_2$Zr$_2$O$_7$/MnS nanocomposites electrode after 1000 successive CV cycles are 116, 700, 261 F/g, correspondingly. The
electrode consisting of SrZrO$_3$ nanorods exhibits remarkably high C$_{sp}$ of 1225 F/g and 65 Wh/kg energy density. The excellent results of SrZrO$_3$ nanorods are owing to its high specific surface area, small pore size and unique morphology.

Cyclic stability analysis reveals an excellent stability of the studied electrodes due to their unique morphologies and conductive nature of the substrate (Ni foam). C$_{sp}$ remains constant in Ce$_2$Zr$_2$O$_7$/PbS, while in case of CeO$_2$/CeS$_2$ and Y$_2$Zr$_2$O$_7$/MnS, the C$_{sp}$ increases continuously up to 1000 successive CV cycles. The SrZrO$_3$ nanorods shows high cyclic stability up to 1000 cycles. Above studies, suggest a significant promise of aforementioned materials for their use in future generation supercapacitors electrodes.
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</tr>
<tr>
<td>SCs</td>
<td>Supercapacitor</td>
</tr>
<tr>
<td>E</td>
<td>Energy Density</td>
</tr>
<tr>
<td>P</td>
<td>Power Density</td>
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<td>$C_{sp}$</td>
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<td>EIS</td>
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1. Introduction

The energy crisis is one of the biggest challenges and we are not far when we will run out the energy sources, which are in use since ages as these are limited. These resources are critical to bring life in industrial society and demand is increasing every day. It took hundreds and thousands of years for fossils to turn into fuel naturally. Many research institutes and individuals are working on renewable energy resources and some governments are encouraging these initiatives. We are largely dependent on petroleum and coal to fulfill our energy needs which is also causing irreversible damages to our planet’s environment. Priority is to reduce the use of these natural resources and move to alternate energy resources. We want our fossil fuel resources to last longer by limiting their use and at the same time make our planet a better place to live for our future generations. During the past few years more and more interest is being observed in renewable energy methods and techniques.

Currently, fossils fuels and nuclear power plants meet the energy needs of the world. Lesser part of energy needs has drawn from renewable energy sources. Renewable resources is one of the most suitable and reliable source of alternative energy. Renewable energy can derived from sources like wind, solar, water and air. The energy generated from aforementioned resources can generate electricity, which can fulfil many daily needs of human kind including powering up our transportation and industrial system. In addition to generation, efficient storage of produced electricity is very important because of irregular supply of sources like wind, air and solar. We can use cost effective and efficient batteries and capacitors to store the energy.

1.1 Types of Energy Devices

Energy devices can be broadly classified into two categories.

I. Energy harvesting devices
II. Energy storage devices (ESD)

1.1.1 Energy Harvesting Devices

Energy harvesting devices include those devices, which directly harvest the solar energy into useable form of energy. The most common form of energy harvesting is solar power system. Solar cells works on photovoltaic effect, and convert the solar light directly into electricity.
The second form of energy harvesting is fuel cells. Fuels cells convert the fuel into electricity, and its actually electrochemical cells\textsuperscript{23}. Fuel cells have similar working strategy as batteries, but fuels cells cannot recharged like batteries. The most recognized form of fuel cells now a day is hydrogen fuel cell.

**1.1.2 Energy Storage Devices**

ESD are further characterized into two types.

I. Electrical ESD

II. Non-electrical ESD

The electrical ESD include batteries, capacitors and superconducting magnetic energy storage system. While the non-electrical ESD include those devices that convert the kinetic and thermal energy into electrical energy like flywheels, pumped hydro and pumped air storage systems.

The chemical ESD include batteries and capacitors. Batteries are charged to store the chemical energy by a chemical reaction that is triggered within the cells by applying a potential. Batteries are discharged and convert the chemical energy into electrical energy. Batteries have many uses due to its portability, ease of use, and have ability of wide power storage capacity ranging approximately from 100 W to 20 MW. Batteries are available in many types like Ni-Cd battery and Li-ion battery etc.\textsuperscript{23,24}. Batteries

Capacitors are another chemical ESD that can charge and discharge instantaneously\textsuperscript{25}. Capacitors have the ability to store the energy for long term with negligible loss of energy.

The other from of capacitor is supercapacitor (SCs) and these are termed as ultra-capacitors. SCs could achieve high power density (P) with combination of porous electrodes and active electrolyte\textsuperscript{26,27}. SCs have higher energy (E) and P than conventional capacitors. The working principle of energy storage in batteries, capacitors and SCs is depicted in Fig. 1.1.
Figure 1.1: Schematic illustration of storage mechanism of batteries, capacitors and supercapacitors.\textsuperscript{i,ii}

When we compared the SCs with batteries, it remain relatively unchanged during the successive charging and discharging. The overall performance of SCs can be determined by proper selection of the electrode, electrolyte and cell configuration.

In recent times the researcher focus on the SCs materials due to its excellent and extraordinary electrochemical properties. They have high $P$, high specific capacitance ($C_{sp}$) and long cyclic ability\textsuperscript{29,30}. SCs have a high $P$ but low $E$ than batteries and fill the gap between batteries and capacitors in Ragone plot\textsuperscript{31-33}.


Figure 1.2: General description of supercapacitor’s cell\textsuperscript{iii}.

Ragone plot, the performance evaluator of the energy storage and harvesting devices is given in Fig. 1.3, which, indicate the specific $P$ vs $E$. Ragone plot shows that batteries and fuel cells have lower $P$ as compared to conventional capacitor (106 W/kg) but have higher $E$. The $E$ of SCs is greater than the conventional capacitors\textsuperscript{27}. Conventional capacitor store energy on plates that have low surface area, while SCs store the charges in double layer setup\textsuperscript{34}.

SCs when compared to batteries can supply the hundred to many thousand time more power density. They can store charges by fast and reversible faradaic redox and electrostatic reaction that is why SCs have longer life than batteries\textsuperscript{35, 36}. Batteries have a limited life as charges are stored by the redox reaction of the active masses and longtime are required for charging or discharging a battery. Therefore, SCs in term of energy and power density, fall between battery and conventional capacitor and have an important position in the Ragone plot.

1.2 Types of Supercapacitors

SCs can be classified into three types on the basis of their working principle of energy storage.

I. Electrical double layer capacitor (EDLC)
II. Pseudocapacitor
III. Hybrid capacitor

1.2.1 Electrical Double Layer Capacitor (EDLC)

EDLCs store the electrostatic charges in the form of double layer at the interface of the electrolyte and electrode. EDLC physically store the charges by adsorption and desorption of ions. No chemical reaction (Faradaic reaction) is involved in the EDLC storage mechanism and cyclic voltammograms (CVs) have typical rectangular shape. EDLC electrode materials consist of carbon materials like activated carbon, carbon nanotubes etc. EDLC usually have more P than the pseudocapacitors but have low E. It usually exhibits fast charging and discharging process and galvanostatic charge

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discharge curve (GCD) have a fast IR drop. Fig. 1.4 (a) and (b) have a typical CVs and GCD of EDLC materials.

![Figure 1.4: Typical (a) cyclic voltammograms and (b) charge-discharge curves of EDLC materials.](image)

1.2.2 Pseudocapacitors

The electrode materials which store the charges though reversible redox chemical reactions are called pseudocapacitors. Reversible redox reactions are actually fast faradaic redox reactions that occur at the surface of the active materials. Oxidation and reduction reactions occur during faradaic reaction and appear in the form of peaks in CVs as obvious in Fig. 1.5(a). Charge-discharge process are shown in GCD profiles indicating the redox reaction in materials (Fig. 1.5b). Pseudocapacitors usually have high $C_{sp}$ and E than EDLCs. The active electrode materials in the pseudocapacitors are usually metal oxide, sulfide and conducting polymers.

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Figure 1.5: Typical (a) cyclic voltammograms and (b) charge-discharge curves of pseudocapacitive materials.

1.2.3 Hybrid Supercapacitors

Hybrid SCs have the properties of both EDLC and pseudocapacitors. In hybrid SCs both faradaic and non-faradaic reactions are involved for charge storage mechanism. So due to the effect of both EDLC and pseudocapacitance mechanism, hybrid SCs maintain the energy and power density, but have the low values than EDLC and pseudocapacitors. The CVs have a slightly different shape than EDLC and a small bump is due the faradaic redox reactions.

1.3 Working Principle of Supercapacitors

The SCs are usually composed of three basic components i.e. active material electrolyte and counter electrode. The $C_{sp}$ of the SCs materials have been accessed by either two or three electrode system. In three electrode system, active material used as working, while a counter and reference electrode is used for capacitance measurement. Reference electrode in three electrode systems is Ag/AgCl or Hg/HgCl, while platinum or graphite wire as a counter and active material as working electrode. Two-electrode setup is also used for capacitance measurement in SCs materials. Symmetric SCs have both electrodes of same active materials while

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asymmetric SCs have two electrodes of different suitable materials in capacitance measurements\textsuperscript{47}.

The choice of proper electrolyte has an important role in achieving a superior $C_{sp}$ with high E. In non-aqueous (organic) electrolyte, large potential window can be used for $C_{sp}$ measurements; it also allows the active electrode materials to deliver a high E. However, organic electrolyte has the disadvantage of low ionic conductivity. Aqueous electrolyte in comparison with non-aqueous electrolyte has an advantage of high ionic conductivity and can provide high E. Beside this, aqueous electrolytes are ecofriendly and they don’t need any anhydrous atmosphere as in case of organic electrolyte\textsuperscript{48}.

Nanostructured materials have a lot of application in various fields including in energy devices like solar cells, fuel cells, batteries and SCs etc. The energy harvesting devices such as solar cells have the difficulty to work on all the days of the years due to limited supplies of the sun light. So only one energy harvesting devices is not enough to meet the energy demands of the world, and we need to develop the efficient ESD to overcome the energy crises of the modern world. Beside this, materials used in energy devices, badly effect the environment. Therefore, we need to develop and synthesize such energy devices materials that can, not only meet the energy demands but are ecofriendly as well. Furthermore, the energy devices should be cost effective and easily accessible. SCs are superior ESD due to higher efficiency and are environment friendly too, as the materials used as active electrodes of SCs device harvest electrical energy without harmful chemicals\textsuperscript{49-51}.

Many materials has been under investigation to enhance the efficiency of the SCs, and to use it as a primary source of energy instead of batteries in electrical vehicles. Some SCs electrode materials show high $C_{sp}$ but they have low E and P and have low cyclic stability. Therefore, to improve the efficiency of the electrode materials, we need to explore such materials, which have high $C_{sp}$ and E without sacrificing P and stable enough to replace the batteries. In order to achieve and optimize the aforementioned properties a lot of metal oxide, metal sulfide, hydroxide, polymers and epoxide gels have been widely studied in past decade. To fabricate high performance SCs devices, several researcher tried to synthesize metal oxides, sulfides and composite material with
improved electrochemical capacitance, E and high cyclic stability. Some of the reported materials are discussed below.

1.4 Brief Overview of Existing Materials

Subramanian et al.\textsuperscript{52} synthesized anhydrous RuO$_2$ and investigated it as an electrode of SCs device. The CV studies were performed to evaluate its potential application under varying conditions of scan rate and concentration of the electrolyte. The $C_{sp}$ of studied RuO$_2$ electrode was 58 F/g at 2 mv/s scan rate. Although it showed a better pseudocapacitance but still needed to improve its capacitance. The stability measurements should also conducted for aforementioned material.

Tao et al.\textsuperscript{53} had synthesized the CoS$_x$ through chemical co-precipitation scheme and tested as SCs’s electrode. CoS$_x$ electrode can deliver the $C_{sp}$ of 474 F/g at 5mA and even a higher $C_{sp}$ of 369 F/g at applied current of 50 mA in 6 M KOH solution. Although the $C_{sp}$ studied electrode material is high but the results are preliminary and still needs improvement to use a metal sulfide as an electrode material for SCs’s applications.

Reddy et al.\textsuperscript{54} studied the monocrystalline metal oxide dispersed in multiwalled carbon nanotubes (MWCNT) as an electrode of SCs. The measured $C_{sp}$ of the studied composite electrode was 138, 160 and 93 F/g for RuO$_2$, TiO$_2$ and SnO$_2$ composites with MWCNT respectively. The results indicate the potential application for developing double layer capacitors. However, the results show improvements but further studied required for practical application of the electrode materials.

Bao et al.\textsuperscript{5} synthesized the CoS nanowires by an efficient and economic method and studied its application as SCs electrode. They modified the structure by varying the concentration of the precursor and studied the effect of morphology on the electrochemical properties of the material. It has been found that the nanowire assembled by nanoflower provide a high value of 508 F/g $C_{sp}$ with high E and high stability and can compete the best SCs RuO$_2$ electrode. The synthesized nanostructured material was low cost as well. Due to these qualities, CoS nanostructured material was considered as a promising candidate for SCs electrode application.

Dubal et al.\textsuperscript{55} prepared a thin films of polycrystalline Mn$_3$O$_4$ on the glassy substrate by chemical bath deposition method. The $C_{sp}$ value (193 F/cm$^2$) reveals the
potential application of \( \text{Mn}_3\text{O}_4 \) as SCs electrode materials. The \( C_{sp} \) of \( \text{Mn}_3\text{O}_4 \) was poor and \( E, P \) and stability measurements was not measured to establish its practical utility as future SCs electrode.

Li et al.\(^5^6\) synthesized a novel mesoporous MnO\(_2\)/carbon aerogel composite and studied the composite material as a SCs electrode. The studied Composite electrode materials showed the better \( C_{sp} \) than the constituent material. It showed a high \( C_{sp} \) of 515.5 F/g. High \( C_{sp} \) with good cyclic stability and environmental friendly nature of the composite electrode suggests its utility as an electrode for SCs application.

Wei et al.\(^5^7\) prepared the nickel cobaltite aerogel. The low cost synthesis method had been used for electrode preparation. The nickel cobaltite aerogel achieved a high \( C_{sp} \) of 1400 F/g after 650 cycles. The high stability and low cost synthesis method reveals that nickel cobaltite aerogel should have a capacity to use an electrode for future SCs.

MnO\(_2\) coated on SnO\(_2\) nanowires studied for their capacitive performance by Yan et al.\(^5^8\). A very easy and quick immersion method had been employed for the coating of amorphous MnO\(_2\) on SnO\(_2\) nanowires. A high \( C_{sp} \) of 800 F/g at a current density of 1 A/g was attained by GCD method. \( E \) and \( P \) suggest the good rate capability. The temperature dependent capacitive behavior was also studied. The core-shell structure was responsible for high cyclic stability of the studied electrode material. Their study showed that amorphous MnO\(_2\) coated on SnO\(_2\) has an excellent electrochemical properties and a good candidate to be used in SCs.

Wang et al.\(^5^9\) demonstrated the electrochemical properties of Ni(OH)\(_2\)/Graphene sheet (GS) composite as a pseudocapacitor electrode. The studied electrode had a high energy and \( P \) with long cycle life. The monocrystalline Ni(OH)\(_2\) grown on GS showed a high \( C_{sp} \) with an excellent rate capability. Their studies showed that the electrochemical properties are largely dependent on morphology, crystallinity and the composite materials.

Layered graphene oxide sandwiched with the conducting polymer had been studied as a SCs electrodes by Zhang et al.\(^6^0\). They demonstrated a feasible approach for the preparation of conducting polymer with pillared GO sheets that exhibited excellent electrochemical properties. They explored the advantages of a composite material for SCs applications. GO sheets provided the large surface area for the
attachment of the conducting polymer and hence improved the electrochemical properties. The composite electrode achieved a high $C_{sp}$ of 500 F/g with high rate capability and cyclic stability. The studied composite give a new way and opened up a general method for synthesis of graphene composite.

Hu et al.$^{61}$ studied the hierarchical nanostructure of amorphous MnO$_2$, Mn$_3$O$_4$ and nanocrystallites single crystal MnOOH nanowires for SCs applications. They concluded that for constructing a highly porous nanocomposite, the ideal substrate is wire like Mn$_3$O$_4$/MnOOH. Cyclic stability of MnO$_2$ was enhanced by the addition of Mn$_3$O$_4$ due to transformation of a nanocrystalline structure to amorphous phase. The ternary nanocomposite achieved a high $C_{sp}$ of 470 F/g with high power capacity and high stability. The improved electrochemical performance suggested that ternary nanocomposite could be used as an electrode material for SCs.

A facile synthesis method had been employed to prepare a binder free ternary electrode of MnO$_2$/carbon nanomaterial by Wang et al.$^{62}$. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) results revealed the porous nature of the ternary nanocomposite, which ensured the fast redox reaction and ease the electrolyte ions access to the entire surface of the active material. These factors ultimately enhanced the electrochemical properties of ternary nanocomposite, achieved a $C_{sp}$ of 357 F/g and increased up to 1190 F/g due to presence MnO$_2$. The nanocomposite had an excellent cyclic performance with capacitance retention of 98.5% after 2000 cycles. Ternary nanocomposite with a porous nature nanostructure and its excellent electrochemical properties suggested a promising candidate for the SCs applications.

Yu et al.$^{63}$ studied the nanocomposite of graphene/MnO$_2$ nanostructured electrode for SCs application. Graphene/MnO$_2$ nanocomposite was wrapped by 3 D carbon nanotubes or with conducting polymers to enhance the electrochemical properties of the nanocomposite. The wrapped nanocomposite had an exceptionally high cyclic stability, high $C_{sp}$ with high rate capability. The wrapping of electrode materials proved to be an efficient technique and could be used to increase the electrochemical properties of different metal oxide. This technique can be widely applicable to insulate the electrode materials of ESD.

Bao et al.$^{64}$ demonstrated the fabrication of hybrid nanocomposite electrode for the SCs application. Ultrathin film of MnO$_2$ was coated on the highly conductive
substrate of Zn$_2$SnO$_4$ (ZTO) nanowires. ZTO nanowires grown on the surface of carbon microfibers (CMFs). The fabricated hybrid MnO$_2$/ZTO/CMF nanocomposite had a high $C_{sp}$ of 621.6 F/g. The amorphous MnO$_2$ layers improved the $C_{sp}$ by fast redox reactions, while ZTO nanowires grown on CMFs offer the conductive substrate and improves the overall electrochemical properties of the hybrid composite. The hybrid MnO$_2$/ZTO/CMF composite had a high rate capability, good GCD stability and high $C_{sp}$. The above-mentioned properties suggest the practical utility of the hybrid composite in future SCs electrode.

Yang et al.\textsuperscript{26} synthesized the hollow CoS hexagonal nanosheets as a SCs electrode. CoS hollow nanosheets electrode achieved $C_{sp}$ of 326.4 F/g with $E$ of 13.2 Wh/kg and $P$ of 17.5 kW/kg at a current density of 64.6 A/g. The specific capacitance retention of 85.4% had been reported after 10000 charge-discharge cycles. The excellent capacitance retentions suggested the practical use of CoS nanosheets in SCs instead of widely studies MnO$_2$ and graphene electrodes. The other factor of this study is high mass loading capacity of the electrode with 9.7mg/cm$^2$ and deliver a high capacitance of 138 F/g, suggested a practical use of CoS nanosheets in energy storage device, in electrical vehicle and computers.

Wang et al.\textsuperscript{65} synthesized a nanostructured mesoporous MnO$_2$ and studied as an electrode for SCs applications. A series of MnO$_2$ nanomaterials with porous structure had been synthesized by one-pot reaction. The synthesized nanoparticles had a high surface area, mesoporous size and 3D network. The electrochemical properties of the electrode revealed its potential; application in SCs. MnO$_2$ had a high $C_{sp}$ of 200 F/g. Hybrid SCs had been fabricated containing MnO$_2$ and activated carbon as a positive electrode and activated carbon as a negative electrode. Hybrid SCs revealed $C_{sp}$ of 23.1 F/g with an $E$ of 10.4 Wh/kg and $P$ of 14.7 kW/kg after 1200 cycles. The results revealed the potential use of MnO$_2$ as a positive electrode in hybrid SCs.

Sun et al.\textsuperscript{66} employed the solid state reaction route to prepare graphene/Ni(OH)$_2$ nanocomposite and studied as a SCs electrode. The Ni(OH)$_2$ nanoparticles was dispersed on the surface of functionalized reduced graphene oxide (F-rGO). The nanocomposite electrode had a $C_{sp}$ of 1568 F/g at a current density of 4 A/g. The developed synthesis route in this work was considered as a green chemical synthesis.
The electrochemical performance of nanocomposite suggested its practical use in SCs electrode.

Xia et al.\textsuperscript{67} prepared the Co\textsubscript{3}O\textsubscript{4}/NiO and ZnO/NiO core-shell nanowire arrays by simple solution method on different substrate and studied their electrochemical properties for ESD. The studied electrode grown on Ni foam exhibited an excellent electrochemical performance with high cyclic stability and high specific capacitance.

Shao et al.\textsuperscript{68} employed the in-situ growth method for the preparation of layered double hydroxide (LDH) microsphere with 3D architecture. 3D architecture include core-shell, yolk-shell and hollow interior. Hollow LDH exhibited the excellent pseudocapacitance performance. In comparison with yolk-shell and core-shell, hollow LDH achieved high specific capacitance, high cyclic stability, good charge-discharge stability and high rate capability. These qualities of hollow LDH credited to high surface area and mesoporous nature of the material. NiAl-LDH hollow microspheres met the requirement of high $C_{sp}$ and cyclic stability for SCs electrode.

He et al.\textsuperscript{69} developed a freestanding 3D graphene/MnO\textsubscript{2} electrode for flexible SCs. 3D graphene network was prepared from pressed Ni foam. Uniform mass of MnO\textsubscript{2} coated on to the 3D graphene skeleton by electrodeposition. Hybrid SCs electrode showed high specific capacitance, high rate capability and remarkable cyclic stability. The high electrochemical performance ascribed to the conductive porous feature of 3D graphene and secondly due to the good contact between the graphene and MnO\textsubscript{2}. Because of these fascinating features of hybrid, graphene/MnO\textsubscript{2} composite electrode considered promising candidate for future application in small flying devices, adhesive tape-like SCs, wearable SCs etc.

Zhang et al.\textsuperscript{70} grown interconnected mesoporous NiCo\textsubscript{2}O\textsubscript{4} nanosheets on the conductive substrate. Mesoporous NiCo\textsubscript{2}O\textsubscript{4} nanosheets supported on Ni foam served as a binder free SCs electrode. NiCo\textsubscript{2}O\textsubscript{4} showed an improved electrochemical performance with an extraordinary cyclic stability and high specific capacitance. Mesoporous bimetal oxide (NiCo\textsubscript{2}O\textsubscript{4}) nanosheets supported on Ni foam as a binder free electrode showed better performance than the single metal oxide for SCs electrode application.

Yu et al.\textsuperscript{71} studied the bimetal oxide (NiCo\textsubscript{2}O\textsubscript{4}/MnO\textsubscript{2} composite as core-shell heterostructured nanowires supported on conductive substrate as an electrode for SCs
applications. As fabricated core-shell heterostructured, nanowire arrays delivered a high $C_{sp}$ of 1.66 F cm$^{-2}$ at a high current density of 20 mA cm$^{-2}$ with high rate capability and high cyclic stability. The improved capacitive performance of NiCo$_2$O$_4$/MnO$_2$ composite ascribed to the unique core-shell heterostructured nanowire arrays formations and the synergistic contribution of the constituent of the nanocomposite electrode.

Vijayakumar et al.$^{72}$ synthesized and studied the electrochemical properties of Co$_3$O$_4$ electrode. CV study confirmed the pseudocapacitive nature of the synthesized cubic phase nanomaterials. High $C_{sp}$ of 346 F/g at 5mV/s and 519 F/g at 0.5mA/cm$^2$ with an excellent cyclic stability up to 1000 charge-discharge cycles. The studied electrochemical behavior suggest that Co$_3$O$_4$ might be a promising electrode materials for SCs applications.

Jiang et al.$^{73}$ studied the MnO$_2$ ternary nanocomposite for SCs applications. Ternary nanocomposite composed of 3D nanostructure of reduced graphene oxide/carbon nanotubes/MnO$_2$ (rGO/CNTs/MnO$_2$). Optimized ternary nanocomposite achieved a $C_{sp}$ of 319 F/g high rate capability and cyclic stability, 85.4% capacitance retention was recorded after 3000 cycles. The outstanding electrochemical performance was due to redox reaction at the surface of the MnO$_2$, fast electron transfer due to 3D conductive network and strong interaction of the ternary nanocomposite.

Birnessite type MnO$_2$ nanosheets were synthesized by hydrothermal approach and had been reported by Zhang et al.$^{74}$. MnO$_2$ showed a large surface area (160 m$^2$/g) and uniform pore size distribution. Due to high surface area, MnO$_2$ achieved a high $C_{sp}$ of 269 F/g at 0.3A/g current density. MnO$_2$ electrode showed a high cyclic stability with 94% capacitance retention after 2000 cycles at 1 A/g current density. MnO$_2$ nanosheets electrode reported in this study showed the remarkable electrochemical properties and considered as a promising candidate for SCs applications.

Mondal et al.$^{75}$ reported a facile and cost effective chemical method for the fabrication of porous βCo(OH)$_2$ 3D nanostructured flower electrode materials. BET study showed the mesoporous nature of nanoflower with high surface area that enabled the fast redox reaction and intercalation of the electrolyte ions though out the surface of the electrode. The unique and impressive flower like morphology due to shape selective, green and cost effective method could be used at an industrial level for future
energy storage applications. The nanoflower electrode showed a better electrochemical performance in aqueous KOH electrolyte in comparison to other morphologies.

Pu et al.\textsuperscript{76} synthesized a hexagonal NiCo\textsubscript{2}O\textsubscript{4} porous nanoplates via hydrothermal method and calcinated at 300 °C. Nanoplates of NiCo\textsubscript{2}O\textsubscript{4} had an average diameter of 100 nm with thickness of about 25 nm. NiCo\textsubscript{2}O\textsubscript{4} nanoplates were activated to 800 cycles and measured the specific capacitance. It showed a $C_{sp}$ of 294 F/g at 1 A/g current density with a capacitance retention of 89.8% after the next 2200 cycles. The electrochemical stability of NiCo\textsubscript{2}O\textsubscript{4} nanoplate’s electrode suggests its potential application in SCs.

Padmanathan et al.\textsuperscript{77} reported the hydrothermal synthesis of two different shapes CeO\textsubscript{2}. The nanohexagon CeO\textsubscript{2} and CeO\textsubscript{2}/C nanorods possessed a large exposed surface area with porous microstructures. The porous nature of the synthesized CeO\textsubscript{2} and CeO\textsubscript{2}/C electrodes achieved a high $C_{sp}$ of 381 F/g and 400 F/g at a current density of 20 A/g. The synthesized electrodes had an excellent and long-term stability as well. The electrochemical performance of the electrodes were attributed to the porous microstructures, large surface area and electrical conductivity. The enhanced $C_{sp}$ and stability of nanorods CeO\textsubscript{2}/C were due to the conductivity of the carbon layer. The studied materials due to their unique morphology and excellent electrochemical properties suggested its use for high performance SCs.

Microwave synthesis route had been employed to synthesize and studied electrochemical properties of NiO nanoflakes by Vijayakumar et al.\textsuperscript{78}. XRD analysis revealed the cubic phase while SEM images showed the nanoflakes structure of NiO. The NiO nanoflakes possessed a high $C_{sp}$ of 401 F/g due to the ion buffering reservoir structure of the electrode. Specific nanoflakes structure reduces the diffusion length of the electrolyte ion and hence reduce the charge transfer resistance. Due to smaller charge transfer resistance and high specific capacitance, NiO nanoflakes electrode were considered an efficient candidate of SCs applications.

Peng et al.\textsuperscript{79} fabricated the novel planner high performance SCs composed of 2D MnO\textsubscript{2}/graphene ultrathin nanosheets. The hybrid 2D planner SCs demonstrated the remarkable $C_{sp}$ of 267 F/g at current density of 0.2 A/g with high cyclic performance and high rate capability. The 92% capacitance retention was reported after 7000 charge-discharge cycles. Fabricated SCs showed an extra ordinary mechanical strength and
capacitance retention was greater than 90%. The extra ordinary electrochemical performance and high mechanical stability of the planner SCs suggested a promising direction for future generation energy storage device for the power backup.

Rakhi et al. synthesized mesoporous $\text{Co}_3\text{O}_4$ nanosheets grown on carbon cloth. $\text{Co}_3\text{O}_4$ demonstrated an exceptional SCs performance in two-electrode system. Electrochemical properties of $\text{Co}_3\text{O}_4$ were improved by the uniform dispersion of $\text{RuO}_2$ particles. Performance of the $\text{Co}_3\text{O}_4/\text{RuO}_2$ composite electrode had been optimized by varying the electrodeposition time and hence optimized the electrochemical performance of the electrode. High $C_\text{sp}$ with high cyclic stability and rate capability were achieved in two-electrode configuration.

Zhou et al. studied the electrochemical response of TiO$_2$ nanotube arrays (NTAs). Their study demonstrated a novel method for the fabrication of the electrode. A simple cathodic polarization treatment was done on the pristine TiO$_2$ NTAs. The resultant electrode demonstrated an improved capacitance performance of TiO$_2$. Capacitance of TiO$_2$ NTAs was 39 times higher than the simple TiO$_2$, and capacitance retention of 93.1% was recorded after 2000 cycles.

Yu et al. synthesized metal sulfide double shell hierarchal structure. To prepare the unique hollow box in box structure of metal sulfide, they used template-assisted method. X. Yu et al. evaluated the electrochemical properties of double shell NiS for SCs application and found its remarkable properties due to its complex structure. NiS double shell hollow structure exhibited the high $C_\text{sp}$ (668 F/g) with high cyclic stability and high rate capability. Metal sulfide synthesized by template assisted multi shell hollow structure, had significantly improved electrochemical performance especially cyclic stability suggested that metal sulfides should be promising candidate for different application.

Gosh et al. used two-step hydrothermal method to synthesized the Ni fam/rGO/Ni$_3$S$_2$ and Ni foam/rGO/Co$_3$S$_4$ composite. Synthesis method was explained properly for the composite formation. Electrochemical investigation had been carried out after the successful formation of the hybrid porous Ni$_3$S$_2$ nanorods and Co$_3$S$_4$ nanoplates on the Ni foam/rGO substrate. 6M KOH electrolyte was used for electrochemical studies. The synthesized composites showed a high $C_\text{sp}$ with high cyclic stability. They investigated the electrochemical performance of synthesized
material by fabricating an asymmetric SCs. Ni foam/rGO/Co$_3$S$_4$ was used as a positive while Ni foam/rGO/Ni$_3$S$_2$ as a negative electrode. Fabricated asymmetric SCs exhibited a high E of 55.16 Wh/kg with high power delivery rate of 975 W/kg. Symmetric SCs also exhibited high cyclic stability.

Ni-Co-layered double hydroxide nanosheets (LDH) supported on Ni foam had been fabricated by Chen et al.$^{84}$ through facile hydrothermal co-deposition strategy. CTAB was used a nucleation assistant agent without using any alkali or oxidants for synthesis. Due to porous nature of the synthesized nanosheets exhibited high electrochemical properties. The as synthesized electrode revealed a high $C_{sp}$ of 2682 F/g with high E and P. Due to excellent electrochemical properties compared to previously reported Ni or Co oxide based materials, the Ni-Co-LDH nanosheets supported on Ni foam could be a promising candidate for future SCs.

Hu et al.$^{85}$ reported the synthesis of CoNi$_2$S$_4$ nanosheets on Ni foam substrate through two-step facile and low cost hydrothermal strategy. Nanosheets supported on Ni foam revealed a high $C_{sp}$ of 2906 F/g with high rate capability and cyclic stability. High performance of the electrode material was attributed to its good mechanical contact with the substrate, low crystallinity, high redox reaction and high conductivity for the electrolyte ions and electrons. The as synthesized electrode was tested for asymmetric SCs application as well. CoNi$_2$S$_4$ nanosheets was used as positive while activate carbon as a negative electrode in an asymmetric SCs cell. It demonstrated high E of 33.9Wh/kg with 409 W/kg power density.

Dai et al.$^{86}$ reported a template assisted synthesis of NiS hollow prism structure for SCs applications. NiS prism like structure was used as an active electrode material and electrochemical performance was evaluated. Electrode material displayed a high $C_{sp}$ of 1725 F/g at 5 A/g current density, and it showed a high rate capability with $C_{sp}$ of 1193 F/g at 40 A/g current density. Hollow prism showed a remarkable cyclic stability and the capacitance was increased after 100,000 charge/discharge cycles. The extraordinary cyclic stability and high $C_{sp}$ of the NiS hollow prism suggested its suitability as future SCs electrode.

Tang et al.$^{87}$ developed an anode material for the asymmetric SCs. Hybrid electrode consisted of Fe$_3$O$_4$ as a core while Fe$_2$O$_3$ as a shell deposited on a titanium substrate for asymmetric SCs. To boost the electrochemical performance of asymmetric...
SCs, the synergistic effect of core ($\text{Fe}_3\text{O}_4$) and shell ($\text{Fe}_2\text{O}_3$) had been utilized. $\text{Fe}_3\text{O}_4$ served as fast electron transporter, while $\text{Fe}_2\text{O}_3$ provided the large surface area for the fast redox reaction and to store the charges. As a result, $\text{Fe}_3\text{O}_4$/Fe$_2$O$_3$ core shell nanoarrays structure deliver a high $C_{sp}$ than the constituents. The composite electrode material also exhibited high rate capability due to the combination of the conductive and porous materials. Asymmetric SCs device of $\text{Fe}_3\text{O}_4$/Fe$_2$O$_3$ was also fabricated to evaluate the electrochemical performance of the materials. Electrochemical measurements of asymmetric device comprised of $\text{Fe}_3\text{O}_4$/Fe$_2$O$_3$ and $\text{Fe}_3\text{O}_4$/MnO$_2$ confirmed the superior performance of the materials. The reported work demonstrated the use of hematite for the first time to encounter its conductivity issues.

Singh et al.$^{46}$ reported an easy and cost effective method for the synthesis of ternary composite of metal oxides. Nanotube (NTs) arrays of Co$_3$O$_4$/MnO$_2$/NiO composite exhibited an extraordinary capacitive performance for SCs applications. The synthesized NTs electrode due to its unique morphology have high surface area, which is accessible for electrolyte ion diffusion, ultimately facilitating the redox reactions. The unique ternary nanocomposite achieved a high $C_{sp}$ of 2525 F/g with long cyclic stability up to 5700 charge-discharge cycles. Ternary NTs composite demonstrated a potential application as a SCs electrode due to enhanced electrochemical properties.

Wu et al.$^{88}$ synthesized a WO$_3$ nanotubes on carbon cloth by hydrothermal approach. WO$_3$ Electrode materials displayed a high $C_{sp}$ of 2,575 mF/cm$^2$ at a current density of mA/cm$^2$. Electrode material revealed an extra ordinary cyclic stability after 6,000 cycles. Asymmetric SCs devices was fabricated to explore the potential applications of the synthesized WO$_3$ nanotubes. The fabricated device showed an excellent cyclic stability up to 10,000 cycles and high energy density. Furthermore, the synthesized material was also used as an electrode for Li-ion batteries and showed a remarkable reversible capacity. The outstanding electrochemical properties of hexagonal WO$_3$ nanotubes in energy devices was ascribed to its morphology that enables the electrolyte ion to access to inner surfaces of the electrode.

Bai et al.$^{89}$ hydrothermally synthesized three different morphology of CS@MnO2 composite with the help of KMnO$_4$ concentration and revealed their potential application in supercapacitor devices. The synthesized Carbon sphere@MnO$_2$ were electrochemically tested and columnar morphology shoed the nest
electrochemical performance and achieved a high $C_{sp}$ of 178 F/g at 1 A/g current density due to high surface area.

Ambare et al.\textsuperscript{90} successfully synthesized the Bi$_2$O$_3$ nanoplates electrode by spray-pyrolysis methods on Ni foam substrate. The electrochemical measurements showed the best capacitive behavior of synthesized material. The Bi$_2$O$_3$ nanoplates achieved a $C_{sp}$ of 322.5 F/g at 5 mV/s scan rate. The materials revealed a high cyclic stability up to 5000 cycles at 100 mV/s scan rate. The nanoplates electrode achieved an $E$ and $P$ of 702.97 Wh/kg, 334.7 kW/kg.

A brief literature review revealed that metal oxide material usually have high stability but poor conductivity, while metal sulfide have a high conductivity and show the better pseudocapacitive performance. It was concluded from the literature too that the composite materials of metal oxide/sulfide and hybrid composite showed better electrochemical performance than the individual materials. Composite materials due to the synergistic effect of the constituents show improved capacitive, $E$ and cyclic stability. Secondly, the binary and ternary composite on conductive substrate like Ni foam are more effective than nonconductive substrate. So the electrode consisting of composite materials of bimetal oxide and sulfide on Ni foam expected to exhibit high electrochemical performance for SCs applications.
The main findings of the studied materials for supercapacitor applications is summarized in Table 1.1 given below.

**Table 1.1. Summary of the main findings of studied materials.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Materials</th>
<th>Specific Capacitance F/g</th>
<th>Current density A/g</th>
<th>Scan rate mV/s</th>
<th>Reference number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>RuO₂</td>
<td>58</td>
<td>-</td>
<td>2</td>
<td>52</td>
</tr>
<tr>
<td>2.</td>
<td>CoSₓ</td>
<td>474</td>
<td>5</td>
<td>-</td>
<td>53</td>
</tr>
<tr>
<td>3.</td>
<td>RuO₂, TiO₂ and SnO₂/MWCNT</td>
<td>138, 160 and 93, respectively.</td>
<td>-</td>
<td>2</td>
<td>54</td>
</tr>
<tr>
<td>4.</td>
<td>CoS</td>
<td>508</td>
<td>-</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>5.</td>
<td>Mn₃O₄</td>
<td>193</td>
<td>-</td>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td>6.</td>
<td>MnO₂/ carbon aerogel</td>
<td>515.5</td>
<td>-</td>
<td>2</td>
<td>56</td>
</tr>
<tr>
<td>7.</td>
<td>Nickel Cobaltite aerogel</td>
<td>1400</td>
<td>-</td>
<td>25</td>
<td>57</td>
</tr>
<tr>
<td>8.</td>
<td>MnO₂/ SnO₂</td>
<td>800</td>
<td>1</td>
<td>-</td>
<td>58</td>
</tr>
<tr>
<td>9.</td>
<td>Ni(OH)₂/Graphene sheets</td>
<td>1335</td>
<td>2.8</td>
<td>-</td>
<td>59</td>
</tr>
<tr>
<td>10.</td>
<td>GO/ Conducting polymer</td>
<td>500</td>
<td>5</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>11.</td>
<td>MnO₂, Mn₃O₄/ MnOOH</td>
<td>391</td>
<td>-</td>
<td>25</td>
<td>61</td>
</tr>
<tr>
<td>12.</td>
<td>MnO₂/ carbon nanomaterial</td>
<td>357</td>
<td>1</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>13.</td>
<td>Graphene/MnO₂/ carbon nanotubes</td>
<td>380</td>
<td>0.1mA/cm²</td>
<td>-</td>
<td>63</td>
</tr>
<tr>
<td>14.</td>
<td>MnO₂/ Zn₂SnO₄/ carbon microfibers</td>
<td>621.6</td>
<td>-</td>
<td>2</td>
<td>64</td>
</tr>
<tr>
<td>15.</td>
<td>CoS</td>
<td>326.4</td>
<td>64.6</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>16.</td>
<td>MnO₂</td>
<td>200</td>
<td>-</td>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>17.</td>
<td>Graphene/Ni(OH)₂</td>
<td>1568</td>
<td>4</td>
<td>-</td>
<td>66</td>
</tr>
<tr>
<td>18.</td>
<td>Co₃O₄/NiO and ZnO/NiO</td>
<td>2.5 Fcm⁻²</td>
<td>0.02 Acm⁻³</td>
<td>-</td>
<td>67</td>
</tr>
<tr>
<td>19.</td>
<td>Hollow, yolk–shell, core–shell microspheres, and NiAl- layered</td>
<td>735, 524, 406, and 177, respectively</td>
<td>2</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>Material Description</td>
<td>Capacity (F/cm²)</td>
<td>Current Density (mA/cm²)</td>
<td>Capacity (mA/cm²)</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---------------------------------------------------------------</td>
<td>------------------</td>
<td>--------------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>3D graphene/MnO₂</td>
<td>1.42</td>
<td>-</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>21.</td>
<td>NiCo₂O₄</td>
<td>3.51</td>
<td>1.8</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>NiCo₂O₄/MnO₂</td>
<td>1.66</td>
<td>20</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>23.</td>
<td>Co₃O₄</td>
<td>346</td>
<td>-</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>24.</td>
<td>Reduced graphene oxide/Carbon nanotubes/MnO₂</td>
<td>319</td>
<td>0.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>25.</td>
<td>MnO₂</td>
<td>269</td>
<td>0.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>26.</td>
<td>3D βCo(OH)₂</td>
<td>416</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>NiCo₂O₄</td>
<td>294</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>28.</td>
<td>CeO₂ and CeO₂/C nanorods</td>
<td>381 &amp; 400</td>
<td>200</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>29.</td>
<td>NiO</td>
<td>401</td>
<td>0.5m Acm⁻²</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>30.</td>
<td>2D MnO₂/graphene ultrathin nanosheets</td>
<td>267</td>
<td>0.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>31.</td>
<td>Co₃O₄/RuO₂</td>
<td>905</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>32.</td>
<td>TiO₂ nanotube arrays</td>
<td>1232</td>
<td>50µA/cm⁻²</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>33.</td>
<td>NiS</td>
<td>668</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>34.</td>
<td>Ni fam/rGO/Ni₃S₂ and Ni foam/rGO/Co₃S₄ composite</td>
<td>987.8 and 1369, respectively</td>
<td>1.5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>35.</td>
<td>Ni-Co-layered double hydroxide nanosheets</td>
<td>2682</td>
<td>3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>36.</td>
<td>CoNi₂S₄ Nanosheets</td>
<td>2906</td>
<td>5mA/cm⁻²</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>37.</td>
<td>NiS</td>
<td>1725</td>
<td>5</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>38.</td>
<td>Fe₃O₄/Fe₂O₃ core shell</td>
<td>231.9</td>
<td>-</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>39.</td>
<td>Co₃O₄/MnO₂/NiO</td>
<td>1224.5</td>
<td>12.2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>40.</td>
<td>WO₃ nanotubes/Carbon Cloth</td>
<td>2.575 mF/cm²</td>
<td>mA/cm²</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>41.</td>
<td>CS@MnO₂</td>
<td>178</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>42.</td>
<td>Bi₂O₃</td>
<td>322.5</td>
<td>-</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
1.5 Aims and Objectives

The improper use of energy and the limited sources of energy led to the energy crises in the world since decades. There is an urgent need to utilize efficiently the available sources of energy and to replace the natural sources to renewable energy resources. Efficient ESD are the need of the modern world besides harvesting energy from renewable sources. SCs are one of the efficient modern ESD due to excellent properties. They are not only environmental friendly but cost effective energy storage device as well. Many materials have been studied for their practical use as electrode for SCs in order to make efficient SCs devices. The aim of the study is to synthesize nanostructured composite materials, which have the following properties to be utilized them as an efficient electrode for SCs devices.

- To synthesize a nanostructured material with well define morphology by facile, cost effective and ecofriendly method.
- Electrode material with hierarchal morphology that improve the surface area, mesoporosity and conductivity.
- To fabricate an electrode material that have high electrical conductivity, high $C_{sp}$ and high $E$ without sacrificing the $P$ and high cyclic stability


Chapter 2  Experimental & Characterization Techniques

2. Experimental

This chapter contains the list of materials that are used for the synthesis of the nanostructured materials, experimental procedures and characterization techniques. The morphology, structural and electrical properties had been studied using the techniques which are given in this chapter in forthcoming sections.

2.1 List of Chemicals

Table 2.1 contains the list of chemicals used for the synthesis procedure. The chemical used for the synthesis of nanostructured materials were of analytical grade. All materials used as received and no further processing has been employed for purification of the chemicals.

Table 2.1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
<th>Percentage Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cerium(III) nitrate hexahydrate</td>
<td>Ce(NO$_3$)$_3$·6H$_2$O</td>
<td>99.9%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>2.</td>
<td>Zirconyl chloride hydrate</td>
<td>ZrOCl$_2$·8H$_2$O</td>
<td>99.9%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>3.</td>
<td>Lead(II) nitrate</td>
<td>Pb(NO$_3$)$_2$</td>
<td>99.9%</td>
<td>Merck</td>
</tr>
<tr>
<td>4.</td>
<td>Sodium Sulfide nonahydrate</td>
<td>Na$_2$S·9H$_2$O</td>
<td>≥99.9%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>5.</td>
<td>Yttrium(III) nitrate hexahydrate</td>
<td>Y(NO$_3$)$_3$·6H$_2$O</td>
<td>99.8%</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
### 2.2 Synthesis of Nanostructured Materials

Nanostructured materials have been synthesized by following simple, economical and well-known wet chemical synthesis methods.

I. Hydrothermal method
II. Co-precipitation method

#### 2.2.1 Hydrothermal Method

The shape and morphology of the nanostructured materials has been controlled by simple and economical hydrothermal method. Hydrothermal method is a wet chemical method that is employed to achieve the desired properties of materials for SCs applications\(^91,92\). This method uses high temperature and vapor pressure to crystallize the compound in nanometer dimensions. The high temperature and pressure provide the energy for the crystal nucleation and growth. The advantage of the hydrothermal method is that it does not require any extra heat treatment for phase purity.

The general description of hydrothermal method is given below.
2.2.2 Co-precipitation Method

Chemical co-precipitation is a simple and cost-effective method for the synthesis of nanomaterials\(^9\). Metal sulfide prepared by the co-precipitation method do not require any further heat treatment. Following is the simple description of the chemical co-precipitation method.

![Diagram of the co-precipitation method](image)

**Figure 2.2:** Schematic description of co-precipitation method.

The following equation 2.1 has been used to calculate the yield of the synthesized nanostructured materials.
Chapter 2  Experimental & Characterization Techniques

\[
\% \text{Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100
\]  

(1)

2.3 Synthesis of Materials

2.3.1 Synthesis of Ce\(_2\)Zr\(_2\)O\(_7\)

The Ce\(_2\)Zr\(_2\)O\(_7\) was prepared by solvothermal method. The solutions of Ce(NO\(_3\))\(_3\)·6H\(_2\)O and ZrOCl\(_2\)·8H\(_2\)O were mixed with 1:1 molar ratio in reaction vessel. The pH of the solution was adjusted to 12 by 2 M KOH solution with magnetic stirring. The solution was mixed about an hour and then transferred to 100 mL Teflon lined stainless steel autoclave. The autoclave was sealed and placed in an oven preheated at 180 °C for 14 hours. The precipitate were collected by centrifugation and washed with deionized water and at the end with ethanol to remove the possible impurities. The calculated yield of the synthesized Ce\(_2\)Zr\(_2\)O\(_7\) was 75%.

2.3.2 Synthesis of PbS

The nanostructured PbS was synthesized by simple co-precipitation method. The solution of Na\(_2\)S·5H\(_2\)O and Pb(NO\(_3\))\(_2\) were mixed in a 1:1 molar ratio with magnetic stirring at room temperature for 3 hours. The product was separated by centrifugation and washed with deionized water to remove the impurities. Precipitates were dried in a vacuum oven at 50 °C and used as such for further characterization. The yield of the PbS was 80%.

2.3.3 Synthesis of PbS/Ce\(_2\)Zr\(_2\)O\(_7\) Nanocomposite

The composite of Ce\(_2\)Zr\(_2\)O\(_7\)/PbS was prepared by one step process as follows. The already synthesized Ce\(_2\)Zr\(_2\)O\(_7\) (0.435 mmol) were mixed in a solution of Pb(NO\(_3\))\(_2\) (6.25 mmol) with 1:1.5 molar ratios, and homogenized by magnetic stirring. After that, the solution of Na\(_2\)S·5H\(_2\)O (6.25 mmol) was added dropwise as precipitating agent. The rest of the procedure was same as discussed earlier in PbS section. The yield of nanocomposite was 78%.

2.3.4 Synthesis of CeO\(_2\)

The chemical reagents and solvents used for the synthesis of nanomaterials were of analytical grade and used as such without further processing and purification. The CeO\(_2\) nanoparticles were synthesized by a simple hydrothermal method. 25ml of (0.5 M) solution of Ce(NO\(_3\))\(_3\) was placed in a reaction vessel under constant magnetic
stirring. Subsequently, the pH of the solution was maintained by 2 M solution of KOH. The pH was adjusted to 12 with continuous magnetic stirring for 1 hour. The above mixed solution was then transferred to a 100 mL Teflon lined stainless steel autoclave. The Teflon was filled up to 70 % of its total volume, heated at 180 °C in an oven for 14 hours. After completion of reaction, the reaction vessel was cooled down to room temperature. Afterwards the product was washed to remove the impurities with deionized water and ethanol. The resultant nanoparticles were dried in vacuum oven at 60 °C and stored in a desiccator for further characterization.

2.3.5 Synthesis of CeS₂

The CeS₂ nanoparticles were synthesized by a hydrothermal method. The molar ratios of Ce and S precursor was 1:2 and 25 mL of (1 M) solution of Na₂S was slowly added to 25 mL of (0.5 M) solution of Ce(NO₃)₃ under constant magnetic stirring. After mixing thoroughly for 30 minutes, the solution was transferred to 100 mL Teflon lined stainless steel autoclave. The further procedure was the same as described above in section 3.2.1.1

2.3.6 Synthesis of CeO₂/CeS₂ Nanocomposite

For synthesis of CeO₂/CeS₂ composite, previously synthesized 0.215 g of CeO₂ was dispersed into 25ml (0.25M) solution of Ce(NO₃)₃ (in a molar ratio of 1:2) by magnetic stirring for 30 minutes. Afterwards, the 25ml (0.5M) solution of Na₂S was added as a precipitating agent with continuous magnetic stirring. The resultant solution was shifted to a 100 mL Teflon lined autoclave, and placed in a preheated oven at 180 °C for 14 hours. The product was washed and dried in a vacuum oven at 60 °C.

2.3.7 Synthesis of Y₂Zr₂O₇

The required stoichiometric amounts of Y(NO₃)₃ and ZrOCl₂ were dissolved in deionized water and mixed in a reaction vessel at constant magnetic stirring. Subsequently, the pH of the mixture was adjusted to 12 by drop wise addition of 2 M KOH solution and kept stirring on for another 1 hour. The above mixture was then shifted to100 mL Teflon lined stainless steel autoclave. The Teflon cup was filled up to 50 % of its total volume and kept it at 180 °C in an oven for 14 hours. After completion of the reaction, the autoclave was cool down to room temperature naturally. Afterwards, the product was centrifuged, washed several times with deionized water and finally
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with ethanol to remove the impurities. The synthesized nanoparticle were dried in vacuum oven at 60 °C and stored in a desiccator for further characterization.

2.3.8 Synthesis of MnS

MnS nanoparticles were also synthesized by hydrothermal method. For this purpose 0.5 M solution of Na₂S was added drop wise to 0.5 M solution of Mn(NO₃)₂ with constant magnetic stirring. After 1 hour stirring, the solution was transferred to 100 mL Teflon line stainless steel autoclave. The further procedure was same as discussed earlier in section 3.3.1.2.

2.3.9 Synthesis of Y₂Zr₂O₇/MnS Nanocomposite

For synthesis of a composite, the previously synthesized Y₂Zr₂O₇ (0.59 g) was mixed in 0.25 M solution of Mn(NO₃)₂ (1:2 molar ratio) and stirred the mixture for 30 minutes. After 30 minutes of continuous stirring, the 0.25 M solution of Na₂S was added slowly to the above solution and was stirred for another 30 minutes. The resultant mixture was transferred to 100 mL Teflon lined stainless steel autoclave and heated to 180 °C in an oven for 14 hours. The product was washed with deionized water and dried in vacuum oven at 60 °C.

2.3.10 Synthesis of SrZrO₃

Perovskite SrZrO₃ nanorods were synthesized by hydrothermal method. For this purpose the stoichiometric solution of Sr(NO₃)₂ and ZrOCl₂ were mixed and slowly added 2 M KOH solution until the pH of the solution reached to 12. Vigorous magnetic stirring was continued for an hour, and then transferred solution to the stainless steel autoclave with Teflon lined have a capacity of 100 mL. Afterward, the sealed autoclave was transferred to pre-heated oven at 180 °C for 14 hours. In the next step, the cooled autoclave was opened and precipitates were collected by centrifugation. The impurities were removed by washing several times with deionized water and finally with the ethanol. The precipitates of SrZrO₃ were air-dried at 80 °C and the dried powder was used for further characterization.

2.4 Characterization Techniques

The synthesized nanostructured materials are characterized structurally, morphologically and electrochemically to evaluate their practical applications as SCs electrode materials.
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2.4 Structural Characterization

For structural analysis the nanostructured materials are characterized by

I. X-Ray Diffraction (XRD)
II. Raman Spectroscopy
III. Fourier Transform Infrared Spectroscopy (FTIR)
IV. X-Ray Photoelectron Spectroscopy (XPS)

2.4.1.1 X-ray Diffraction (XRD)

The crystal structure and the phase purity of the nanostructured materials has been analyzed by powder X-ray diffraction (XRD) technique. The D8 advance Cu K$_\alpha$ with wavelength of 0.154 nm, Bruker's X-ray powder diffractometer was used for structural analysis. The acquired patterns were compared with standard ICSSD cards and confirmed the specific crystal structure and the purity of the synthesized materials. The powder samples were characterized in the 2$\theta$ range of 10-80$^\circ$.

2.4.1.2 Raman Spectroscopy

The rotational and low vibrational frequency modes in the system can be identified by the Raman spectroscopy. The structural fingerprint provides the information about the structure of the material. Raman spectra was recorded using Raman Reinsha RM100 spectrometer. The excitation wavelength used was 532 nm Ar$^+$ laser.

2.4.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR technique has been employed to further confirm the chemical structure of the nanomaterials. IRTracer-100 Fourier Transform Infrared SHIMADZU spectrometer was used for FTIR analysis. The scan range were 4000-400 cm$^{-1}$ and the transmittance mode has been used for structural analysis. KBr pellets were employed for sample analysis.

2.4.1.4 X-Ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectrometer (XPS) study was employed to confirm the elemental composition of the synthesized compounds. The Kratos' Axis Ultra DLD delay line detector coupled with photoelectron spectrometer was used for XPS
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measurements. The acquired spectrum was calibrated using carbon spectrum as a reference.

2.4.2 Morphological Characterization

I. Scanning electron microscopy (SEM)
II. Transmission electron microscopy (TEM)
III. Brunauer-Emmett-Teller (BET)

2.4.2.1 Scanning Electron Microscopy (SEM)

The morphology study was conducted by scanning SEM. SUPRA 40 ZEISS Germany, scanning electron microscope has been used collect SEM images. The SEM images furnished information about the morphology and homogeneity of the materials.

2.4.2.2 Transmission Electron Microscopy (TEM)

Further confirmation of the morphology of the nanostructured materials has been done by TEM analysis. The TEM images were obtained by JEOL 2010F at 200 kV transmission electron microscope. High resolution transmission electron microscopy (HRTEM) images confirms the high crystallinity of the synthesized materials.

2.4.2.3 Brunauer-Emmett-Teller (BET) Measurements

The surface area and the pore size distribution of the samples are important parameters to find out the practical utility of the materials as SCs electrodes. Brunauer-Emmett-Teller (BET) study was used to find out the surface area and mesoporosity of the materials. The study was carried out by the physical adsorption and desorption of inert gases at the surface of the materials as mono or multilayer formation. Nitrogen gas is commonly used for BET study. The ASAP 2020 physiosorption analyzer was used for BET analysis.

2.4.3 Electrochemical Characterization

2.4.3.1 Electrochemistry

Electrochemistry is the study of faradaic and non-faradaic reactions, which occur at the surface of the electrode of an energy storage devices. The electrochemical phenomenon in the electrode material is followed either through ions or through electrons conduction mechanism. In electron conduction mechanism, electron move
between electrodes, and in ions conduction mechanism, electrolyte ions involved in current generation\textsuperscript{94}. In charging of the energy device, electron move from cathode to anode, while in discharging opposite phenomenon is involved. The electrode of energy devices are mostly solids, but it can be in liquid- and gas-phase too.

PGSAT12 Autolab electrochemical workstation has been used for electrochemical testing of the materials. Three-electrode system has been employed for the electrochemical measurements. System consisted of reference, counter and working electrode. Figure 2.3 shows the three and two electrode set up for electrochemical measurements. Ag/AgCl, HgCl\textsubscript{2} and calomel electrode can be used as reference electrode, while Pt wire as a counter electrode. The compound under investigation applied on a substrate is used as working electrode.

Two operating system has been used for the electrochemical experiments i.e. potentiostatic and galvanostatic system. In galvanostatic mode, the \( C_{sp} \) has been measured by applying the current across the working and counter electrode and the response in the form of potential is observed between working and reference electrode. While, in potentiostatic, the voltage is applied and the response in the form of current is observed between the respective electrodes.

There is slight difference between the configurations of three- and two-electrode system as evident from the Fig. 2.3. In two-electrode system, Reference electrode is adjusted with the counter one while in three-electrode system all electrodes are separately adjusted.

In Fig. 2.3 WE, CE and RE stands for working, counter and reference electrode respectively.

2.5 Electrochemical Techniques

The electrochemical behavior of the synthesized nanomaterials has been studied by CV, electrochemical impedance spectroscopy (EIS) and GCD measurements.
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2.5.1 Cyclic Voltammetry (CV)

The CV has been employed to find the out electrochemical behavior of the materials. The CV measurements elucidated the types of the SCs i.e. EDLC or pseudocapacitor. Shapes of the CVs depict the nature of the reaction mechanism occurring at the surface of electrode material. The CV usually demonstrate the redox potential of the electrode material and is used to find out qualitative information about the material of interest. The CV studies are carried out in potentiostatic mode. Voltage is applied across the respective electrode and current response is recorded in the form of voltammograms (CVs) at a constant scan rate within a defined potential window. The CVs show the oxidation and reduction peaks of the faradaic reactions involved at the surface of the materials. The specific capacitance of different materials has been calculated using following equation

\[ C = \int \frac{I}{vmV} \]  \hspace{1cm} (2)

Where I is the current, V is the potential window, m is the mass of the active electrode and v is the scan rate.

The CV for bare Ni foam was measured in the potential range of 0-0.75 V in 0.1 M KOH electrolyte using 3-electrode system and Fig. 2.3 displayed the CVs at

Figure 2.3: Typical three and two electrode setup.
different scan rates. The electrochemical signal for bare Ni foam was measured and the specific capacitance was calculated using equation 2 and is given in Table 2.2. The calculated specific capacitance was less than 1F/g.

![Figure 2.4: CV curves of bare Ni foam at different scan rates.](image)

**Table 2.2.** Specific capacitance of bare Ni foam at different scan rates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Scan Rate</th>
<th>Specific Capacitance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Foam</td>
<td>10</td>
<td>0.477</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.419</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.158</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.090</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.060</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.020</td>
</tr>
</tbody>
</table>

**2.5.2 Galvanostatic Charge-Discharge**

GCD are carried out to evaluate the performance of the energy storage devices. The $C_{sp}$ measurements were performed in two modes e.g. potentiostatic charge/discharge or
Chapter 2   Experimental & Characterization Techniques

galvanostatic charge/discharge mode. In potentiostatic mode, current is generated at constant potential, while in galvanostatic mode, potential varies at constant current. The GCD mode has been used to calculate the specific capacitance, energy and P of the studied materials.

2.5.3 Electrochemical Impedance Spectroscopy

EIS technique has been employed to further clarify the electrochemical nature of the materials. EIS explains the charge transfer behavior of the materials and provide information regarding the kinetics of the electrochemical reactions occurring at the surface of the electrode. EIS studies were performed within a frequency range of 0.1 Hz to 100 KHz at an external applied potential of 2 mV to find out the several resistances components existed within the electrode materials. EIS data may be presented as a Bode or a complex (Nyquist) Plot. Nyquist plot is based on the real and imaginary resistance components. The real component is taken along x-axis while imaginary component along y-axis. A semicircle is appeared at a high frequency region while, straight line at the low frequency range. A straight line in low frequency region represents the Warburg resistance, while semicircle show the charge transfer resistance. If semicircle is larger, then materials are more resistive, but if it is smaller than materials are conductive
3.1. Mesoporous Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS Nanocomposite with Excellent Stability for High-Performance Supercapacitor Electrode

In this section of the thesis, we report the synthesis of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, PbS and Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS nanocomposite and the fabrication of electrodes for SCs application. These electrode materials demonstrate high specific capacitance and excellent cycle stability. The as prepared nanocomposite electrode exhibits superior performance as compared to lead sulfide and cerium zirconate. A combination of high density and active sites allow fast distribution of ions within the nanostructures and rapid transfer of electrons. Consequently, the nanostructured SCs electrode exhibit a high $E$ of 6.7 Wh/kg with a $C_{sp}$ of 219 F/g at a current density of 1 A/g. These findings suggest that Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS electrode material has a practical applicability in SCs devices.
3.1.1 Fabrication of Electrodes

Working electrode were prepared by grinding solid powder with few drops of ethanol and 1 µL of Nafion solution to produce a homogeneous slurry, then it was loaded on Ni-foam and dried at 50 °C for 24 hours. The loading mass of active materials were ~0.1 mg for each electrode.

3.1.2 Characterization Methods

3.1.2.1 Structural and Morphological Characterization

The crystal structure of nanostructured material has been analyzed by the X-ray diffraction (XRD) and the specifications of the instrument are given in chapter 2, section 2.3.11. IRTracer-100 Fourier Transform Infrared SHIMADZU Spectrometer and Renishaw Invia Raman Microscope were used for FTIR and Raman analysis, respectively. The further details regarding aforementioned spectrometers are given in sections 2.3.1.3 and 2.3.1.2. Microstructure and the morphology of synthesized Ce₂Zr₂O₇, PbS and Ce₂Zr₂O₇/PbS nanocomposite were characterized by FESEM and HRTEM. The further details and the specifications of FESEM and HRTEM are given in sections 2.3.2.1 and 2.3.2.1, respectively. Compositional information of Ce₂Zr₂O₇, PbS and Ce₂Zr₂O₇/PbS was obtained by X-ray photoelectron spectrometer (XPS) and surface analysis was performed by surface area analyzer to calculate the surface areas. The specifications of X-ray photoelectron spectrometer and surface analyzer are described in sections 2.3.1.4 and 2.3.2.3 respectively.

3.1.2.2 Electrochemical Characterization

All electrochemical characterizations were conducted by using a three-electrode system in 0.1 M electrolyte (aqueous KOH) solution with an Ag/AgCl and Pt as reference and counter electrode, respectively. As mentioned in section 2.3.3.1, an Autolab PGSAT12 electrochemical workstation was used to carry out the electrochemical measurements. The $C_{sp}$ of the fabricated electrode has been calculated from CVs and GCD by using the following equations:\(^{49}\),

\[
C = \int \frac{1}{vm} dV
\]  

\[
C = \frac{I \Delta t}{\Delta Vm}
\]
Chapter 3

Results & Discussion

Where I is the current, V is the potential window, m is the mass of the active electrode, v is the scan rate and Δt is the discharge time. E and P are calculated from the following two equations.

\[ E = \frac{1}{2} (C_p \Delta V^2) \]  
\[ P = \frac{E}{t} \]

Where \( \Delta V \) is the discharge potential and \( t \) is the time for a sweep segment.

3.1.3 Structure and Morphology of Ce\(_2\)Zr\(_2\)O\(_7\), PbS and Ce\(_2\)Zr\(_2\)O\(_7\)/PbS

XRD patterns of as-prepared Ce\(_2\)Zr\(_2\)O\(_7\), PbS and Ce\(_2\)Zr\(_2\)O\(_7\)/PbS are shown in Fig. 3.1a, b and c, respectively. The diffraction patterns (Fig. 3.1a & b) matched well with those given in the ICSD cards # 00-008-0221 and 00-001-0880 for cerium zirconate and lead sulfide, respectively without any impurity phases.

![XRD patterns](image)

Figure 3.1: XRD patterns of (a) Ce\(_2\)Zr\(_2\)O\(_7\), (b) PbS and (c) nanocomposite of Ce\(_2\)Zr\(_2\)O\(_7\)/PbS.
The peaks at 2θ values of 28.967°, 33.601°, 48.131°, 57.129°, 59.940° and 70.420° in Fig. 3.1a are attributed to the (222), (400), (440), (622), (444), and (800) crystal planes of cubic Ce₂Zr₂O₇. It matched with the cubic structure of Ce and Zr compound that already has been reported by A. Arias et al., whereas the peaks at 2θ values of 25.956°, 30.064°, 43.254°, 50.978°, 53.547°, 62.728°, 68.999°, 70.785° and 79.079° in Fig. 3.1b are ascribed to the (111), (200), (220), (311), (222), (400), (331), (420) and (422) crystal planes of cubic PbS. In case of Ce₂Zr₂O₇/PbS, both Ce₂Zr₂O₇ and PbS were identified (Fig. 3.1c), indicating the successful formation of nanocomposite.

FTIR spectra of as-synthesized Ce₂Zr₂O₇, PbS and Ce₂Zr₂O₇/PbS are given in Fig. 3.2a, b and c, respectively. The band located at ~3400 cm⁻¹ can be attributed to the O-H stretching mode of physically adsorbed H₂O on the surface of the samples.

Figure 3.2: FTIR spectra of (a) Ce₂Zr₂O₇, (b) PbS and (c) nanocomposite of Ce₂Zr₂O₇/PbS.
The scissoring bending mode of H-O-H displays a broad absorption band at about 1400 cm\(^{-1}\). The strong band located at \(~680\) cm\(^{-1}\) can be assigned to pyrochlore band. The pyrochlore band originates from stretching and the bending vibrations of metal and oxygen bonds.

The band at 600 cm\(^{-1}\) (Fig. 3.2b) is assigned to Pb-S stretching mode. In the case of Ce\(_2\)Zr\(_2\)O\(_7\)/PbS (Fig. 3.2c), characteristic bands from both Ce\(_2\)Zr\(_2\)O\(_7\) and PbS, are observed, thus confirming the formation of the composite.

Fig. 3.3a, b and c display Raman spectra for Ce\(_2\)Zr\(_2\)O\(_7\), PbS and Ce\(_2\)Zr\(_2\)O\(_7\)/PbS, respectively. The sharp and dominant peak at 467 cm\(^{-1}\) (Fig. 3.3a) results from the symmetrical stretching vibrational mode of [Ce–O\(_8\)]. The bands at around 305 and 623 cm\(^{-1}\) are related to the B\(_{1g}\), B\(_{3g}\) modes of vibration and stretching vibration mode of Zr-O in Ce\(_2\)Zr\(_2\)O\(_7\), respectively.

**Figure 3.3:** Raman spectra of (a) Ce\(_2\)Zr\(_2\)O\(_7\), (b) PbS and (c) nanocomposite of Ce\(_2\)Zr\(_2\)O\(_7\)/PbS.
In the Raman spectrum of PbS (Fig. 3.3b), the peaks at around 80 and 137 cm\(^{-1}\) are attributed to the longitudinal and diagonal acoustic modes, whereas those at 271 and 434 cm\(^{-1}\) are linked, respectively, to the two-phonon process and probably 2 longitudinal optical phonon modes\(^{102,103}\). In the case of Ce\(_2\)Zr\(_2\)O\(_7\)/PbS (Fig. 3.3c), as expected, vibrational modes of both constituent cerium zirconate and lead sulfide are observed.

FESEM images of as-prepared Ce\(_2\)Zr\(_2\)O\(_7\), PbS and Ce\(_2\)Zr\(_2\)O\(_7\)/PbS samples reveal spherical shape of Ce\(_2\)Zr\(_2\)O\(_7\) and flower like morphology of PbS, while the Ce\(_2\)Zr\(_2\)O\(_7\)/PbS nanocomposite have both morphologies and confirms the formation of a composite material (Fig. 3.4).

**Figure 3.4:** FESEM images of (a) Ce\(_2\)Zr\(_2\)O\(_7\) (b), PbS and (c) nanocomposite of Ce\(_2\)Zr\(_2\)O\(_7\)/PbS.
HRTEM images (Fig. 3.5) further reveal the lattice fringes and verify the crystalline nature of as-prepared nanomaterials.

**Figure 3.5:** HRTEM images of (a) Ce$_2$Zr$_2$O$_7$, (b) PbS and (c) nanocomposite of Ce$_2$Zr$_2$O$_7$/PbS.

In order to assess the pore size and specific surface area of Ce$_2$Zr$_2$O$_7$, PbS and Ce$_2$Zr$_2$O$_7$/PbS nanocomposite nitrogen adsorption–desorption measurements were carried out, as displayed by Fig. 3.6a, b and c, respectively. The calculated Brunauer–Emmett–Teller (BET) surface area of Ce$_2$Zr$_2$O$_7$, PbS and Ce$_2$Zr$_2$O$_7$/PbS, is 39.53, 46.67 and 46.09 m$^2$/g respectively, whilst the pore size estimated by the
Barrett–Joyner–Halenda (BJH) method is 8.86, 8.02 and 11.15 nm, respectively. PbS has a greater surface area and smaller pore size than cerium zirconate and composite due to its flower like morphology. High porosity and surface area greatly facilitate redox reactions\textsuperscript{104}, implications of which will be discussed in forthcoming paragraphs.

![Image of nitrogen adsorption-desorption isotherms](image)

**Figure 3.6:** Nitrogen adsorption–desorption isotherms of (a) Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, (b) PbS and (c) nanocomposite of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS.

The elemental composition and oxidation state of as-synthesized nanomaterials were investigated by XPS measurement. Apart from Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, PbS and Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS, no other peak appeared in the XPS survey spectra (Fig. 3.7a, b and c), confirming the high purity of the samples. Fig. 3.8 shows Ce 3d, Zr 3d, O 1s, and Pb 4f and S 2p spectra. The binding energies at around 917.06, 907.83, 901.15, 898.61, 889.25 and
882.70 eV indicate that cerium is in +3 oxidation state, while the 920.52 and 918.067 eV binding energy are related to +4 oxidation state of zirconium (Fig. 3.8a).

**Figure 3.7:** Survey spectra of (a) Ce$_2$Zr$_2$O$_7$, (b) PbS and (c) nanocomposite of Ce$_2$Zr$_2$O$_7$/PbS.

The peaks at 142.146 and 137.32 eV in the Pb 4f spectra (Fig. 3.8b) are attributed to Pb$^{2+}$ and those at binding energies of 139.72 and 138.47 eV in the S 2p spectra (Fig. 3.8b) confirm that sulfur is in -2 oxidation state. These are in accordance with the valence states of cerium zirconate and lead sulfide reported previously.$^{105}$
3.1.4 Electrochemical Performance of Ce$_2$Zr$_2$O$_7$, PbS and Ce$_2$Zr$_2$O$_7$/PbS

To reveal the potential applications of Ce$_2$Zr$_2$O$_7$, PbS and Ce$_2$Zr$_2$O$_7$/PbS nanocomposite in SCs we conducted the electrochemical analysis. The electrochemical performance of electrode consisting of nanostructured materials is mainly dependent on the structure and morphology because it offers larger surface and mesoporous structure, which enables better diffusion of charges into the material$^{106}$. Active material loaded Ni foam was used as a working electrode. The electrochemical signal for bare Ni foam was measured and the calculated specific capacitance was less than 1 F/g.

Fig. 3.9a, b, c and d show the typical CV curves of spherical Ce$_2$Zr$_2$O$_7$, nanoflower PbS and Ce$_2$Zr$_2$O$_7$/PbS nanocomposite, supported on Ni-foams (vs Ag/AgCl) as a function of scan rates ranging from 10 to 100 mV/s. The shapes of CVs of EDLC electrode materials is a nearly rectangular, while the pseudocapacitor have CVs with a pair of redox peaks$^{107-109}$.

These measurements are carried out at different scan rates and the $C_{sp}$ are calculated using Eq. 1, which are reported in Table 3.1. The CVs displayed in Fig. 3.9a-c suggest that by increasing the scan rate the current increases, thus indicating the involvement of slow diffusion-controlled process for electrode material. It is also apparent from the CVs that an increase in scan rate slightly shifts the redox peaks and enhances the peak separation. The enhancement in peak separation by increasing the
scan rate suggests that a quasi-reversible process is involved. Fig. 3.9d displays the change in $C_{sp}$ as a function of scan rate. As the scan rate increases the specific capacitance decreases. The high values of $C_{sp}$ at low scan rate can be attributed to the involvement of slow faradaic reaction because the diffusion of ions help to access the inner and outer surface through the pores of the electrode.\(^{72}\)

**Figure 3.9:** CV curves of (a) Ce$_2$Zr$_2$O$_7$, (b) PbS, (c) nanocomposite of Ce$_2$Zr$_2$O$_7$/ PbS at various scan rates and (d) variation of specific capacitance with scan rate.

A shift in potential changes the current response owing to the solution and electrode resistance. Consequently, CVs profile changes by increasing the scan rate due to switching potential. These findings suggest that the redox mechanism is operative for the devised electrode and generate the resultant capacitance.\(^{106,110,111}\) The scan rate effect the diffusion of electrolyte ions, it can be inferred from $C_{sp}$ values (table 3.1). In the case of the nanocomposite, the synergistic effect of both oxide and the sulfide
facilitate ions diffusion and result in high capacitance. The values of capacitance are intermediate between those of Ce$_2$Zr$_2$O$_7$ and PbS.

Table 3.1. Specific capacitance of Ce$_2$Zr$_2$O$_7$, PbS and Ce$_2$Zr$_2$O$_7$/PbS at different scan rates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Scan Rate</th>
<th>Specific Capacitance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mV/s</td>
<td>F/g</td>
</tr>
<tr>
<td>Ce$_2$Zr$_2$O$_7$</td>
<td>10</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>99</td>
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<td></td>
<td>50</td>
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<td>60</td>
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<td></td>
<td>80</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>PbS</td>
<td>10</td>
<td>451</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>436</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>410</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>385</td>
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<tr>
<td></td>
<td>50</td>
<td>364</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>345</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>304</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>270</td>
</tr>
<tr>
<td>Ce$_2$Zr$_2$O$_7$/PbS</td>
<td>10</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>245</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>221</td>
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<td></td>
<td>50</td>
<td>199</td>
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<tr>
<td></td>
<td>60</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>116</td>
</tr>
</tbody>
</table>
Galvanostatic charge-discharge profiles (GCD) are shown in Fig. 3.10a, b and c, which further investigate electrochemical behaviors of Ce$_2$Zr$_2$O$_7$, PbS and nanocomposite of Ce$_2$Zr$_2$O$_7$/PbS at current densities of 1, 1.5, 2 and 2.5 A/g, respectively. At higher current density, PbS becomes more polarizable as compared to Ce$_2$Zr$_2$O$_7$ due to its higher conductivity. However, the composite shows higher $C_{sp}$ than Ce$_2$Zr$_2$O$_7$ calculated from charge/discharge profile and the results are in good agreement with that obtained from CV curves which confirms pseudocapacitive behavior (Fig. 3.10c).

**Figure 3.10:** Galvanostatic charge-discharge profile of (a) Ce$_2$Zr$_2$O$_7$, (b) PbS, (c) nanocomposite of Ce$_2$Zr$_2$O$_7$/ PbS at different current density and (d) variation of specific capacitance as a function of current density.

It has been further revealed by Fig. 3.10d that as the current density increase the $C_{sp}$ decreases. This can be attributed to the diffusion effect of ions. The higher current
density inhibits diffusion and transportation of electrolyte ions into the electrode material and decrease the specific capacitance$^{49,109,112,113}$.

$C_{sp}$ of $\text{Ce}_2\text{Zr}_2\text{O}_7$, PbS and nanocomposite was also measured from GCD using Eq. 2 and E and P were calculated by using Eq. 3 & 4 and their values are reported in Table 3.2. It demonstrates that both the parameters i.e. E and P values are in accordance with the specific capacitance.

**Table 3.2.** Energy and power density of $\text{Ce}_2\text{Zr}_2\text{O}_7$, PbS and $\text{Ce}_2\text{Zr}_2\text{O}_7$/PbS at different current density.

<table>
<thead>
<tr>
<th>Material</th>
<th>Current density A/g</th>
<th>Specific Capacitance F/g</th>
<th>Energy density Wh/Kg</th>
<th>Power density W/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}_2\text{Zr}_2\text{O}_7$</td>
<td>1</td>
<td>193</td>
<td>9.67</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>140</td>
<td>7</td>
<td>458</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>120</td>
<td>6</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>100</td>
<td>5</td>
<td>750</td>
</tr>
<tr>
<td>PbS</td>
<td>1</td>
<td>204</td>
<td>6.23</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>217</td>
<td>6.66</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>136</td>
<td>4.17</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>122</td>
<td>3.74</td>
<td>587</td>
</tr>
<tr>
<td>$\text{Ce}_2\text{Zr}_2\text{O}_7$/PbS</td>
<td>1</td>
<td>219</td>
<td>6.72</td>
<td>235</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>102</td>
<td>3.13</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>76</td>
<td>2.35</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>58.5</td>
<td>1.80</td>
<td>589</td>
</tr>
</tbody>
</table>

These results suggest that $\text{Ce}_2\text{Zr}_2\text{O}_7$ shows less polarization even at higher current densities as compared to PbS, while the nanocomposite of $\text{Ce}_2\text{Zr}_2\text{O}_7$ and PbS exhibits better electrochemical performance as compared to its constituents.

The electrochemical stability of mesoporous $\text{Ce}_2\text{Zr}_2\text{O}_7$/PbS nanocomposite was examined by subjecting the electrodes to 1000 CV cycles (CVs). The cycling process was evaluated at a scan rate of 100 mV/s. Fig. 3.11a displays the behavior of $C_{sp}$ as a
function of cycle number. Three stages are involved in the cyclic behavior of \( \text{Ce}_2\text{Zr}_2\text{O}_7/\text{PbS} \) nanocomposite electrode, i.e., (i) electrode got activated first, (ii) then it a constant capacitance was observed and (iii) after 455 CV cycles, a decrease in capacitance is noticed. In the start when electrode material is activated, the \( C_{sp} \) of the electrode material is increased from 116.13 F/g to ~154 F/g up to 55 CVs cycles and then remains almost constant. The capacitance increases with CVs as more and more electrode material become activated due to the intercalation of electrolyte ions. A slight decrease in \( C_{sp} \) is noticed throughout 1000 cycles but capacitance retention was almost 100% (116.13 F/g). The studied electrode can tolerate up to 1000 successive CV cycles. So it can be concluded that redox reaction on the surface of electrode do not affect the structures of electrode. After 1000 CV cycles mesoporous electrodes are still suitable for further pseudocapacitance performance. The high stability suggests that the mesoporous nanostructured composite is a good candidate for SCs electrode.

Fig. 3.11b shows the Ragone plots of the synthesized electrodes, revealing that the P increases with energy density. Ragone plot indicate the suitability of the studied electrode for SCs application due to high rate capability of the electrodes materials.

The electrical behavior the fabricated electrodes was investigated by using the EIS. The EIS scans were performed in the frequency range of 0.1 Hz - 100 KHz. The Nyquist plots are shown in Fig. 3.11c, and the corresponding equivalent circuit diagram of the system is shown in Fig. 3.11d, which reveals that the nanocomposite shows charge transfer resistance (\( R_{ct} \)) of 40 \( \Omega \), which is less than \( R_{ct} \) of \( \text{Ce}_2\text{Zr}_2\text{O}_7 \) (43.63 \( \Omega \)) and PbS (47.60 \( \Omega \)). These results suggest that PbS and \( \text{Ce}_2\text{Zr}_2\text{O}_7 \) provide active cites to each other and made the composite more conductive as compare to individual counter parts, which matched well with the CV and GCD results. However, a straight line in the low frequency region corresponds to Warburg impedance, which reveals that PbS has smaller Warburg impedance than \( \text{Ce}_2\text{Zr}_2\text{O}_7 \). However, the nanocomposite has an improved Warburg impedance than PbS and \( \text{Ce}_2\text{Zr}_2\text{O}_7 \). These findings indicate that the composite shows greater charge conductivity due to low \( R_{ct} \) and it exhibits a good capacitive performance.
Figure 3.11: Cyclic stability of (a) Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS at 1000 cycles, (b) Ragone plots of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, PbS and Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS, (c) Nyquist plots of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, PbS and Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS and (d) Equivalent circuit diagram of the system.

3.1.5 Summary of Main Findings of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, PbS and Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS as Electrode Materials

The nanocomposite of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS displayed higher specific surface area, porosity, electronic conductivity, electrochemical activity as well as high cyclic stability as compared to its constituent counterparts i.e. Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and PbS. The Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS electrode material had a high C\textsubscript{sp} of 116 F/g after 1000 CVs. The C\textsubscript{sp} was almost constant up to 1000 CVs indicating an excellent stability of the electrode. These results suggest that the practical usability of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS nanocomposite as an electrode material in SCs devices.
3.2 Highly Stable Mesoporous CeO$_2$/CeS$_2$ Nanocomposite as Electrode Material with Improved Supercapacitor Electrochemical Performance

The present study reports the synthesis and the fabrication of a novel CeO$_2$/CeS$_2$ nanocomposite electrode for pseudo-type SCs. The synthesized nanocomposite material not only exhibits high pseudocapacitive performance than the constituent oxide (CeO$_2$), but also revealed fast charge transportation arising from the sulfide (CeS$_2$). As a result, SCs electrode composed of CeO$_2$/CeS$_2$ composite demonstrates high E than CeO$_2$ and higher cyclic stability than CeS$_2$. The voltametric study, charge-discharge investigation and EIS studies suggest the CeO$_2$/CeS$_2$ nanocomposite is an excellent energy storage material.
3.2.1 Characterization Methods

3.2.1.1 Structural and Morphological Characterization

The crystal structure of the synthesized nanomaterials have been investigated by X-ray diffraction (XRD) (Bruker’s X-ray powder diffractometer, D8 Advance, Cu Kα, λ = 0.154 nm). The chemical structure of the nanomaterials is investigated by FTIR studies by using IR Tracer-100 Fourier Transform Infrared SHIMADZU Spectrometer. X-ray Photoelectron Spectroscopy (XPS) studies has been conducted for the confirmation of the oxidation state of the elements present in the nanomaterials. The Kratos’ Axis Ultra delay line detector photoelectron spectrometer was used for XPS studies and carbon spectrum is used as a reference to calibrate the spectra. The morphology of the nanomaterials has been characterized by using scanning electron microscope (SEM) (SUPRA 40 ZEISS, Germany) and a transmission electron microscope (TEM), JEOL 2010F at 200 kV. Nitrogen adsorption–desorption technique (ASAP 2020 Physisorption Analyzer) has been used for BET measurements.

3.2.1.2 Electrochemical Characterization

The three-electrode system has been used for CV, GCD and EIS measurements. An active material loaded on Ni-foam was used as a working, while a platinum wire as a counter and Ag/AgCl was used as a reference electrode. 0.1 M KOH solution was used as an electrolyte. The loading capacity of each working electrode was 0.1 mg. Electrochemical signal for bare Ni foam was recorded and the measured specific capacitance was less than 1F/g.

CV, GCD and EIS measurements were employed using a PGSAT12 autolab electrochemical workstation. All measurements were performed at room temperature. Cyclic voltammograms (CVs) were recorded at scan rates ranging from 10 - 100 mV/s. GCD profiles were scanned at various current densities ranging from 1 - 4 A/g. EIS was conducted within frequency range from 100 kHz to 10 mHz. \( C_{sp} \) of the fabricated electrodes was calculated from CV and GCD curves by using the following equations:\(^{49}\)

\[
C = \int \frac{IdV}{smV} \quad (1)
\]

\[
C = \frac{I\Delta t}{\DeltaVm} \quad (2)
\]
Where, \( \int (Idv) \) is the integrated area. \( V, I, \Delta t, \Delta V, s, \) and \( m \) are the potential window, current, discharge time, potential change during discharge process, scan rate in V/s and mass (g) of active material, respectively. Following equations are employed to calculate the \( E \) (Wh/kg) and \( P \) (W/kg) of the electrode materials:

\[
E = \frac{1}{2} (C_{sp} \Delta V^2) 
\]

(3)

\[
P = \frac{E}{t} 
\]

(4)

Where, \( \Delta V \) and \( t \) are the potential window of discharge process and discharge time, respectively.

### 3.2.2 Structure and Morphology of CeO\(_2\), CeS\(_2\) and CeO\(_2\)/CeS\(_2\)

Fig. 3.12a shows the XRD pattern of CeO\(_2\) nanoparticles synthesized via hydrothermal route. The pattern is well matched with the cubical bulk CeO\(_2\).\(^{98}\) The labelled ‘hkl’ values match with those given in the standard ICSD card no. 00-001-0800 and correspond to cubic fluorite structure of CeO\(_2\). Absence of any additional peak confirms the synthesis of phase pure nanoparticles of CeO\(_2\). Fig. 3.12b displays the XRD pattern of the synthesized CeS\(_2\) nanoparticles. The ‘hkl’ values match well with those given in the standard ICSD card no 01-075-1109 suggesting orthorhombic phase of the CeS\(_2\). The XRD pattern of CeO\(_2\)/CeS\(_2\) nanocomposite sample are displayed in Fig. 3.12c, which shows the characteristic peaks of both the cerium oxide and sulfide, indicating the successful formation of nanocomposite material. The diffraction peaks correspond either to CeO\(_2\) or CeS\(_2\) composition with no additional peak and thus evidently supports the CeO\(_2\)/CeS\(_2\) composite formation.

FT-IR spectra of CeO\(_2\), CeS\(_2\) and nanocomposite of CeO\(_2\)/CeS\(_2\) are shown in Fig. 3.13 a, b and c, respectively. The broad absorption feature at \( \sim 3448 \) cm\(^{-1}\) can be attributed to the O-H stretching mode of the adsorbed water and hydroxyl groups. The absorption band close to 1600 cm\(^{-1}\) is due to the scissoring mode of associated water that is absorbed on the surface of the material. The band at 500 cm\(^{-1}\) in Fig. 3.13a corresponds to the Ce-O stretching vibration\(^{114}\).

The weak band at around 850 cm\(^{-1}\) in Fig. 3.13b is ascribed to metal - sulfur bonding. Fig. 3.13c is the FTIR spectrum of CeO\(_2\)/CeS\(_2\) nanocomposite that encompasses the features of both the constituent materials.
The XPS measurements are conducted to analyze the elemental composition and chemical state of the CeO2, CeS2, and CeO2/CeS2 nanomaterials and the corresponding results are presented in Fig. 3.14. The survey spectra (Fig. 3.14a) indicate the presence of Ce, S, and O, as well as C as a reference\textsuperscript{115}. All the labelled peaks in Fig. 3.14a correspond to the elements present in the synthesized materials. Fig. 3.14b, c and d show XPS spectra of Ce 3d, S 2s and O 1s, respectively.

The peaks at binding energies around 916, 907, 900 and 898, 882 eV can be ascribed to 4+ oxidation state of Ce. In the S 2s spectrum (Fig. 3.14c), the peaks at around 231, 238, 220 and 213 eV represent the S$^{2-}$ ions in the synthesized CeS2 nanomaterials. Fig. 3.14d represents the oxygen spectrum of O 1s. The presence of O$^{2-}$ species in CeO2 is confirmed by spin-orbit splitted peaks of O 1s at the binding energies of 529.7 eV and 531.2 eV.
Figure 3.13: FTIR spectra of (a) CeO$_2$, (b) CeS$_2$ and (c) nanocomposite of CeO$_2$/CeS$_2$.

SEM images of CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ are presented in Fig. 3.15a, b and c, respectively. CeO$_2$ particles (Fig. 3.15a) are cubical, while CeS$_2$ particles are spherical in shape (Fig. 3.15b). In the case of CeO$_2$/CeS$_2$ composite, both cubical and spherical particles can be seen (Fig. 3.15c), confirming the presence of both CeO$_2$ and CeS$_2$ in the nanocomposite material.

To further reveal morphologies of synthesized nanomaterials TEM analysis is carried out. Fig. 3.16a, b and c present high magnification TEM images of CeO$_2$, CeS$_2$, and CeO$_2$/CeS$_2$ nanocomposite, respectively. Cubical CeO$_2$ nanoparticles (with sizes $\sim 20 - 50$ nm) and spherical CeS$_2$ nanoparticles (with sizes about 5 – 20 nm) are more clearly visible (Fig. 3.16a and b). In CeO$_2$/CeS$_2$ composite cubical nanoparticles coexist with spherical nanoparticles (Fig. 3.16c).
Figure 3.14: XPS Survey spectra of (a) CeO$_2$, CeS$_2$ and nanocomposite of CeO$_2$/CeS$_2$, XPS spectra of (b) Ce 3d, (c) S 2s and (d) O 1s.

High-resolution transmission electron microscope (HRTEM) images of CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ nanomaterials are displayed in Fig. 3.17a, b and c, respectively. These images clearly exhibit the resolved lattice fringes, which indicate the high crystallinity of the synthesized nanomaterials.
Figure 3.15: SEM images of (a) CeO$_2$, (b) CeS$_2$ and (c) nanocomposite of CeO$_2$/CeS$_2$. 
Figure 3.16: TEM images of (a) CeO$_2$, (b) CeS$_2$ and (c) nanocomposite of CeO$_2$/CeS$_2$. 
Figure 3.17: HRTEM images of (a) CeO$_2$, (b) CeS$_2$ and (c) nanocomposite of CeO$_2$/CeS$_2$.

BET surface areas of the CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ samples were determined by N$_2$ adsorption-desorption isotherms, and Barrett–Joyner–Halenda (BJH) method has been employed to calculate the pore size distributions, as shown in Fig. 3.18a, b and c. All the samples have same isotherm with distinct hysteresis loop and can be categorized as type-IV isotherm$^{116}$. The mesoporous nature of the materials has been confirmed by the Type-IV isotherm. The calculated BET surface areas are 56.7, 75.8, and 65.5 m$^2$/g for CeO$_2$, CeS$_2$, and CeO$_2$/CeS$_2$, respectively, indicating that the specific surface area of the CeS$_2$ nanoparticles is higher than that of the CeO$_2$ cubical nanoparticles while the nanocomposite of CeO$_2$/CeS$_2$ has surface area in between of the two.

The corresponding BJH pore size distributions are 7.62 nm, 8.54 nm and 17.39 nm for the CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ nanocomposite respectively, indicating that the
pore sizes of the synthesized nanomaterials are mainly in the mesoporous range (2–50 nm). The increased pore size in the composite material could be ascribed to the formation of heterostructures due to constituent elements in the resultant material. The mesoporous structure is beneficial in a sense that small pore size and large surface area enhance the electrolyte ion diffusion and could increase the energy storage at high current density.

![Image](image)

**Figure 3.18:** N\textsubscript{2} adsorption-desorption isotherm of (a) CeO\textsubscript{2}, (b) CeS\textsubscript{2} and (c) nanocomposite of CeO\textsubscript{2}/CeS\textsubscript{2}.

### 3.2.3 Electrochemical Performance of CeO\textsubscript{2}, CeS\textsubscript{2} and CeO\textsubscript{2}/CeS\textsubscript{2}

The electrochemical performance of an electrode largely depends upon the structure and morphology of the materials. The electrodes consisting of CeO\textsubscript{2}, CeS\textsubscript{2}, and CeO\textsubscript{2}/CeS\textsubscript{2} nanocomposite were fabricated by employing three electrode set up to carry out CV studies. Fig. 3.19 a, b and c display CV curves of the CeO\textsubscript{2}, CeS\textsubscript{2}, and CeO\textsubscript{2}/CeS\textsubscript{2} nanomaterials, respectively. In the case of CeO\textsubscript{2} an anodic peak
centered at 0.48 V and a cathodic peak at 0.35 V were observed in the potential range of 0 to 0.70 V. In case of CeS$_2$ the cathodic and anodic peaks appeared at the 0.52 V and 0.33 V, respectively. While in the composite the peak potential shifts towards lower values. This indicates a fast and more reversible charge transfer process for the composite electrode in comparison to the constituent materials.

![Figure 3.19](image)

**Figure 3.19:** CV curves of (a) CeO$_2$, (b) CeS$_2$ (c) nanocomposite of CeO$_2$/CeS$_2$ at different scan rates and (d) variation of specific capacitance as function of scan rate.

The CVs of CeO$_2$, CeS$_2$, and CeO$_2$/CeS$_2$ reflect that the redox mechanism is involved in energy storage reaction where Ce is reduced from +4 to +3 oxidation state. For each case, one electron is involved in the redox process and the measured capacitance results from this redox reaction. The shape of the CVs is different from the electrochemical response of EDLCs. It is well established that EDLCs have rectangular shaped CVs with no charge transfer process involved, while in case of pseudocapacitors
the CVs have specific anodic and cathodic signatures. The redox behavior of our synthesized electrode materials evidently indicates pseudocapacitive mechanism. Further the non-symmetric behavior of the CVs is suggesting kinetically a quasi-reversible redox process.

The CV measurements were conducted at different scan rates for CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ and their specific capacitance values were calculated using eq.1. The CeO$_2$ has $C_{sp}$ values of 237, 191, 143, 115, 97, 85.6 F/g, the $C_{sp}$ values of CeS$_2$ are 1030, 808, 713, 615, 539 476 F/g and of CeO$_2$/CeS$_2$ composite the values are 402, 316, 246, 221, 203, 193 F/g at scan rates of 10, 20, 40, 60, 80 and 100 mV/s, respectively. Fig. 3.19d represents the $C_{sp}$ of CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ as a function of scan rate. It has been observed that by increasing scan rate the current increases, while specific capacitances decreases. Further, it indicates that the $C_{sp}$ values of CeS$_2$ are higher than those of CeO$_2$ and CeO$_2$/CeS$_2$ nanocomposite. It has been proposed that high BET surface area and crystallinity help in improving the $C_{sp}$ of a material\textsuperscript{120}. In this work, amongst the fabricated electrodes, the BET surface area of spherical CeS$_2$ is greater than cubical CeO$_2$ and CeO$_2$/CeS$_2$ nanomaterials. Greater surface area, low crystallinity and mesoporosity allows better intercalation of charges and results in higher values of $C_{sp}$ for CeS$_2$ and nanocomposite than CeO$_2$ nanoparticles. The change in $C_{sp}$ for different microstructure of the materials can also be explained on the basis of diffusion of electrolyte ions and the resistance offered due to kinetic energy of the ions. The ions with low kinetic energy and low resistance at low scan rate have maximum time to diffuse into the electrode surface, and hence results into high specific capacitance. On the other hand, at high scan rate the resistance of ions increases due to high kinetic energy. They have minimum time to interact with the electrode surface, thus resulting in low values of specific capacitance. Thus, it can be concluded the porous nature of the electrode material facilitates the diffusion of ions and improves the charge capacitance ability.

To further evaluate the specific capacitance and to assess the feasibility of nanomaterials as a SCs electrode, GCD measurements are conducted. Fig. 3.20a, b and c show the GCD profiles of the as-synthesized CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ nanocomposite respectively, performed at a current density of 1, 2, 3 and 4 A/g. Values of $C_{sp}$ at different current densities for CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ nanocomposite are given in Table 3.3. The pseudocapacitive property of the nanomaterials is confirmed by
the curved nature of the GCD profiles, which is in accordance with the already discussed results of CV. The potential versus time profiles clearly demonstrate the capacitive nature of the analyzed materials, where the potential of the materials drops while giving a plateau after certain time. Fig. 3.20d displays a decrease in the $C_{sp}$ by increasing the current density for all the three nanomaterials. This decrease in $C_{sp}$ can be attributed to higher electrolyte ions resistance that increases at higher current density.

**Figure 3.20:** Galvanostatic charge-discharge curves of (a) CeO$_2$, (b) CeS$_2$ (c) nanocomposite of CeO$_2$/CeS$_2$ at different current density and (d) variation of specific capacitance as function of current density.

Apart from high specific capacitance, the stability of the electrode material is equally important to be assessed for its practical utility. In order to check the stability the synthesized nanomaterials were subjected to 1000 CV cycles and their $C_{sp}$ was monitored (Fig. 3.21). The $C_{sp}$ of CeO$_2$ remains almost unchanged up to 300 cycles. Then it exhibits a slow rise up to 625 cycles and afterwards it remains almost
unchanged. The $C_{sp}$ of CeS$_2$ show a slight rise for 100 cycles indicating activation of material and afterwards it does not show any appreciable change up to 1000 cycles.

**Table 3.3.** Specific capacitance of CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ at different current density.

<table>
<thead>
<tr>
<th>Name of Materials</th>
<th>Current Density (A/g)</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>1</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>72</td>
</tr>
<tr>
<td>CeS$_2$</td>
<td>1</td>
<td>924</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>776</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>684</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>584</td>
</tr>
<tr>
<td>CeO$_2$/CeS$_2$</td>
<td>1</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>253</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>195</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>186</td>
</tr>
</tbody>
</table>

On the contrary, the CeO$_2$/CeS$_2$ nanocomposite exhibits almost a linear increase in the $C_{sp}$ as the number of cycles increases. The outstanding SCs performance of CeO$_2$/CeS$_2$ nanocomposite can also be manifested by their remarkable cycling stability. The stability measurements specify that additional cycles are needed to fully activate the CeO$_2$/CeS$_2$ electrode nanomaterials.
Figure 3.21: Cyclic stability behavior of CeO$_2$, CeS$_2$ and nanocomposite of CeO$_2$/CeS$_2$ 1000 CV cycles.

The Ragone plots that indicate the E vs P of the SCs electrode materials are shown in Fig. 3.22 and the corresponding data is presented in Table 3.4. The maximum E calculated for CeO$_2$ is 5.1 Wh/kg and have a power delivery rate of 250 W/kg. By increasing the current density, the E decreases from 5.1 to 2.5 Wh/kg, while P increases from 250 to 1000 W/kg. The CeS$_2$ electrode achieves a very high P of 9000 W/kg at an E of 20.28Wh/kg. The nanocomposite electrode material have an E and P in-between of the constituents materials. It achieves an E of 21.2 Wh/kg with a P of 303 W/kg and the maximum P is achieved 1200 W/kg for corresponding E of 9 Wh/kg. Thus, our CeO$_2$/CeS$_2$ nanocomposite electrode exhibits reasonable energy densities and power densities between current densities ranging from 1-4 A/g.
Figure 3.22: Ragone plot of CeO₂, CeS₂ and CeO₂/CeS₂ nanocomposite.

To further evaluate the electrochemical behavior of CeO₂, CeS₂ and CeO₂/CeS₂ nanocomposite electrodes, the EIS study has been performed at an applied potential of 2 mV. Fig. 3.23a, b and c displays the Nyquist plots of the synthesized electrode nanomaterials, while the Fig. 3.23d shows the corresponding equivalent circuit of the electrochemical system.

Table 3.4. Energy and power density of CeO₂, CeS₂ and CeO₂/CeS₂ nanocomposite at different current density.

<table>
<thead>
<tr>
<th>Name of Materials</th>
<th>Current Density (A/g)</th>
<th>Energy Density (Wh/kg)</th>
<th>Power Density (W/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>1</td>
<td>5.1</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.9</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.1</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2.5</td>
<td>1000</td>
</tr>
<tr>
<td>CeS₂</td>
<td>1</td>
<td>32.0</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>26.9</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>23.8</td>
<td>3750</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.3</td>
<td>9000</td>
</tr>
<tr>
<td>CeO₂/CeS₂</td>
<td>1</td>
<td>21.2</td>
<td>303</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>12.7</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.8</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>9.3</td>
<td>1200</td>
</tr>
</tbody>
</table>
Chapter 3 Results & Discussion

The component of high frequency region of the Nyquist plot is compressed and the typical semicircle is not obvious. However, it can be seen that all the electrodes exhibit SCs behavior, as the imaginary part increases vertically and this increase is more obvious in the case of the CeO$_2$/CeS$_2$ nanocomposite electrode, thus indicating better capacitive nature of the electrode as compared to CeO$_2$ and CeS$_2$ electrodes. Table 3.5 displays the values of capacitance, solution resistance, charge transfer resistance and Warburg impedance calculated from EIS measurements. The tabulated values suggest the composite material offers higher $R_{ct}$ than its constituents that is a signature of good capacitive material. Moreover, the substantial change in $R_s$ values is also unusual. Nevertheless, the variation in the resistance components ($R_s$, $R_{ct}$ and W) by changing the material is an indication of the change of chemical interaction that confirms the pseudocapacitive nature of the material. Relatively, high $R_{ct}$ value of the CeO$_2$/CeS$_2$ nanocomposite material than CeO$_2$ and CeS$_2$ are complementary to the CV and GCD studies.

Table 3.5. Capacitance, solution resistance, charge transfer resistance and Warburg impedance.

<table>
<thead>
<tr>
<th>Name of Material</th>
<th>Capacitance (mF)</th>
<th>Solution Resistance (Rs) Ω</th>
<th>Charge Transfer Resistance (Rct) Ω</th>
<th>Warburg Impedance (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>0.395</td>
<td>9.96</td>
<td>61.4</td>
<td>0.329x10$^{-2}$</td>
</tr>
<tr>
<td>CeS$_2$</td>
<td>13.9</td>
<td>18.9</td>
<td>57</td>
<td>0.206x10$^{-1}$</td>
</tr>
<tr>
<td>CeO$_2$/CeS$_2$</td>
<td>0.518</td>
<td>23</td>
<td>170</td>
<td>0.24x10$^{-2}$</td>
</tr>
</tbody>
</table>
3.2.4 Summary of Main Findings of CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ as Electrode Materials

This body of work reported the electrochemical analysis of three types of (CeO$_2$, CeS$_2$ and CeO$_2$/CeS$_2$ nanocomposite) nanomaterials supported on Ni-foam electrodes for SCs application. High specific capacitances (1030, 402, and 237 F/g), excellent cycling stability and high P (9000, 1200 and 1000 W/kg) were achieved with CeS$_2$, CeO$_2$/CeS$_2$ nanocomposite and CeO$_2$ electrodes, respectively. The $C_{sp}$ of the nanocomposite electrode increased with successive number of cycles and was highest (700 F/g) at 1000 cycle and this behavior was ascribed to two phenomena. Firstly, high electrical conductivity of CeS$_2$ is responsible for providing a well-defined track for transportation of outer electrons between the ions of the electrolyte and the surface of the electrode material. Secondly, in addition to providing the stability to the
nanocomposite electrode, the activation of CeO$_2$ after penetration of electrolyte with successive cycles further facilitated the charge transport in the bulk. An appreciable increase of $C_{sp}$ as compared to CeO$_2$ and remarkable stability of the CeO$_2$/CeS$_2$ mesoporous nanocomposite suggested a significant promise for its practical utility as a SCs electrode.
3.3. Y$_2$Zr$_2$O$_7$/MnS Nanocomposite: A Binder Free High Performance Supercapacitor Electrode

In this section of the thesis, we report the synthesis of bimetal oxide yttrium zirconate (Y$_2$Zr$_2$O$_7$) nanorods, manganese sulfide (MnS) nanoparticles and the composite of both nanostructured materials by simple hydrothermal method. To the best of our information, first time, we fabricate an electrode consisting of aforementioned nanocomposite and investigate it for SCs application. The electrochemical studies are conducted to check its suitability for electrode materials in SCs energy storage devices. Y$_2$Zr$_2$O$_7$/MnS electrode material, exhibits high E of 10 Wh/kg, with excellent cyclic stability demonstrating the potential application of such nanocomposite material in energy devices. The stability of the metal oxide enables it can tolerate the volume changes during charging and discharging process, thus proving good cyclic stability to the nanocomposite electrode up to 1000 CVs cycles.
3.3.1 Fabrication of Electrodes

The working electrode were fabricated by mixing 0.1mg powders of synthesized nanomaterials in 1-2 mL of absolute ethanol. The resultant slurry was then applied on Ni-foam and dried at 50 °C for 24 hours.

3.3.2 Characterization Methods

3.3.2.1 Structural and Morphological Characterization

The information regarding the structure of each powder sample was obtained by X-rays diffractometer. Chemical and constituent materials information was obtained by FTIR and XPS analysis. Transmission electron microscopy was used to examine the morphology of all samples. Nitrogen adsorption–desorption technique was used for the analysis of specific surface area, pore size distribution and pore volume. BET isotherm has been calculated by using ASAP 2020 Physisorption Analyzer. The specification details of aforementioned instruments are given in chapter 2, section. 2.3.

3.3.2.2 Electrochemical Characterization

The electrochemical properties of the Y$_2$Zr$_2$O$_7$ nanorods, MnS and Y$_2$Zr$_2$O$_7$/MnS electrodes were investigated using Ni-foam as a substrate in three-electrode cell configuration at room temperature in 0.1 M solution of KOH as electrolyte. Platinum wire is used as a counter, while Ag/AgCl is used as a reference electrode. The CV, GCD and EIS measurements were conducted on a PGSAT12 autolab electrochemical workstation.

The $C_{sp}$ was calculated from CV and GCD profile using following equations.

$$C = \int \frac{I dV}{vmV}$$

$$C = \frac{I\Delta t}{\Delta Vm}$$

Where $I$, $V$, $m$, and $v$ are the current density, potential window, mass of active materials and the scan rate, respectively. While $\Delta t$ is the discharge time. The $e$ and $P$ are obtained from the following equations,

$$E = \frac{1}{2}(C_{sp}\Delta V^2)$$

$$P = \frac{E}{t}$$
Where $\Delta V$ is the discharge potential and $t$ is the time for a sweep segment.

### 3.3.3 Structure and Morphology of $Y_2Zr_2O_7$, MnS and $Y_2Zr_2O_7$/MnS

X-ray diffraction patterns (XRD) of $Y_2Zr_2O_7$, MnS and $Y_2Zr_2O_7$/MnS are displayed in Fig. 3.24a, b and c, respectively. XRD pattern of $Y_2Zr_2O_7$ nanorods matches well with the standard pattern ICSD-00-029-1389 and crystallized into rhombohedral structure (Fig. 3.24a), while MnS crystallized into hexagonal structure and matches perfectly with the standard reference ICSD-00-002-1268, Fig. 3.24b. The XRD pattern of $Y_2Zr_2O_7$/MnS (Fig. 3.24c) confirms the formation of nanocomposite, as the XRD pattern has clear features of both constituent materials.

![Figure 3.24](image)

**Figure 3.24**: XRD patterns of (a) $Y_2Zr_2O_7$, (b) MnS and (c) nanocomposite of $Y_2Zr_2O_7$/MnS.

The FTIR spectra of $Y_2Zr_2O_7$, MnS and $Y_2Zr_2O_7$/MnS are presented in Fig. 3.25a, b and c, respectively. The bands are located at around 3600, 2350, 1400, 730 cm$^{-1}$.
and 1100 cm\(^{-1}\), 600 cm\(^{-1}\), 500 cm\(^{-1}\) for Y\(_2\)Zr\(_2\)O\(_7\) and MnS, respectively. The band at \(~3600\) cm\(^{-1}\) is assigned to the \(\sim\)O-H stretching vibration of water molecule, while the band at 1400 cm\(^{-1}\) is due to the scissoring bending mode of surface water molecule. The band at around 730 cm\(^{-1}\) is due to the pyrochlore phase. It may be associated to the stretching and bending vibration of Y-O (Fig. 3.25a) bond\(^{121}\). The band at 1100 cm\(^{-1}\) is due to Mn–OH (Fig. 3.25b) stretching mode\(^{122}\). The absorption band at around 600 cm\(^{-1}\) corresponded to Mn-S stretching vibrations\(^{123}\). The FTIR spectrum of composite exhibited peaks of both the constituent materials i.e. yttrium zirconate and manganese sulfide.

Figure 3.25: FTIR spectra of (a) Y\(_2\)Zr\(_2\)O\(_7\), (b) MnS and (c) nanocomposite of Y\(_2\)Zr\(_2\)O\(_7\)/MnS.

X-ray photoelectron spectroscopic (XPS) measurements were performed to inspect the chemical composition and the oxidation states of the elements in the synthesized nanomaterials. Fig. 3.26a, b and c displays the XPS survey plot of Y\(_2\)Zr\(_2\)O\(_7\),
MnS and Y₂Zr₂O₇/MnS, respectively. The survey spectra (Fig. 3.26a, b and c) indicates the presence of Y, Zr, O, Mn and S as well as C as a reference and confirm that all corresponding elements are present in the synthesized materials without impurities.

![XPS Survey spectra](image)

**Figure 3.26:** XPS Survey spectra of (a) Y₂Zr₂O₇, (b) MnS and (c) nanocomposite of Y₂Zr₂O₇/MnS.

Fig. 3.27a, b and c shows the XPS spectra of Y 3p, Zr 3d and O 1s, respectively. The Y 3p spectrum shows the peaks at binding energies around 312, 300 and 284 eV and correspond to +3 valance state of yttrium (Fig. 3.27a). The peaks at binding energy of 184, 182, 159 and 157 eV correspond to the +4 oxidation state of Zr (Fig. 3.27b), while the peak of O 1s at binding energies of 529.7 and 531.2 eV (Fig. 3.27c) are ascribed to O²⁻ species in the Y₂Zr₂O₇.

The Mn 2p spectrum displays peaks at binding energies of 642 and 653 eV, that match to spin-orbit splitted Mn 2p₃/₂ and Mn 2p₁/₂, correspondingly (Fig. 3.28a). The S 2p₃/₂ peak at 161.20 eV in Fig. 3.28c is also consistent with the reference value of MnS and confirms that Mn exists in +2, while S exist in -2 oxidation state."
Figure 3.27: XPS spectra of (a) Y 3p, (b) Zr 3d and (c) O 1s.

Figure 3.28: XPS spectra of (a) Mn 2p, (b) S 2s and (c) S 2p.
Chapter 3

Results & Discussion

To get information regarding the morphologies of synthesized nanomaterials, Fig. 3.29a, b and c present transmission electron microscopy (TEM) images of $\text{Y}_2\text{Zr}_2\text{O}_7$, MnS and $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS, respectively. Nanorods of $\text{Y}_2\text{Zr}_2\text{O}_7$ and spherical nanoparticle of MnS are clearly seen in Fig. 3.29a and b. In case of nanocomposite, both nanorods and spherical particles coexist, confirming the formation of nanocomposite of $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS.

Figure 3.29: TEM images of (a) $\text{Y}_2\text{Zr}_2\text{O}_7$, (b) MnS and (c) nanocomposite of $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS.
The two key factors, which determine the performance of electrode materials in SCs applications, are surface area and pore-size distribution. Therefore, the surface area and the porosity of Y$_2$Zr$_2$O$_7$, MnS and Y$_2$Zr$_2$O$_7$/MnS samples were investigated by N$_2$-adsorption/desorption measurement (Fig. 3.30a, b and c). It showed that Y$_2$Zr$_2$O$_7$ nanorods, MnS and Y$_2$Zr$_2$O$_7$/MnS exhibited a BET surface area of 75.83, 104.4215, 81.66 m$^2$/g with a pore size of 25, 24.4 and 9.07 nm, respectively. The presence of mesoporous structure is confirmed by the typical IV isotherms with H$_3$-type hysteresis loops$^{125}$. All samples have the same isotherm as indicated in Fig. 3.30. The H$_3$ type hysteresis loops does not display any restriction in adsorption at high P/P0 region, and this is due to the particles, which have a combination of split shape pore$^{126}$.

**Figure 3.30:** N$_2$ adsorption-desorption isotherm of (a) Y$_2$Zr$_2$O$_7$, (b) MnS and (c) nanocomposite of Y$_2$Zr$_2$O$_7$/MnS.
Mostly mesopores and macropores present in the materials that is in agreement with the Barrett–Joyner–Halenda (BJH) pore size distribution calculated from the nitrogen isotherm. The $\text{Y}_2\text{Zr}_2\text{O}_7/\text{MnS}$ nanocomposite with mesopores would be beneficial to increase the pseudocapacitance behavior due to easy passage of ions through the mesopores. The distinctive mesoporous structure of the synthesized nanostructured materials is expected to offer low resistance to the flow of electrons and exhibit excellent electrical conductivity.

### 3.3.4 Electrochemical Performance of $\text{Y}_2\text{Zr}_2\text{O}_7$, MnS and $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS

CV measurement was performed to evaluate the electrochemical performance of $\text{Y}_2\text{Zr}_2\text{O}_7$, MnS and $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS. Fig. 3.31a, b and c signify the typical CVs for the mesoporous $\text{Y}_2\text{Zr}_2\text{O}_7$, MnS and $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS nanocomposite on Ni foam as working electrode with various scan rates ranging from 10 -100 mV/s in the potential range of 0 - 0.75 V. The electrochemical response of bare Ni foam was measured and the specific capacitance was less than 1F/g. The CVs of $\text{Y}_2\text{Zr}_2\text{O}_7$ nanorods, MnS and $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS nanocomposite clearly demonstrate the pseudocapacitive performance resulting from Faradaic reactions. A couple of redox peaks is situated at about 0.48 and 0.39 V when scan rate is 10 mV/s (Fig. 3.31a). The location of the cathodic peak moves somewhat from 0.39 to 0.38 V, when scan rate varies from 10 to 100 mV/s.

This finding proposes that $\text{Y}_2\text{Zr}_2\text{O}_7$ material has a low resistance due to the good contact between the electrode and the substrate material. The Fig. 3.31b and c represent the CVs of MnS and $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS, respectively. The CVs shows the same pseudocapacitive behavior as in case of $\text{Y}_2\text{Zr}_2\text{O}_7$. MnS CVs shows a higher current response than $\text{Y}_2\text{Zr}_2\text{O}_7$ due to high conductivity of sulfide nanomaterials. Fig. 3.31c shows the CVs of $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS that displays the intermediate behavior due to the contribution of both constituents’ materials. Comparison plot at 100mV/s (Fig. 3.31d) displays the high current response of MnS due to its high conductivity as compared to $\text{Y}_2\text{Zr}_2\text{O}_7$ and $\text{Y}_2\text{Zr}_2\text{O}_7$/MnS materials.
Figure 3.31: Cyclic voltammograms of (a) $Y_2Zr_2O_7$, (b) MnS, (c) nanocomposite of $Y_2Zr_2O_7$/MnS and (d) comparison of CV plot at 100 mV/s.

The CV measurements for $Y_2Zr_2O_7$, MnS and $Y_2Zr_2O_7$/MnS nanocomposite were performed at different scan rates and their corresponding $C_{sp}$ was calculated using Eq. 1, and given in Table 3.6. The following structural features help in understanding electrochemical performance of the synthesized nanostructured materials. Firstly, the mesoporous structure of the materials helps to increase the amount of electro-active sites, additionally the electrolyte can intercalate easily through this mesoporous structure of the electrode material. Secondly, the mesoporous structure helps in setting a good mechanical contact with the substrate. Therefore, the mesoporous electrode with conductive substrate perform well as a SCs electrode. From the CVs of all electrode material, it can be concluded that the shape does not alter much with increasing the scan rate. As we increase the scan arte from 10 to 100mV/s, only a slight change is observed.
in the position of cathodic and anodic peaks. This can be explained on the basis of fast transportation of electron and a good mechanical contact between the electrode material and the substrate. The $C_{sp}$ of $Y_2Zr_2O_7/MnS$ nanocomposite is greater than $Y_2Zr_2O_7$ but less than MnS. This behavior can be explained on the basis of the fact that the nanocomposite has properties of both the constituents. The assembly of $Y_2Zr_2O_7$ and MnS makes a better electrode than its constituents. Fig. 5d represent the comparison of CVs plot of $Y_2Zr_2O_7$, MnS and $Y_2Zr_2O_7/MnS$ nanocomposite at 100 mV/s. It can be seen clearly that the nanocomposite has an intermediate behavior of current response due to the presence of both constituents.

GCD plots is the most reliable and steady technique to assess the $C_{sp}$ of the electrode material at a constant current density. Fig. 3.32 demonstrates the representative GCD curves of the nanocomposites at different current densities of 1, 2, 3 and 4 A/g. The values of $C_{sp}$ for the electrode materials were calculated from the GCD profile using of Eq. 2, and the values for all electrodes are given in Table 3.7. The pseudocapacitance nature can also be manifested by the shapes of GCD profiles, and can be concluded the pseudocapacitance behavior that is in accordance with CV results$^{131}$. The plateaus in the GCD profiles is in accordance with anodic peaks in the CVs. So above findings suggest pseudocapacitance nature of all the electrode materials.
Table 3.6. Specific capacitance of \( \text{Y}_2\text{Zr}_2\text{O}_7 \), \( \text{MnS} \) and \( \text{Y}_2\text{Zr}_2\text{O}_7/\text{MnS} \) at different scan rates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Scan Rate mV/s</th>
<th>Specific Capacitance F/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Y}_2\text{Zr}_2\text{O}_7 )</td>
<td>10</td>
<td>177</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>95.8</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>87.5</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>75.6</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>67.8</td>
</tr>
<tr>
<td>( \text{MnS} )</td>
<td>10</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>359</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>296</td>
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<tr>
<td></td>
<td>40</td>
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<td></td>
<td>50</td>
<td>235</td>
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<td></td>
<td>60</td>
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</tr>
<tr>
<td></td>
<td>80</td>
<td>184</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>163</td>
</tr>
<tr>
<td>( \text{Y}_2\text{Zr}_2\text{O}_7/\text{MnS} )</td>
<td>10</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>232</td>
</tr>
<tr>
<td></td>
<td>30</td>
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<td>80</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>145</td>
</tr>
</tbody>
</table>
Figure 3.32: Galvanostatic charge-discharge curves of (a) Y$_2$Zr$_2$O$_7$, (b) MnS and (c) nanocomposite of Y$_2$Zr$_2$O$_7$/MnS.

Fig. 3.33a specifies the variation of $C_{sp}$ with scan rate. All three electrode materials have a similar trend of specific capacitance. The $C_{sp}$ decreases with increase in scan rate. This can be explained on the basis of the fact of electrolyte ion diffusion and internal electrode resistance. At higher scan rate, there is an increase in internal resistance, while low electrolyte ion diffusion. At higher scan rate, the ions are kinetically excited and circulate only to outer surfaces of the electrode, while at low scan rate, electrolyte ions are kinetically less excited and have a sufficient time to reach both outer and inner surfaces of the electrode material. The higher $C_{sp}$ at low scan rate
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arises due to the good contact of electrolyte ions with electrode material and the same trend was already discussed in the reported literature\textsuperscript{132, 133}.

Table 3.7. Specific capacitance, energy and power density of $\text{Y}_2\text{Zr}_2\text{O}_7$, $\text{MnS}$ and $\text{Y}_2\text{Zr}_2\text{O}_7/\text{MnS}$ at different current density.

<table>
<thead>
<tr>
<th>Material</th>
<th>Current density A/g</th>
<th>Specific Capacitance F/g</th>
<th>Energy density Wh/Kg</th>
<th>Power density W/Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Y}_2\text{Zr}_2\text{O}_7$</td>
<td>1</td>
<td>187.50</td>
<td>10.67</td>
<td>330.00</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>87.50</td>
<td>4.98</td>
<td>642.86</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>60.94</td>
<td>3.47</td>
<td>969.23</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>56.25</td>
<td>3.20</td>
<td>1280.00</td>
</tr>
<tr>
<td>$\text{MnS}$</td>
<td>1</td>
<td>321.15</td>
<td>12.06</td>
<td>258.68</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>273.08</td>
<td>10.26</td>
<td>522.25</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>236.54</td>
<td>8.88</td>
<td>790.24</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>184.62</td>
<td>3.93</td>
<td>1050.00</td>
</tr>
<tr>
<td>$\text{Y}_2\text{Zr}_2\text{O}_7/\text{MnS}$</td>
<td>1</td>
<td>221.05</td>
<td>9.97</td>
<td>285.71</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>214.04</td>
<td>9.67</td>
<td>572.46</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>178.95</td>
<td>8.08</td>
<td>847.06</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>168.42</td>
<td>7.60</td>
<td>1140.00</td>
</tr>
</tbody>
</table>

The plateau profile moves towards higher potential as the current density increases due to the strong polarization of ions\textsuperscript{128}. The electrode and electrolyte interaction increases due to the presences of mesoporous structure. Mesoporous structure increases the overall surface area, thus easing the redox process during the GCD cycle\textsuperscript{134}. The specific capacitances of the $\text{Y}_2\text{Zr}_2\text{O}_7$, $\text{MnS}$ and $\text{Y}_2\text{Zr}_2\text{O}_7/\text{MnS}$ nanocomposites calculated at different current densities are shown in Fig. 3.33b. The nanocomposites can deliver a high $C_{sp}$ of 221 F/g at a current density of 1 A/g and the value decreases to 168 F/g, subsequently the current density rises to 4 A/g maintaining 76% of the initial specific capacitance.

However, when MnS is used as the electrode for SCs, it delivers a $C_{sp}$ of 321 F/g at a current density of 1 A/g and only a low $C_{sp}$ of 184 F/g is remained. Subsequently the current density increases to 4 A/g, which is greater than the nanocomposites at the same
current density. However, nanocomposite has a greater $C_{sp}$ than $Y_2Zr_2O_7$. The increase in the $C_{sp}$ is attributed to the conductive nature of MnS. Combination of $Y_2Zr_2O_7$ and MnS helps to construct a porous, mechanically stable and conductive structure that enhance the electrical conductivity and electron/charge transfer pathways as compare to pure $Y_2Zr_2O_7$.

Figure 3.33: Variation of specific capacitance as function of (a) scan rate (b) current density and (c) Ragone plot of $Y_2Zr_2O_7$, MnS and $Y_2Zr_2O_7$/MnS.

The values of specific capacitance highly depend on the current density. At higher value of current density the resistance of electrode material and electrolyte ion diffusion is increased and result in low specific capacitance and the tendency is an accordance with the reported literature\cite{135}. It is also important to mention that the good retention in capacitance is observed with increase in current density from 1 to 4 A/g (Fig. 3.33b), indicating the good rate performance of all electrode materials ($Y_2Zr_2O_7$, MnS, $Y_2Zr_2O_7$/MnS).
Moreover, a Ragone plot, which is a performance assessor for energy storage devices, was used to evaluate the performance of $Y_2Zr_2O_7$, MnS and $Y_2Zr_2O_7$/MnS nanocomposite electrodes (Fig. 3.33c). It was found that the MnS exhibits $E$ of 12 Wh/kg and $P_{of}$ of 1050 W/kg, while the other electrodes based on $Y_2Zr_2O_7$ and $Y_2Zr_2O_7$/MnS nanocomposite exhibit energy densities of ~ 11 and ~ 10 Wh/kg and $P_{of}$ of 1280 and 1140 W/kg. The $P$ of $Y_2Zr_2O_7$/MnS nanocomposite is greater than $Y_2Zr_2O_7$ and MnS. Thus, the values obtained for $E$ and $P$ for $Y_2Zr_2O_7$/MnS nanocomposite show improved performance due to the synergistic effect of constituent materials. The calculated values of $E$ and $P$ of the fabricated electrodes are given in Table 3.7.

Cyclic stability of a SCs electrode is an essential feature for its practical usability. The CV measurement at 100 mV/s was performed for the fabricated electrodes (Fig. 3.34). Brilliant specific capacitance retention is found after 1000 CV cycles. The good mechanical contact between the active material and the substrate is encouraging for long cycle life of the electrode. The amazing electrochemical stability performance of $Y_2Zr_2O_7$ electrode can be explained on the basis following three possible reasons, (a) the good mechanical contact between electrode and the substrate, (b) the uniform covering of active material on Ni foam can provide an efficient transport of electron and ions and (c) the stability of $Y_2Zr_2O_7$ nanorods electrode due to its unique morphology. The $Y_2Zr_2O_7$ is stable enough to deliver a high $C_{sp}$ up to 1000 CVs\textsuperscript{12}. The cyclic stability behavior of MnS is explained on the fact of following reason. There are two stages in cyclic life of MnS i.e. a steady state and activation of electrode material after a certain period. The $C_{sp}$ remains constant up to 580 cycle, after that electrode material gets activated and $C_{sp}$ increases up to 1000 CV cycles, which indicates the good cyclic performance of MnS electrode\textsuperscript{136}. The improved electrochemical and pseudocapacitive performance conveyed by $Y_2Zr_2O_7$/MnS nanocomposite electrode is absolutely due to good association between $Y_2Zr_2O_7$ and MnS.
EIS studies were performed within a frequency range of 0.1 Hz to 100 KHz at an external applied potential of 2 mV to find out the several resistances present within the electrode materials. The EIS analysis and the resultant Nyquist plots are displayed in Fig. 3.35. Nyquist plot shows a semicircle for each electrode material at high frequency region which corresponds to charge transfer and solution resistance, while a straight line in low frequency region indicates the diffusion process is involved in the transfer of electron and this in accordance with the reported literature\textsuperscript{127,137,138}. The values of different resistance parameters are calculated and presented in Table 3.8. The illustrative equivalent circuit of the system is given in inset of Fig. 3.35. The $R_s$ is the solution resistance, $R_{ct}$ describes the charge transfer resistance C is the capacitance and W represent the Warburg impedance. The results suggest that charge transfer resistance of $Y_2Zr_2O_7$/MnS is lower than that of $Y_2Zr_2O_7$ (44.9 $\Omega$ versus 119.3 $\Omega$), we tentatively attribute it to the shifting of Fermi energy level towards conduction band due to MnS, which increases the conductivity of $Y_2Zr_2O_7$/MnS nanocomposite.
Figure 3.35: Nyquist plot of Y$_2$Zr$_2$O$_7$, MnS and Y$_2$Zr$_2$O$_7$/MnS.

It further suggests that the addition of MnS into the Y$_2$Zr$_2$O$_7$ clearly increases the electrical conductivity of the nanocomposite. Moreover, with the addition of MnS, the C$_{sp}$ also increases, which further confirms the good combination compatibility of Y$_2$Zr$_2$O$_7$ and MnS nanoparticles in nanocomposite electrode.

Table 3.8. Capacitance, solution resistance, charge transfer resistance and Warburg impedance of Y$_2$Zr$_2$O$_7$, MnS and Y$_2$Zr$_2$O$_7$/MnS nanocomposite.

<table>
<thead>
<tr>
<th>Name of Material</th>
<th>Capacitance (C) (mF)</th>
<th>Solution Resistance (Rs) Ω</th>
<th>Charge Transfer Resistance (Ret) Ω</th>
<th>Warburg Impedance (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$Zr$_2$O$_7$</td>
<td>0.2535</td>
<td>24.71</td>
<td>99.3</td>
<td>0.24x10$^{-2}$</td>
</tr>
<tr>
<td>MnS</td>
<td>5.73</td>
<td>31.2</td>
<td>34.1</td>
<td>067x10$^{-1}$</td>
</tr>
<tr>
<td>Y$_2$Zr$_2$O$_7$/MnS</td>
<td>4.27</td>
<td>25.4</td>
<td>44.9</td>
<td>0.7x10$^{-2}$</td>
</tr>
</tbody>
</table>
3.3.5 Summary of the Main Findings of Y$_2$Zr$_2$O$_7$, MnS and Y$_2$Zr$_2$O$_7$/MnS Nanocomposite as Electrode Materials

In conclusion, Y$_2$Zr$_2$O$_7$, MnS and Y$_2$Zr$_2$O$_7$/MnS nanocomposite electrode materials have been prepared and we addressed the cyclic stability issues of SCs electrode materials. The contribution of Y$_2$Zr$_2$O$_7$ and MnS increased the overall electrochemical performance and cyclic stability of SCs electrode. The Y$_2$Zr$_2$O$_7$/MnS nanocomposite C$_{sp}$ was 221 F/g with an E of 10Wh/kg. There was negligible decrease in C$_{sp}$ and energy with increase in current density, due to the less polarization of Y$_2$Zr$_2$O$_7$/MnS electrode material. The C$_{sp}$ of Y$_2$Zr$_2$O$_7$/MnS nanocomposite electrode was increased from 145.25 to 261.51 F/g at 100mV/s after successive 1000 CVs, which indicated the excellent cyclic stability of the electrode material. The long-lasting stability and high tolerance of C$_{sp}$ suggested that the mesoporous nanocomposite is a promising candidate for SCs electrode.

In the present work, we explore the electrochemical properties of SrZrO$_3$ nanorods in aqueous electrolytes. The SrZrO$_3$ nanorods achieve high surface area of 146 m$^2$/g with small pore size $\sim$1.48 nm distribution. Due to high surface and mesoporosity, the fabricated electrode consisting of SrZrO$_3$ nanorods achieves a $C_{sp}$ of 1225.8 F/g at a current density of 10A/g with an excellent cyclic stability up to 1000 CV cycles. High $C_{sp}$ and excellent cycle stability demonstrate its potential application as a SCs electrode.
3.4.1 Fabrication of Electrode

Working electrode was prepared by mixing solid powder with ethanol and Nafion solution. The 1 mg SrZrO$_3$ were thoroughly mixed in ethanol followed by subsequent addition of 1 µl 5% Nafion solution that makes a homogenous slurry. The working electrode was fabricated by applying the slurry on Ni foam and then dried at 60 $^\circ$C for 24 hours. The loading capacity of working electrode was 0.01, 0.1, 0.15 and 0.2 mg.

3.4.2 Characterization Methods

3.4.2.1 Structural and Morphological Characterization

X-ray diffraction (XRD) (D8 advance, Bruker's X-ray powder diffractometer, Cu $K_\alpha$, $\lambda = 0.154$ nm) was used to study the crystal structure of SrZrO$_3$ nanorods. IRTracer-100 Fourier Transform Infrared SHIMADZU Spectrometer was used for FTIR analysis. RAMAN spectra was recorded using Raman Reinsha RM100 spectrometer excited with a 532 nm Ar$^+$ laser. X-ray Photoelectron Spectroscopy studies was carried using Kratos' Axis Ultra delay line detector photon spectrometer. Oxidation state of the elements were confirmed by XPS studies. Morphological analysis of the SrZrO$_3$ nanorods were carried out by scanning electron microscopy (SEM, JEOL JSM-7500F and transmission electron microscopy (TEM, JEOL JEM-2100). The multipoint Braunauer-Emmett-Teller (BET) technique has been used for the assessment of surface area and pore size of the SrZrO$_3$ nanorods.

3.4.2.2 Electrochemical Characterization

Electrochemical studies has been employed to find out the potential application of SrZrO$_3$ nanorods as a SCs electrode. PGSAT12 autolab electrochemical workstation has been used for CV, GCD and EIS measurements. Three-electrode system in aqueous 0.1 M KOH electrolyte was used to study the electrochemical measurements. Pt wire was used as a counter, Ag/AgCl as a reference while, active material loaded on Ni foam as a working electrode. EIS measurements were carried at the frequency range of 100 kHz to 10 mHz.
3.4.3 Structure and Morphology of SrZrO$_3$

Crystallinity of SrZrO$_3$ is revealed through XRD spectrum as shown in Fig. 3.36. The spectrum is well matched with standard ICSD card (ICSD- 00-044-0161). In Fig. 3.36 all the diffraction patterns at the 2θ values of 21.621, 24.219, 30.699, 32.619, 36.206, 39.546, 41.108, 44.074, 45.493, 49.647, 54.784, 60.621, 64.124, 69.571 and 7.766 correspond to Miller indices of (101), (111), (200), (210), (211), (131), (221), (202), (230), (222), (042), (331), (242), (313) and (323), respectively. Thus, suggesting that perovskite SrZrO$_3$ nanorods crystallizes in an orthorhombic structure. The XRD pattern further reveals that there is no impurity in the synthesized SrZrO$_3$ nanorods.

![XRD spectra of SrZrO$_3$.](image)

**Figure 3.36:** XRD spectra of SrZrO$_3$.

FTIR spectrum of the SrZrO$_3$ nanorods is displayed in Fig. 3.37. The broad absorption peak near 3400 cm$^{-1}$ can be attributed to O-H stretching of of water molecule, while a sharp band near 1400 cm$^{-1}$ is due to scissoring vibrations of absorbed water molecule.$^{96}$ The sharp peak at about 860 cm$^{-1}$ is due to metal oxygen bonding. The spectrum also displays a broad absorption feature between 500–600cm$^{-1}$ that is attributed to ZrO$_6$ octahedral stretching vibrations.$^{99}$
Figure 3.37: FTIR spectra of SrZrO$_3$.

The Raman spectrum (Fig. 3.38) of SrZrO$_3$ exhibits peaks at 245, 410, 550 and 700 cm$^{-1}$. The band at 245 cm$^{-1}$ is attributed to $A_g$ mode, while the broad peak at 550 cm$^{-1}$ is due to the $A_g$ and $B_{3g}$, while the feature at 410 cm$^{-1}$ is due to the $A_g$ mode of SrZrO$_3$. The sharp band at 700 cm$^{-1}$ is assigned to the second order scattering features resulting from the superposition of various combinational modes$^{139}$.

Figure 3.38: Raman spectra of SrZrO$_3$.
X-ray photoelectron spectroscopic (XPS) analysis was applied to find out the oxidation state and composition of the SrZrO$_3$ nanorods. Fig. 3.39a represent the XPS survey spectrum of SrZrO$_3$. The XPS survey spectra confirms that Sr, Zr and O are present in the samples. All the peaks correspond to constituent elements of the synthesized SrZrO$_3$ nanorods and there in no other peak of any impurity.

Figs. 3.39b-f represent the XPS spectra of Sr 3p, Sr 3d, Zr 3d, Zr 3p and O1s, respectively. The Sr 3p and 3d spectra confirms the +2 oxidation state of Sr, while Zr in SrZrO$_3$ present in +4 oxidation state according to 3d and 3p XPS spectra. The O is in -2 oxidation state according to 1s XPS spectra and has spin-orbit splitted peaks at 529.7 and 531.2 eV (Fig. 3.39f)$^{140}$.

The SEM image indicates that SrZrO$_3$ are nucleated in nanorods shape, Fig. 3.40a. The SEM image of nanorods further indicates that nanorods diameter and length varies substantially. Such morphology could be beneficial as it might has high surface area and porosity due to inhomogeneity in the morphology. High surface area and porosity enhance the electrochemical performance of nanomaterials, see later sections.

TEM image further clarify the morphology of SrZrO$_3$ nanorods. It confirms SrZrO$_3$ exists in the nanorods shape, Fig. 3.40b. The high-resolution transmission electron microscopy (HRTEM) image (Fig. 3.40c &d) display clear lattice fringes and confirms the high crystallinity of the material, these findings are in agreement with the XRD measurements.
Figure 3.39: (a) XPS Survey of SrZrO$_3$, (b) XPS Spectra of Sr 3p, (c) 3d, (d) Zr 3p, (e) Zr 3p and (f) O1s.
The materials, which are used as electrode in SCs, are characterized for its mesoporosity and surface area. These aforementioned properties are the key parameters of the electroactive materials, which control the performance of electrode of SCs. Therefore, surface area and mesoporous nature of nanorods SrZrO$_3$ has been investigated by N$_2$-adsorption-desorption measurement, Fig. 3.41. The hysteresis loop at P/P$_0$ > 0.4 is observed and characterized as a H3 hysteresis loop according to IUPAC system. This type of hysteresis can be attributed to mesoporous materials and have type IV isotherms$^{141}$. High surface area and mesoporous structure is favorable for electroactive materials. As high surface area and small pore size may help to deliver high C$_{sp}$ and have ability to store the high energy. Large surface area and small pore size also facilitates the diffusion of electrolyte ion into the electrode material and enhance the charge storage capacity at higher current densities. The SrZrO$_3$ nanorods have a specific surface area of 146.13 m$^2$/g, while the pore width and pore volume of the nanorods are 1.48 nm and 0.078 cm$^3$/g, correspondingly.

Figure 3.40: (a) SEM, (b) TEM and (c, d) HRTEM images of SrZrO$_3$ nanorods.
3.4.4 Electrochemical Performance of SrZrO$_3$

The electrochemical measurements were executed to examine the electrochemical performance of the SrZrO$_3$ nanorods. Fig. 3.42a shows the CVs of SrZrO$_3$ at various scan rates ranging from 10 - 100 mV/s at a potential window of 0 to 0.75 V. The following equation is employed to calculate the $C_{sp}$ from CVs\cite{49}.

$$C = \int \frac{IdV}{s mV}$$

(1)

Where, $\int (IdV)$, s, V and m is the integrated area, scan rate, potential window and the mass of the active material, respectively.

Active material loaded Ni foam was used as a working electrode. The electrochemical signal for bare Ni foam was measured and the calculated specific capacitance was less than 1 F/g. The measured value is in accordance with the reported literature\cite{49,142}.

The CV curves have a large integrated area and have a high $C_{sp}$ of 1354 F/g at a scan rate of 10 mV/s. The observed $C_{sp}$ is higher than the other metal oxide electrode materials like reported by R. B. Rakhi et al.\cite{143} and RuO$_2$ electrode (700 F/g). The CV study has been carried out to calculate the specific capacitance of the SrZrO$_3$ nanorods electrode. The loading capacity has been varied to confirm the higher value of $C_{sp}$ as compared to reported oxide materials. The loading capacity of the working electrode was 0.1, 0.15 and 0.2mg. The calculated $C_{sp}$ of electrodes with different loading
capacity was given in Table 3.9. The values confirmed the higher $C_{sp}$ of the SrZrO$_3$ with an average specific capacitance of 1278 F/g.

The shapes of the CVs depict that the capacitance is generated by faradaic reaction. The deliverance of capacitance by Faradaic reactions are different from conventional electric double-layer capacitance. In EDLC capacitance shape of CVs are rectangular. In all CVs curves redox peaks has been clearly observed (Fig. 3.42a). These peaks appear due to faradaic reaction at the surface of the working electrode$^{144,145}$. The redox peaks (anodic and cathodic) were present at about $\sim$0.46 and $\sim$0.38V, correspondingly and suggest the oxidation and reduction process is occurring in the electrode material.

**Figure 3.42:** (a) CV curves at different scan rates and (b) Comparison plot of bare Ni foam, 0.1, 0.15 and 0.2mg of SrZrO$_3$ at 50mV/s.

It can further be observed from the CVs that with increase in scan rates, the current increases and there is a regular increase in the difference of cathodic and anodic peaks potential. This type of behavior designate that the current is produced due to diffusion controlled reaction’s kinetics. This suggest the SrZrO$_3$ nanorods electrode is encouraging the fast redox reactions at the surface of electrode, which is obvious from the shapes of the CVs.

Fig. 3.42 b displays the comparison of CV curves of bare Ni foam, 0.1 mg, 0.15 mg and 0.2 mg active material loaded Ni foam electrodes at 50 mV/s. CVs clearly indicate the effect of mass on integrated area of the CVs and generated current of the electrodes. It confirms by increasing the loading capacity the current increases. Secondly, it indicates that bare Ni foam has little contribution to specific capacitance in electrochemical measurements of the studied electrodes.
Table 3.9. Specific capacitance of bare Ni foam and electrodes with different loading capacity of SrZrO$_3$ at different scan rates.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Scan Rate (mV/s)</th>
<th>Specific Capacitance (F/g) of SrZrO$_3$</th>
<th>Specific Capacitance (F/g) of Ni Foam</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.1mg</td>
<td>0.15mg</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>1354</td>
<td>1165</td>
</tr>
<tr>
<td>2.</td>
<td>20</td>
<td>1127</td>
<td>854</td>
</tr>
<tr>
<td>3.</td>
<td>30</td>
<td>997</td>
<td>714</td>
</tr>
<tr>
<td>4.</td>
<td>40</td>
<td>872</td>
<td>631</td>
</tr>
<tr>
<td>5.</td>
<td>50</td>
<td>728</td>
<td>561</td>
</tr>
<tr>
<td>6.</td>
<td>60</td>
<td>694</td>
<td>515</td>
</tr>
<tr>
<td>7.</td>
<td>80</td>
<td>564</td>
<td>434</td>
</tr>
<tr>
<td>8.</td>
<td>100</td>
<td>477</td>
<td>369</td>
</tr>
</tbody>
</table>

GCD measurements has been performed to further evaluate the energy storage ability of the SrZrO$_3$ electrode. The symmetrical nature of GCD profiles shows the electrochemical reversibility and occurrence of fast redox reaction at the surface of electrode material (Fig. 3.43). The pseudocapacitive behavior of the electrode material is confirmed by the plateau region in GCD profiles and this is in accordance with CV results. The fast redox reaction occurs due to charge transfer and the formation of electrical double layer at the interface of electrode and the electrolyte. The same phenomenon was suggested to be operative in the reported work$^{146}$. 

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The following equation is used to calculate the $C_{sp}$ of the electrode from GCD profiles\textsuperscript{147}.

$$C = \frac{I\Delta t}{\Delta V m}$$  \hspace{1cm} (2)

Where $I$, $\Delta V$, $\Delta t$, and $m$ is the applied current, potential change, discharge time and the mass of active material (0.01mg), correspondingly.

The $C_{sp}$ is calculated at various current densities. The decrease in $C_{sp}$ with the increment of current density, suggesting the fast surface redox reaction. High $C_{sp}$ of 1225.8 F/g is attained at low current density of 10A/g. The nonhomogeneous morphology, mesoporous structure and high surface area are responsible for the fast faradaic redox surface reaction. High surface area indorse the higher surface redox reactions. Higher the surface area increase the possibility for redox reaction to occur and results in higher $C_{sp}$ and ultimately higher E of the electrode material. The observed value of $S_{C_{sp}}$ of SrZrO$_3$ nanorods is higher than the reported metal oxide like RuO$_2$ and other materials that reported in previous studies\textsuperscript{148,149}. The high $C_{sp}$ SrZrO$_3$ nanorods is attributed to hierarchical morphology, high surface area, mesoporous nature and to high conductivity.
The $C_{sp}$ is altered with the variation in scan rate, and the variation is displayed in Fig. 3.44. The $C_{sp}$ is maximum at lower scan rate, while minimum at higher scan rate. This can be explained on the basis of diffusion of electrolyte ion into the electrode surfaces. The electrolyte ion has a maximum time to diffuse into the inner and outer surface of the electrode at low scan rate, and maximum surface of electrode is engaged in the redox reaction, resulting in the higher value of the $C_{sp}$ as compared to higher scan rate. At higher scan rate only outer surfaces of the electrode material is involved in redox reaction. Secondly, the decrease of $C_{sp}$ with scan rate might be described on the basis of current generation with scan rate. The increase in current with scan rate is not pronounced as the scan rate and finally results in decrease in $C_{sp}$ according to Eq.1. $C_{sp}$ is calculated by using Eq. 1 and the values are given in Table 3.10.

Table 3.10. Specific capacitance of SrZrO$_3$ at different scan rates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Scan Rate mV/s</th>
<th>Specific Capacitance F/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrZrO$_3$</td>
<td>10</td>
<td>1354</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1128</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>998</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>873</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>729</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>695</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>564</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>477</td>
</tr>
</tbody>
</table>

Fig. 3.45 represents the change in specific capacitance of the SrZrO$_3$ electrode with current density. The $C_{sp}$ of the electrode decreases following increasing the current density. This might be due to the increase in solution and electrode resistance. The electrolyte ions are less excited and have a sufficient time to reach the electrode material at the low value of current density. While at higher current densities, electrolyte ions are highly excited and suffer time limitation and high resistance and as a result $C_{sp}$ decreases. The $C_{sp}$ from GCD profiles was calculated using Eq. 2, and the calculated values are given in Table 3.10.
Figure 3.44: Specific capacitance as a function of scan rate.

The E and the P of the electrode material is calculated from the $C_{sp}$ acquired from GCD profiles. Following equations are used to calculate the aforementioned values\(^4^9\).

$$E = \frac{1}{2}(C_{sp}\Delta V^2) \quad (3)$$

$$P = \frac{E}{t} \quad (4)$$

Here, $\Delta V$ is the potential window of discharge process, and $t$ is the time of discharge process.

Figure 3.45: Specific capacitance as a function of current density.
Chapter 3 Results & Discussion

The Ragone plot is a performance evaluator for energy storage devices. For SrZrO$_3$ nanorods it is shown in Fig. 3.46. The SrZrO$_3$ has an $E$ of 65Wh/kg, which is higher than the reported oxide material$^{150,17}$, this might be due to the high surface area and nonhomogeneous morphology of the material. The value of specific capacitance, $E$ and $P$ of electrode material are given in Table 3.11.

**Table 3.11.** Specific capacitance, energy and power density of SrZrO$_3$ at different current density.

<table>
<thead>
<tr>
<th>Material</th>
<th>Current density</th>
<th>Specific Capacitance</th>
<th>Energy density</th>
<th>Power density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A/g</td>
<td>F/g</td>
<td>Wh/Kg</td>
<td>W/Kg</td>
</tr>
<tr>
<td>SrZrO$_3$</td>
<td>1</td>
<td>1225.8</td>
<td>65.4</td>
<td>3100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>653.3</td>
<td>34.9</td>
<td>4650</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>516.1</td>
<td>27.6</td>
<td>6100.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>483.9</td>
<td>25.8</td>
<td>7750</td>
</tr>
</tbody>
</table>

The cyclic stability of electrode is a crucial parameter to evaluate the performance of nanostructured material as a SCs electrode. Fig. 3.47 represents the cyclic stability performance of SrZrO$_3$ nanorods electrode. The synthesized nanorods electrode reveal the best electrochemical performance and high cyclic stability, verifying its potential suitability for high performance SCs electrode.

The SrZrO$_3$ needed additional 1000 cycles to fully activate the electrode material. The $C_{sp}$ of SrZrO$_3$ increases up to 1000 CVs, indicating the high stability of electrode material. The $C_{sp}$ increases from 491 F/g (1$^{st}$ CVs) to 866 F/g (1000 CVs) after 1000 successive CVs.

The improved $C_{sp}$ and high cyclic stability of SrZrO$_3$ might be due to the low resistance of electrode material, which can be further explained by EIS data. EIS is another parameter to assess the electrochemical performance of electrode material. Fig. 3.48a shown the Nyquist plot of SrZrO$_3$ electrode, while Fig. 3.48b represent the
equivalent circuit diagram. The values obtained from fitting the impedance data, and values has been given in Table 3.12.

Figure 3.46: Ragone plot (Energy density vs power density) of SrZrO$_3$.

Figure 3.47: Cyclic stability plot of SrZrO$_3$ nanorods.
Table 3.12. Capacitance, solution resistance, charge transfer resistance and Warburg impedance of SrZrO$_3$.

<table>
<thead>
<tr>
<th>Name of Material</th>
<th>Capacitance (C) (mF)</th>
<th>Solution Resistance (Rs) Ω</th>
<th>Charge Transfer Resistance (Rct) Ω</th>
<th>Warburg Impedance (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrZrO$_3$</td>
<td>0.0941</td>
<td>22.34</td>
<td>0.43</td>
<td>0.17x10$^{-2}$</td>
</tr>
</tbody>
</table>

Nyquist plot indicates the low charge transfer resistance of the electrode material in high frequency region, while a straight line in low frequency region indicates the diffusion controlled process is dominant in current generation. Semicircle at high frequency indicates the charge transfer resistance ($R_{ct}$), while straight line indicate Warburg impedance (W). Lower $R_{ct}$ value specifies the high P of the electrode material and propose the potential use of SrZrO$_3$ electrode for SCs application.

Figure 3.48: (a) Nyquist plot and (b) circuit diagram of SrZrO$_3$. 
3.4.5 Summary of Main Findings

In the present work, the synthesis and electrochemical properties of SrZrO$_3$ nanorods for was investigated and the nanorods electrode achieved a high $C_{sp}$ of 1225.8 F/g at a current density of 10 A/g. In addition to high $C_{sp}$ the electrode material exhibited a high $E$ of 65 Wh/kg with high power delivery rate of $\sim$4000 W/kg. The SrZrO$_3$ nanorods electrode has been subjected to successive 1000 CV cycles to assess its stability and results suggested its excellent cyclic stability up to 1000 CV cycles. The $C_{sp}$ increased from 491 to 866 F/g (1$^{st}$ to 1000 CV cycle). The excellent cyclic stability was due to structural changes at the electrode surface and the activation of the electrode material with successive CV cycles. The studied SrZrO$_3$ nanorods electrode achieved a high $C_{sp}$ of 1225 F/g at 10 A/g current density with high cyclic stability. The observed values is higher than the reported value in literatures. These findings demonstrated the potential application and suitability of SrZrO$_3$ nanorods for future energy storage devices.
4.1 Conclusions

The major objective of the present study was the fabrication of electrode material with improved electrochemical performance and high stability for SCs applications. To achieve the objective nanocomposites of metal oxide/sulfide were synthesized by hydrothermal method to explore their electrochemical performance for practical utility.

The nanostructures of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, PbS and the nanocomposite of Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS achieved a \( C_{sp} \) of 193, 204 and 219 F/g and E of \(-9.8, 6.2 \) and \(-6.8 \) Wh/kg, respectively, at 1 A/g current density. Nanocomposite Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/PbS electrode demonstrated better electrochemical performance and stability behavior than Ce\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and PbS due to the synergistic effect of the constituents. The \( C_{sp} \) was almost constant up to 1000 CVs indicating an excellent stability of the electrode.

The electrochemical performance of CeO\textsubscript{2}, CeS\textsubscript{2} and CeO\textsubscript{2}/CeS\textsubscript{2} nanocomposite supported on Ni-foam was evaluated for SCs application. The \( C_{sp} \) of 148, 924 and 420 F/g were achieved in CeO\textsubscript{2}, CeS\textsubscript{2} and CeO\textsubscript{2}/CeS\textsubscript{2} nanocomposite electrodes, respectively with E of 5, 32 and 21 Wh/kg at a constant current density of 1 A/g. Nanocomposite electrode demonstrated high cyclic stability with monotonous increase in \( C_{sp} \) up to 1000 CV cycles.

In case of Y\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, MnS and the nanocomposite of Y\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/MnS electrode, the \( C_{sp} \) of 187, 321 and 221 F/g at a current density of 1A/g were achieved. The \( C_{sp} \) of Y\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}/MnS nanocomposite electrode was increased from 145 to 261 F/g at 100 mV/s after successive 1000 CV cycles, which indicated the excellent cyclic stability of the electrode material.

The electrochemical performance of SrZrO\textsubscript{3} nanorods electrode was studied by three-electrode system in 0.1M KOH electrolyte. A high \( C_{sp} \) of 1225.8 F/g at a current density of 10 A/g was achieved with the E of 65 Wh/kg. Despite of high energy density, nanorods electrode depicted the high delivery rate of\(~4000\) W/kg and high cyclic stability with continuous increase in \( C_{sp} \) up to 1000 successive CV cycles.

In comparison for all the studied systems, a high \( C_{sp} \) has been achieved in case of metal sulfide electrode due to its better electrical conductivity. Metal oxide as
Chapter 4  Conclusions & Future Perspective

compared to metal sulfide revealed an exceptional cyclic stability in successive CV cycles.

As compared to metal sulfide, CeS$_2$ electrode exhibited a superior electrochemical properties and it achieved a high value of $C_{sp}$ (924 F/g) and E (32 Wh.kg) at low current density (1 A/g). While in case of metal oxide, SrZrO$_3$ nanorods electrode exhibited a superior electrochemical performance due to its high specific surface area and small pore size distributions.

Synthesized nanocomposites CeO$_2$/CeS$_2$, Y$_2$Zr$_2$O$_7$/MnS, Ce$_2$Zr$_2$O$_7$/PbS exhibited improved cyclic ability, E and the $C_{sp}$ than individual constituents. The CeO$_2$/CeS$_2$ nanocomposite demonstrated better electrochemical properties than other composites electrodes due to the better redox properties of Ce. Nanocomposite sacrificed the conductivity of the sulfide but, simultaneously gained the stability of the oxide and demonstrated improved properties for pseudocapacitor electrode.
4.2 Future Perspective

In this thesis, metal oxide/sulfide nanocomposites have been synthesized by simple and facile hydrothermal methods and their electrochemical performance have been assessed for supercapacitor applications. The core issue that is addressed in this thesis is stability of the electrode material over successive cycles. The main findings indicate that composite of metal oxide/sulfide electrode is stable enough to use as an alternative electrode for future generation supercapacitors. However, following future studies may require to improve the performance of the electrodes.

- The investigated electrode materials can be tested for further CV cycles to confirm the stability of the materials.
- Some other transition metal based oxides may also be tried to replace the studied metal oxides.
- The electrodes in this thesis are studied by three-electrode system and their electrochemical behavior was assessed. The electrodes can also be studied by two-electrode system to further confirm their applications in supercapacitors.
5. List of Publications


References


114. Kumara, E.; Selvarajan, P.; Muthuraj, D. Synthesis and Characterization of


