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Synthesis and Characterization of Mixed Transition Metal Oxides and their Composites with Carbon for Energy Storage Applications

By

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(Student Number: 215085891)

Thesis in fulfilment of the requirement for the degree

DOCTOR OF PHILOSOPHY(PhD)

in

CHEMISTRY

in the

FACULTY OF SCIENCE

of the

UNIVERSITY OF JOHANNESBURG

Supervisor : Prof P Ndungu
Co-supervisor : Dr. K Pruessner
              Prof D Billing
DECLARATION

I declare that this thesis “SYNTHESIS AND CHARACTERIZATION OF MIXED TRANSITION METAL OXIDES AND THEIR COMPOSITES WITH CARBON FOR ENERGY STORAGE APPLICATIONS” is a presentation of my own original research work. It is being submitted for the degree of Doctor of Philosophy (Ph.D.) in Chemistry at the University of the Johannesburg. It has not been submitted for any degree or examination in any other university. All the sources used are accordingly acknowledged by means of complete references.

Some of the work reported in this thesis has been published in journal articles and presented at conferences, as indicated in the academic output section.

The work was done under the supervision and guidance of Prof. P. Ndungu at the University of Johannesburg and co-supervision of Dr. K. Pruessner and Prof. D. Billing.

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CO-SUPERVISOR DATE

Prof. Dave G. Billing .................. ........... ................................

CO-SUPERVISOR DATE
DEDICATION

This work is greatly dedicated to my late father, Heliso Dolla Dollebo, who made every single effort to be who I am today.
ACKNOWLEDGEMENTS

First and foremost, I thank my principal supervisor, Prof. Patrick Ndungu for his support through the period of my PhD study. I would also like to acknowledge my co-supervisors Prof. David Billing (University of the Witwatersrand) and Dr. Karin Pruessner (University of Kuwazulu-Natal) for their help and suggestions. I would not forget the time I spent at the University of the Witwatersrand with Prof. David Billing’s group learning X-ray diffraction techniques and Retiveld refinement method as well and many thanks goes to all the nice people in that group.

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And of course, none of this work would be possible without the constant cooperation in many ways from colleagues, friends, lab mates, and staff members of the department. I truly want to thank Dr. Isiaka Lawal, a colleague from our research group who has been on my side during my difficult times. I also greatly acknowledge the University of Johannesburg and the National Research Foundation (NRF) for the PhD scholarships and other funds.

God, almighty – finally I thank my Lord, for his provision and guidance in every aspect of my life.
CONFERENCE AND SYMPOSIUM PRESENTATIONS

1. **T. H. Dolla**, D. Billing, K. Pruessner, P. Ndungu, Sol-gel prepared spinel-type \( \text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4 \) as electrode material for a possible application in energy storage in Li-ion battery, 4th International Symposium on Electrochemistry “Pure and Applied Electrochemistry” April 3-5, 2018, University of Johannesburg, Johannesburg, South Africa.


LIST OF PUBLICATIONS


5. **T. H. Dolla**, D. G. Billing, K. Pruessner, P. Ndungu, Mn substituted Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ porous microspheres for high performance energy storage application in supercapacitors. (in preparation)
ABSTRACT

Energy storage technologies play an essential role in efficient use of electrical energy and utilization of sustainable and renewable energy resources such as solar and wind energy, which have intermittent nature. In recent years, with the rapid-growth of portable electronic devices and electric vehicles there is a huge demand for the development of electrical energy storage systems with improved energy and power density, durability, and reduced cost. In connection with this, electrochemical energy storage systems such as electrochemical capacitors (supercapacitors) and batteries have shown great potential. Supercapacitors have been considered as promising technologies due to their higher power density and better safety than batteries, faster charge-discharge processes and longer life time. However, the low energy density has limited their application. Hence, great efforts have been focused on designing and optimizing the electrode material for high performance applications. Owing to their high specific capacitance, low cost, facile and scalable preparation, nanostructured transition metal oxides have been considered as an attractive electrode materials for high-performance supercapacitors. However, several drawbacks including the low electron conductivities, slow ion diffusion rates, and big volume change during the electrochemical measurements limit their further applications.

To overcome the draw backs of transition metal oxides as elecrode materials for supercapacitors, this study is aimed at developing mixed transition metal oxides (MTMOs) and their hybrids with carbon, which can enhance their conductivity and hence enhance electrochemical performances. Therefore, this thesis focuses on the physical, chemical, structural and electrochemical investigation of mixed transition metal oxide based materials as potential electrode materials with enhanced electrochemical performance for supercapacitors to satisfy the requirement of the clean and reliable energy storage devices.

A series of ternary mixed transition metal oxides of the type Mn-Ni-Co and Zn-Mn-Co with different compositions crystallizing in spinel structure (AB₂O₄) and hybrids with carbon are prepared by developing and optimizing different synthesis techniques and are presented in this thesis. Various characterization techniques including XRD, FTIR, TGA, Raman, XPS, BET, SEM, TEM, and VSM have been utilized to fully understand the morphological, structural, electronic, and other properties. Facile citrate sol-gel technique and co-precipitation method
were developed and utilized to prepare the oxides Mn\textsubscript{x}Ni\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4} and Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4}, respectively. They were successfully formed in a spinel crystal structure with a varying compositions. The substitution of Mn in to the binary systems is shown to influence the structural, morphological, and electronic properties of the mixed metal oxides. Compared to the other various synthetic techniques, sol-gel and coprecipitation methods are simple and have proven to be effective in controlling the stoichiometry and ensuring the homogenous mixing of the different elements in the atomic level yielding phase pure oxides.

The ternary carbon coated Mn\textsubscript{0.5}Ni\textsubscript{0.5}Co\textsubscript{2}O\textsubscript{4}/C hybrid nanostructure was successfully prepared through a template assisted sol-gel followed by pyrolysis making use of glucose as a carbon source. The metal oxide nanoparticles were effectively coated with the carbon sheets and were homogenously dispersed in the matrix. The investigation of its electrochemical performance had shown to display better supercapacitive performance than the binary counterparts. This mainly because of the synergistic effect of incorporation of the carbon in the nanostructure enhancing the conductivity and the multimetallic components providing rich redox centres for the electrochemical reactions. The obtained results showed that proper design of hybrid nanostructures of mixed transition metal oxides and carbon would enhance the electrochemical performance of electrode materials for supercapacitors.

Lastly, Mn substituted Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4} (x = 0, 0.3, 0.5, 0.7, 1) porous microspheres obtained by a facile co-precipitation route were investigated for their application as high performance electrode material for supercapacitors. Transmission electron microscopy studies revealed the porous nature of the microspheres and are constituted by well-connected aggregates of nanoparticles. The Mn substitution has played a big role in enhancing the surface area and electrochemical performance of the microspheres. The electrochemical study shows highest specific capacitance of 589.9 F g\textsuperscript{-1} at 1 mA cm\textsuperscript{-2} for Mn\textsubscript{0.7}Zn\textsubscript{0.3}Co\textsubscript{2}O\textsubscript{4} (x = 0.7) with high cycling stability of 92.1% and excellent rate capability at 10 mA cm\textsuperscript{-2}, which is much higher than pristine ZnCo\textsubscript{2}O\textsubscript{4} and MnCo\textsubscript{2}O\textsubscript{4}. This is mainly attributed to the synergetic effect of its morphology and multiple chemical compositions. The results obtained indicate the role of tuning of compositions in mixed metal oxides to optimize their electrochemical performance.
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<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
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<tr>
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<td>Cyclic Voltammetry</td>
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<tr>
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<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>FC</td>
<td>Field Cooled</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GCD</td>
<td>Galvanostatic Charge-Discharge</td>
</tr>
<tr>
<td>GoF</td>
<td>Goodness of Fit</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>MTMOs</td>
<td>Mixed Transition Metal Oxides</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-Pyrrolidone</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene Fluoride</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating Sample Magnetometer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>ZFC</td>
<td>Zero Field Cooled</td>
</tr>
</tbody>
</table>
CHAPTER 1

Introduction

1.1. General background and problem statement

Sustainable development, population growth, access to clean and safe water, health care, and growing energy demand are some of the major challenges facing humanity in a changing society in the 21st century requiring utmost political and scientific attention [1]. Among these challenges, supplying sufficient, consistent, and affordable energy obtained in an environmentally sustainable way thereby tackling global climate change has attracted massive attention globally [2, 3]. Due to the combined effect of increasing population growth, need for sustainable development and the predictions of future uses, energy consumption will keep on increasing in the following decades. Global energy demand is projected to double by 2050 and it is estimated that the world will need 30 Terawatts of energy by then [4].

Current energy generation mainly relies on fossil fuels (coal, oil, and gas), which supply 80% of the world's energy needs [5]. Detailed analyses and reports indicate that fossil fuels are still expected to remain as the dominant primary energy resources for many long decades to come [6]. Global warming, limited supplies of the fossil-fuels, expanding economy and increasing pollution make it imperative that traditional combustion-based energy sources are replaced with clean and renewable energy sources [7, 8]. Some of these renewable energy sources are include hydropower, wind, solar, geothermal, and tidal, of which solar and wind energy are the most abundant and easily available sources [9, 10]. Implementing renewable energy technologies can improve power reliability and provide localization of power generation, diversify the energy supply, improve energy security by mitigating effects of distant political upheavals in fossil fuel producing regions [11]. As more of the renewable energy sources are integrated into grids, their intermittent nature can have a significant effect on the stability of the grid creating a mismatch between supply and demand. More than likely, near future national strategies to integrate renewable energy, will look at using a mixed bag of energy generation strategies and in doing so require efficient energy storage technologies that can successfully integrate with intermittent sources of renewable energy [12].
Energy storage is considered to be indispensable in the modern era of energy value chain in order to improve efficiency and has recently got the attention of governments, researchers and investors [14, 15]. Electrical energy is a readily accessible and main form of energy used for portable devices, transportation, and stationary grid storage [16]. Electrical energy storage systems allow the storage of electricity produced during either low demand or from intermittent energy sources for later use and hence improve the economics and utilization of renewable energy (Fig. 1.1) [13, 15]. The electrical energy storage technologies need continuous improvement to meet the demands and expectations in terms of ease of use and long-lasting portable power. The key factors to assess the performance of energy storage systems and their potential for practical use are how much energy per unit of mass can be stored (energy density in Wh kg⁻¹ or Wh l⁻¹), and how fast this energy can be retrieved and/or stored (power density in Wh kg⁻¹ or Wh l⁻¹) [17]. In addition, other factors like cycle life, cost and environmental friendliness are also considered [18]. Based on the type of energy, the energy storage technologies can be classified into mechanical, thermal, chemical, electrical, and electrochemical [15, 18-20].

Electrochemical energy storage (EES) systems such as electrochemical capacitors (supercapacitors), batteries, and fuel cells are believed to be the most efficient (Theoretical~80%, achievable~50-75%) and highly attractive energy storage systems among others currently playing a key role in the modern society [21-23]. The one exceptional advantage yielded by electrochemical charge storage devices is that they are not restricted by Carnot limitations, which reduces efficiencies (Theoretical~50%, achievable~25-40%) of all thermal energy storage devices. Electrochemical capacitors (supercapacitors) are systems that utilize electrochemical processes to store and discharge energy, and although they are used in conjunction with recharge-able battery systems, they may one day replace the currently dominant rechargeable battery technology [24-27]. They have several advantageous features when compared to batteries; such as, longer lifecycle, environmentally friendly, high power density, excellent shelf life, faster charge/discharge processes, and highly efficient [24, 26, 27]. The need for materials offering high power-high energy density, faster kinetics, longer cycle life, improved safety and having a lower cost has been a driving force in the development of electrochemical energy storage devices.
Figure 1.1 Schematic of applications of electricity storage for generation, transmission, distribution, and end customers and future smart grid that integrates with intermittent renewables and plug-in hybrid vehicles through two-way digital communications between loads and generation or distribution grids [13].
Recently, nanostructured electrode materials have been effectively employed in EES systems offering improved electrical conductivities and enhanced ion diffusion [28]. Nanostructured transition metal oxides have been extensively explored as promising electrode materials for EESs owing to their higher specific capacity/capacitance than the carbon-based materials and better electrochemical stability [29-31]. However, they still cannot meet the requirements of long cycling stability and high rate performance for practical applications. The main drawbacks associated with transition metal oxides (TMOs) as electrode materials for electrochemical energy storage applications include large volume change, low electrical conductivity and large voltage hysteresis, which depreciate their electrochemical performances and consequently limit their applications in EES devices [31]. Some of the strategies employed to address these limitations include fabrication of composite structurers of TMOs with carbon materials and doping with another transition metal to improve its ionic and electrical conductivity and maintain the structural integrity [32, 33].

1.2. Motivation

Spinel structured transition metal oxides, with a general formula of AB$_2$O$_4$, are emerging as promising electrode materials due to the contributions of both metals in the electrochemical energy storage processes [29, 34]. They offer a robust crystalline structure with a large diffusion pathway, which is a desired property in energy storage processes. So far, numerous spinel type transition metal oxides have been examined as electrode materials for supercapacitors, including Co$_3$O$_4$ [35], Mn$_3$O$_4$ [36], Fe$_3$O$_4$ [37], and together with binary mixed transition metal oxides such as NiCo$_2$O$_4$, MnCo$_2$O$_4$, ZnCo$_2$O$_4$, ZnFe$_2$O$_4$, MnFe$_2$O$_4$, and ZnMn$_2$O$_4$ with an improved electrochemical performance than the single metal atoms [38-41]. Because of the promising performances of the binary mixed oxides, there is a current endeavor to further explore the mixed metal oxides with increased complexity in the composition by incorporating more number of elements, aimed at further improving the performance by addressing capacity retention and electrical conductivity. Currently, ternary mixed transition metal oxides have shown enhanced energy-storage capability than single and binary metal oxides, which can offer multiple redox reaction sites during electrochemical reactions [42-44]. Furthermore, fabricating carbon composites for the metal oxides is also considered as a promising strategy in which much better performance can be obtained due to the synergetic effect of the two components with an improved mechanical flexibility and better electronic
conductivity of the active materials [45]. Therefore, designing a nanostructured electrode material based on the above two strategies can be considered as a possible solution to tackle the drawbacks of transition metal oxides.

1.3. Aims and objectives
1.3.1. Aim of the study

The aim of this research is to explore, determine, provide new insights into the development of ternary mixed transition metal oxides and their composites with carbon nanomaterials and investigate the fundamental physical, chemical, and structural aspects and possible applications for electrochemical energy storage systems.

1.3.2. Objectives

The following objectives were formulated to achieve the aim of the study;

a) Develop and optimize facile and effective synthetic methodologies

b) Synthesis of nanostructured ternary mixed transition metal oxides

c) Fabrication of composites of porous carbon nanomaterials and transition metal oxides

d) Physicochemical, structural, and electronic characterization of the fabricated materials using various analytical instruments such as SEM/EDX, TEM, SAED, XRD, TGA, XPS, FTIR, Raman, BET, and VSM

e) Explore their possible applications as electrode materials for supercapacitors comparing the different compositions.

f) Applications of Mn_{x}Zn_{1-x}Co_{2}O_{4} ternary oxides and carbon nano-composites of Mn_{x}Ni_{1-x}Co_{2}O_{4} oxides as electrode materials for supercapacitors
1.4 Outline of the thesis

The following outline gives a brief overview of the thesis. This thesis comprises of eight chapters; some of which have been published, are currently under review, or will be submitted for publication.

Chapter 1: This chapter presents the problem statement, aims, motivation, and objectives of the study.

Chapter 2: This chapter provides a literature review on the fundamentals and types of electrochemical energy storage technologies, specifically focusing on electrochemical capacitors (supercapacitors), and the various attributes of nanostructured electrode materials.

Chapter 3: The detailed explanation of the materials, synthesis methods, characterization tools and the electrochemical performance techniques utilized in this study is presented in this chapter.

Chapter 4: The sol-gel synthesis, study of the structural, magnetic and electronic properties of spinel $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) materials is presented in this chapter. Various techniques such as powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Vibrating-sample magnetometer (VSM) are employed to reveal the composition, structure, morphology, magnetic and electronic properties the of the spinel oxides with respect to the variation in composition.

Chapter 5: presents the electrochemical performances of carbon coated ternary mixed Mn-Ni-Co oxides as electrode materials for supercapacitors. The performance features of the ternary mixed Mn-Ni-Co oxide-based hybrid electrode compared to the mixed binary counterparts are extensively examined using various electrochemical techniques including cyclic voltammetry, galvanostatic charge-discharge test, and electrochemical impedance spectroscopy. The effect of carbon coating on the electrochemical performance is also discussed.
Chapter 6: This chapter describes the synthesis of Mn substituted Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ oxides by the co-precipitation method and explains the effect of doping on the structural, electronic and magnetic properties of the oxides. The effect of Mn substitution on the morphological, structural, and electronic properties of Mn–Zn–Co oxide microspheres is demonstrated employing different characterization methods including scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy.

Chapter 7: This chapter is a report on investigation of the enhancement of electrochemical performance by Mn substitution in Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ porous microspheres as electrode materials for supercapacitors. Extensive electrochemical studies were made to illustrate the effect of Mn substitution on the supercapacitive performance of the mixed ternary oxides with different compositions.

Chapter 8: In this chapter is presented a summary of the thesis with the key findings, conclusions and a future outlook on the development of ternary mixed transition metal oxides in the electrochemical energy storage field.
1.5 References


CHAPTER 2

Literature Review

2.1. Introduction

Energy, and in particular electrical energy, is essential for human beings to keep our standard of living. Globally, the demand for energy is expected to grow by 28% in 2040 [1]. It is forecasted that most of this increase in energy demand will be due to the rapidly developing countries also known as non-OECD (Organization for Economic Cooperation and Development) countries, which desperately need energy resources to drive their economic growth [2]. As the world economy develops and incomes of individuals rise, more people are likely to get connected to the electricity grid and start consuming energy more. According to International Energy Agency (IEA), the World Energy Council and others, fossil fuels are expected to remain as the dominant primary energy resources for many decades to come and are regarded as the major contributors of the CO₂ emission [1, 3].

Shifting power generation from fossil fuels to renewable and sustainable energy sources, such as wind and solar energy, is a main strategy to tackle the environmental problems related to the continuous consumption of nonrenewable resources and the increasing complexity of power distribution systems. A popular strategy to efficiently use these renewable energy sources is to develop advanced energy storage systems for delivering energy on demand [4-6]. Currently, various energy storage systems are available for different applications and are classified into four types: mechanical, chemical, electrical, and electrochemical [7, 8]. Mechanical energy storage by means of pumped hydroelectricity is the main energy storage method at present. However, electrochemical energy storage (EES) systems in the form of electrochemical capacitors (ECs) and batteries have displayed great potential in powering portable electronics and the electrification of the transportation sector due to the advantageous features of high efficiency, long cycle life, and potential to be implemented based on cheap, sustainable and recyclable materials, and low maintenance cost. Therefore, this review gives a description of the principles, types and materials used for the electrochemical energy storage systems.
2.2. Fundamentals of Electrochemical Energy Storage Systems

Historically, the “Parthian Battery”, which was found in 1936 during archaeological excavations near Baghdad, appeared to be the ancient electrochemical energy storage device that dates back to the Parthian empire (247 B.C.- 224 A.D.) [9]. The battery comprised of an iron rod surrounded by a cylinder made of a rolled copper sheet that was inserted in a clay jar filled with a vinegar solution. It might have been used to generate electricity (1.1 to 2.0 V) for the purpose of silver and gold plating. The first modern electrochemical energy storage (EES) device was the voltaic pile, an electrical battery, invented by Alessandro Volta and reported in 1800 [10]. It comprised of an assembly of zinc and copper metals placed alternately in a stack-like manner separated by paper soaked in an aqueous solution, such as brine or vinegar and produced a steady electric current. The processes taking place in the device were only demonstrated later by Humphry Davy and Michael Faraday which described that it is the occurrence of chemical reactions that is responsible for the production of electricity. This finding marked the emergence of the field of electrochemistry. Consequently, the development of electrochemical energy storage technologies such as batteries and supercapacitors became active in the 19th and 20th centuries [11].

The electrochemical energy storage (ESS) systems have got a considerable amount of global interest owing to their promising capabilities. Most remarkably, they can efficiently store and convert energy reversibly between chemical energy and electrical energy in an environmentally friendly way [12, 13]. Therefore, ESSs can serve as a key technology in improving the quality of human life by making convenient use of energy. There are many requirements that ESSs need to fulfill for various applications such as high energy density, long cycle durability, economical, adaptable design, appropriate safety, and easy fabrication. These attributes are mainly dictated by the intrinsic properties of the materials constituting the ESSs [14]. The various types of electrochemical energy storage technologies can be categorized based on their storage principle and performance parameters, such as specific power and specific energy [15]. The amount of energy stored per unit mass is known as specific energy (Wh kg⁻¹), whereas the rate at which a device stores and discharges energy is known as specific power (Wh kg⁻¹). Based on the ratios of energy density vs. power density and the charge storage mechanism, the electrochemical energy storage technologies can be classified into two main categories; electrochemical capacitors (ECs) and batteries as shown in Figure 2.1.
The fundamental concept behind electrochemical energy storage is the reversible process of converting chemical energy into electrical energy [16]. The driving force for this conversion is the Gibbs free energy change, $\Delta G$, of the species at the surface of the electrodes participating in the chemical reaction;

$$A + B = C \quad \Delta G \text{ (kJ mol}^{-1}\text{)}$$  \hspace{1cm} (2.1)

This free energy change is the same if the reactants A and B were to undergo an electrochemical reaction where the reaction involves the transport of ions and electrons across the cell. As these species are electrically charged, the electrostatic energy transported across by a mole of such species is given by $zEF$, where $F$ is Faraday’s constant, $z$ is the charge number of the transporting species, and $E$ is the cell voltage. Under open circuit conditions, the cell voltage is related to the Gibbs free energy change by,

$$\Delta G = -zEF$$  \hspace{1cm} (2.2)
To put it another way, the potential difference between neutral species at the electrodes determines the underlying force driving an electrochemical cell (Figure 2.2) via a chemical reaction among electrically neutral reactants, A and B, to form an electrically neutral product, C.

**Figure 2.2.** Basic operating principle of electrochemical energy storage, illustrating (a) electrical energy to chemical energy conversion, and (b) chemical energy back to electrical energy for reaction $A + B = C$ [12].

### 2.3. Electrochemical Capacitors and Batteries

Electrochemical capacitors (ECs), commonly known as supercapacitors, are energy storage systems that store charge at the electrode-electrolyte interface or through redox reactions on the surface of electrode [17]. These devices are advantageous and potential candidates in a wide range of applications due to their high power densities (>10 kW kg$^{-1}$), exceptional reversibility (≥90-95%) and long life span (>100,000 cycles) [17, 18]. The comparisons between battery and supercapacitor are listed in the Table 2.1. Some important characteristics that must be considered when comparing supercapacitors and batteries are the energy density, power density, self-discharge, cycle life, the operative temperature limits, and charge-discharge durations. Electrochemical capacitors can produce large power and energy density compared...
to a conventional capacitor and longer life cycles than battery because of the surface reactions of electrode materials to store charge [19-21]. Based on the comparisons, both ECs and batteries can provide unique solution to the energy storage and considered as complementary technologies. According to the power and energy density, supercapacitors lie between batteries and conventional capacitors as shown in the Ragone plot in Figure 2.2. Thus, supercapacitors can link the gap between capacitors and batteries [5]. The power density requirements, fast charge/discharge cycle, low self-discharging and high electrochemical stability are beneficial features of supercapacitors [5, 6].

Batteries are another major class of electrochemical energy storage system that store energy through redox reactions at the electrodes [23]. A battery is usually represented as a technology with high energy density and low power density as illustrated on the Ragone plot in Figure 2.3. Among the rechargeable batteries, Lithium ion batteries (LIBs) are the high performing technology used in common portable electronic devices due to their low weight and high energy density and have reasonably attracted the biggest commercial and research interest [24-
They currently dominate more than half of the global battery market because of their high energy density, portability, acceptable life cycle, and their compact size that provides flexibility in product design, especially for portable electronics and communication devices. The first commercial LIB was introduced in 1991 by Sony Corporation, which is based on a graphite anode, a lithium cobaltate (LiCoO₂) cathode, and an organic electrolyte [24]. The principal advantage of LIBs over other battery technologies is its much higher specific power and specific energy.

Table 2.1. Comparison of the performances for a supercapacitor and battery [27, 28]

<table>
<thead>
<tr>
<th>Function</th>
<th>Supercapacitor</th>
<th>Battery (Li-ion battery)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating voltage per cell (V)</td>
<td>0-2.7</td>
<td>3-4.5</td>
</tr>
<tr>
<td>Charge time</td>
<td>ms-min</td>
<td>0.5-10 h</td>
</tr>
<tr>
<td>Discharge time</td>
<td>ms-days</td>
<td>1-15 h</td>
</tr>
<tr>
<td>Energy density (Wh L⁻¹)</td>
<td>10-20</td>
<td>200-400</td>
</tr>
<tr>
<td>Power density (W L⁻¹)</td>
<td>40000-120000</td>
<td>1300-10000</td>
</tr>
<tr>
<td>Cycle life</td>
<td>10000-100000</td>
<td>200-1000</td>
</tr>
<tr>
<td>Charge/discharge efficiency (%)</td>
<td>80-95</td>
<td>85-95</td>
</tr>
<tr>
<td>Temperature range (°C)</td>
<td>-40-70</td>
<td>-20-60</td>
</tr>
<tr>
<td>Self-discharge (%)</td>
<td>20-40</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td>Coulombic efficiency</td>
<td>0.85-0.98</td>
<td>0.7-0.85</td>
</tr>
<tr>
<td>Risk of explosion</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Charge rate</td>
<td>High</td>
<td>kinetically limited</td>
</tr>
</tbody>
</table>
The lithium-ion battery (LIB) is composed of anode, cathode, separator, and electrolyte. Figure 2.4 below shows a diagram of operation principle of a Li-ion battery. In a conventional LIB, the cathode is usually made of layered metal oxides whose composition is denoted by LiMO$_2$, which are the spinel lithiated metal oxides, LiCoO$_2$ (LCO) being the most successful. Graphite is used as the anode and is separated by a porous membrane from the cathode, which allows the Li$^+$ ions and preventing the direct contact of electrodes to avoid short-circuiting. Graphite stores Li$^+$ ions into the spacings found between the graphitic monolayers based on the intercalation mechanism. During charge-discharge process, the Li-ions are shuttled between the lithium metal oxide (LMO$_2$) and a layered graphite anode passing through the electrolyte. Electrons pass through the external circuit in order to combine with the extra positive charge (Li$^+$) in the electrode [13]. Electrolytes used are aprotic, non-aqueous solvents [14].

![Figure 2.4. Structure and principle of operation of a Li-ion battery [29]](image-url)
2.4.  Supercapacitors

2.4.1.  Brief history of supercapacitors

The beginnings or earliest recorded invention of capacitor technology was first reported in 1745 with the development of the Leyden jar, which was made of glass jar and metal foil [30]. The glass jar served as a dielectric material, where its interior and exterior surfaces were covered with metal foils, which acted as electrodes. Since then, the capacitor technology has advanced well through research. The first electrochemical capacitor (electric double layer capacitors-EDLCs) were patented in 1957 by Becker [31], which were made by using activated charcoal plate and a sulfuric acid electrolyte. He found that its capacitance is considerably higher than conventional supercapacitor due to the high specific surface area of porous carbon. The charge storage mechanism was later found to be based on the formation of a double layer known as Helmholtz double layer, which occurs due to the adsorption of electrolyte ions onto the surface of electrode material. Carbon materials like activated carbons (ACs), carbon aerogels, carbon nanotubes (CNTs), and graphene having high specific surface area are unique class of materials for EDLC type supercapacitors and have been applied and investigated [32, 33]. At present, there are various commercially high performing supercapacitors in the market.

2.4.2.  Operation Principle of Supercapacitors

Energy storage in supercapacitors and most electrochemical energy storage systems follows similar principle, which takes place by separating the connection between the two electrodes into two different charge transport paths. One by an ionically conducting but electronically insulating electrolyte and, another electronically conducting but blocking ions (Figure 2.3) [34]. Electrochemical energy storage in electrochemical capacitors (supercapacitors) is based on charge storage at the electrochemical interface in contrast to batteries where it takes place in the electrodes or in the chemical bonds of fuels as in fuel cells.

Capacitors store energy physically as equivalent amounts of opposite charges accumulated on plates, called electrodes, on either side of an insulating (dielectric) material [35]. At the interface of electrode/electrolyte, opposite charges accumulate on the surface of electrode
(within the porous structure) and in the electrolyte forming a Helmholtz double layer. This double layer leads to the formation of a capacitance [36]. Capacitance is the ability of capacitors to store charge as a function of changes in the electric field between electrodes. Capacitance is proportional to the surface area of the material ‘A’ and to the relative permittivity also called dielectric constant ‘ε’ of the medium between the plates, and inversely proportional to the thickness ‘d’ of the double layer according to the equation (2.3):

$$C = \frac{A \cdot \varepsilon}{d}$$

(2.3)

where C is the capacitance in farads (F).

The parameters energy density (E) and power density (P) are important to evaluate the performance of supercapacitors. The maximum amount of energy (E) that can be stored and provided by an electrochemical capacitor is proportional to its capacitance (C) and its operating voltage (V) is given in equation (2.4) as:

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

(2.4)

The peak power (power density) (P) is the energy delivered per unit time to an external load given as:

$$P = \frac{V^2}{4R}$$

(2.5)

where V is the cell voltage (in volts) and R is the equivalent series resistance (ESR) (in ohms). The capacitance of the cell is determined largely by the electrode materials and the cell voltage is limited by the electrolyte solution. The different types of resistances related to the inherent properties of the electrode material and electrolyte solution, charge transfer process, and resistance due ionic-diffusion in the electrode result in the overall equivalent series resistance (ESR) [37]. Therefore, for supercapacitors to achieve high performance, they must fulfill the requirements of having a large capacitance value, high operating cell voltage and minimum
ESR. Hence, the advancement of both the electrode materials and electrolytes is essential in order to improve the overall performance of the supercapacitor.

Generally, supercapacitor devices are composed of two electrodes, an electrolyte, conductive current collectors and a membrane separator to separate the two electrodes within an electrolyte (Figure 2.5). Among the components, electrode materials are an important part in determining the performance of electrochemical capacitors [38]. The energy storage mechanism in supercapacitors takes place through either ion adsorption at the electrode/electrolyte interface [39], or reversible faradaic reactions [40]. Based on their mechanism of charge storage, supercapacitors are classified into two broad categories known as electrochemical double layer capacitors (EDLCs) and pseudocapacitors [6]. Another category which makes use of both mechanisms and exhibiting a much higher capacitance is called hybrid capacitors [41]. In EDLCs, energy is stored by ion adsorption and by forming an electrochemical double layer at the surface of the electrode leading to accumulation of charge at the electrode-electrolyte interface [20]. In contrast, pseudocapacitors store energy through fast surface redox reactions taking place at the surface of electrodes [37].

Figure 2.5. Schematic diagram of a supercapacitor
2.4.3. Electrochemical Double Layer Capacitors (EDLCs)

EDLCs are electrochemical capacitors that store charge electrostatically through adsorption of ions onto the surface of an electrode making use of an electrical double layer of charge developed at the electrode-electrolyte interface [42]. This kind of charge storage involves only atomic scale distances and interaction allowing EDLCs to charge or discharge fully in seconds [43]. Electrode materials for EDLCs require an active material with high accessible specific surface area and high electrical conductivity. The most investigated and favorable materials for EDLCs are mainly carbon materials, like activated carbon, carbon nanotubes, and graphene sheets [32, 44-46].

The arrangement of the charges in the Helmholtz double layer during the charge/discharge processes results in a displacement current. The charge storage mechanism does not occur at a definite potential and thus exhibit no plateaus or peaks as shown in Figure 2.6(a&b). The current has a linear correlation with a sweep rate as given in equation (2.6):

\[ I = C \frac{dV}{dt} \]  

where, \( I \) is the current (A), \( C \) is the capacitance (F), \( V \) is the potential (V) and \( t \) is the time (s). This results in a distinct rectangular cyclic voltammograms (Figure 2.6(a)).

EDLCs can be differentiated from batteries by their unique electrochemical signature, which can be demonstrated by employing potentiostatic and galvanostatic methods, as shown in Figure 2.6. They represent two extreme types of behavior of electrochemical energy storage devices [21]. The different methods for achieving double-layer capacitance are characterized by classic rectangular cyclic voltammograms and a linear time-dependent change in potential at a constant current [47]. In batteries, the cyclic voltammograms are characterized by faradaic redox peaks, often with rather large voltage separation between oxidation and reduction because of phase transitions (panel e in Figure 2.6). The presence of two phases is indicated by the voltage plateau in galvanostatic experiments (panel f).

Owing to the electrostatic type of charge storage at the interfaces, EDLCs show excellent cyclic stability, which is useful in various applications ranging from large scale grid services to hybrid
vehicles to portable electronics [48, 49]. However, due to their low specific energy they can still not meet the strict prerequisites for high energy density devices, restricting their large-scale application and thus prompts the need for storage mechanisms beyond electric double-layer capacitance [48]. The most common strategy to increase their energy storage capability is the integration of electrode materials that utilize fast faradaic redox reactions such as transition metal oxides, redox-active polymers, and hydroxides [50].

Figure 2.6. Typical cyclic voltammogram curves (top) and galvanostatic charge/discharge curves (bottom) for different types of electrode materials a,b) capacitive-type material [51] c,d) pseudocapacitive material [52] and e,f) battery-type material [53] at different sweep rates and current densities, respectively, highlighting their unique electrochemical features.

2.4.4. Pseudocapacitors

Pseudocapacitors store energy by utilizing a reversible, rapid faradaic redox reactions occurring on the surface or at the interface between an electrode and electrolyte, where charge transfer takes place through electrosorption or intercalation processes without bulk phase
transformation [54, 55]. They develop a different type of capacitance at electrodes where the Faradaic charge depends linearly on the applied voltage exhibiting a capacitor-like behavior known as “pseudocapacitance”, which resembles a battery behavior but is different from the capacitive behavior of EDLCs [56]. The pseudocapacitance ($C_{pc}$) is proportional to the charge transferred and can be defined by the equation [57]:

$$C_{pc} = q \frac{dX}{dV}$$

where $q$ is the faradic charge required for sorption of ions, $dX$ is the change in fractional coverage of the surface and $dV$ is the change in potential. From equation (2.7) it can be realized that the pseudocapacitance $C_{pc}$ is not constant. The faradaic process allows them to offer a specific capacitance of ~100 times higher than that of EDLCs and higher energy density [58]. The electrochemical behaviors of pseudocapacitors exhibit features of both a rechargeable battery and an EDLC [59] and thus exhibit both linear and plateau regions in the GCD voltage profile as shown in Figure 2.6(c&d).

Pseudocapacitors have created enormous interest as the next generation energy storage as they exhibit favorable features of both EDLCs and batteries and have great potential to address the critical gaps between chemical and capacitive energy storage devices [60]. Although both rechargeable batteries and pseudocapacitors store energy through redox reactions, pseudocapacitive behavior is not diffusion-controlled unlike batteries making them advantageous in terms of power density [61]. Despite these beneficial features, they display poor life cycles. Therefore, to understand the full potential of pseudocapacitors, novel electrode materials and new physical/chemical processes are needed to improve both their energy and power densities [62].

The electrode materials commonly employed for pseudocapacitors include transition metal oxides, hydroxides and conducting polymers [63, 64]. In the past decades, transition metal oxides were investigated as attractive pseudocapacitive materials due to their multiple oxidation states, which allows for the occurrence of fast faradic redox reactions that can improve the capacitive behavior [65, 66]. Transition metal oxides such as RuO$_2$, NiO, MnO$_2$, IrO$_2$, Co$_3$O$_4$, Fe$_2$O$_3$, NiCo$_2$O$_4$ have been intensively studied for use as pseudocapacitive electrode materials because they exhibit fast charge and discharge like a conventional double-
layer capacitor, but with much higher specific capacitances than EDLCs [67]. RuO$_2$-based electrodes offer one of the best examples of pseudocapacitance because they exhibit almost constant capacitance over a wide voltage range with excellent reversibility and cycle life [68]. Nevertheless, the acute toxicity, high cost and less availability of ruthenium elements have hindered its wide range applications. Pseudocapacitive materials hold the promise of achieving battery-level energy density combined with the cycle life and power density of EDLCs.

2.4.5. Electrochemical performance evaluation for EES

Generally, the electrochemical characteristics of electrode active materials for EES devices are evaluated in either a three-electrode (3E) or a two-electrode (2E) configurations [69]. The three-electrode configuration focuses on the evaluation of electrode materials by screening electrode materials with minimal amounts of the active material. The two-electrode system, resembling the structure of fully assembled supercapacitors, evaluates the performance of a cell under nearly ideal conditions.

The three-electrode system consists of a working electrode, reference electrode, and counter electrode, which are all connected to a potentiostat, which controls the electrode potential while recording the change in electrode current with potential, or controlling the current passing through the electrode and then recording the change in electrode potential with current. A two-electrode cell setup is composed of a pair of closely spaced electrodes containing the electrode active materials and separated by an ion permeable, but electrically insulating, separator [70]. Electrochemical performance of a 2E cell configuration depends on both the electrodes in a given electrolyte. Depending on the type of the electrode active material on each of the electrodes, supercapacitors can be grouped into two major categories known as symmetric and asymmetric. In an asymmetric configuration, the positive and negative electrodes operate in different potential ranges, thus the operating potential window of the device can be significantly extended [71].

A 2E cell setup does not provide any information about the components of the cell and only considers the device as a whole. Thus, for an in-depth study of the active materials, and for
obtaining detailed information on the individual components of a device, the 3E cell configuration is the only choice.

To evaluate the performance of supercapacitors, three essential parameters, specific capacitance $C_{sp}$, operating voltage $V_o$, and equivalent series resistance $R_{ES}$, are often used to assess their energy and power performance [72]. These parameters are measured by cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy techniques. The parameters are usually sufficient for commercial products where the materials, fabrication, and cell design are all fixed. In addition to the aforementioned parameters, there are some other tests, namely, retention capability, cycling stability, coulombic efficiency, self-discharge, and time constant that provide insights into the performance of an energy storage system and is summarized Figure 2.7.

![Figure 2.7](image_url)  
*Figure 2.7. An illustration of key performance metrics, test methods, major affecting factors for the evaluation of supercapacitors [72].*
2.5. Nanostructured electrode materials for supercapacitors

The main challenge for supercapacitors is their low energy density. Since their electrochemical performance is strongly correlated to the structure and intrinsic properties of the electrode materials, the energy density can be improved by using electroactive materials having high specific capacitance and optimized structures [73]. Designing high-performance supercapacitor electrodes requires considering parameters such as accessible surface area and porosity, electrical conductivity, specific capacitance, rate capability, cycle stability, and thermodynamic stability for a wide operational potential range [74]. Moreover, the cost of the active materials used in an electrode and their effect on the environment should also be considered as well.

Nanostructured electrode materials have displayed outstanding electrochemical properties in realizing high-performance supercapacitors and help in overcoming several difficulties associated with bulk materials [38]. They can offer enormous advantages in rate enhancement and storage capacity. The main benefits of nanostructured electrode materials compared to their bulk counterparts include:

(1) **Large surface area**: Nanostructured materials have large surface-to-volume ratio and hence large surface free energy. This in turn enhances the contact area at the electrode/electrolyte interface and increase the number of active sites for electrode reactions leading to improvement in power density (or rate capability), energy density and life cycle of the electrode materials [75].

(2) **Short diffusion length**: Materials with the nano-size dimensions can potentially enhance the transport of ions and electrons by reducing the path length in the electrode materials and thus significantly increasing the rate of electrochemical processes. Nanostructuring of materials can reduce the diffusion time ($\tau$) of ions in electrode materials according to the equation (2.7) [76]:

$$\tau = \frac{L^2}{4\pi D}$$

---

27
where \( L \) is diffusion length and \( D \) is diffusion coefficient. The diffusion time varies directly with the square of diffusion length and thus nanomaterials can greatly enhance ion diffusivity to achieve fast charge storage and high rate capability.

(3) **Enhanced ionic and electronic conductivity**: The low size dimensionality of nanomaterials can lead to a redistribution of atomic charges on the surface and improve the contact between electrode and electrolyte, which enhances the charge transfer process [77].

(4) **Enhanced structural stability**: Materials at the nanoscale dimensions may cause modification of phase transformations upon electrochemical reactions and provide improved tolerance to the pulverizing volumetric changes. This will minimize or eliminate performance fading occurring due to electrical isolation of active electrode materials. [77-79].

**2.5.1. General overview of electrode materials for supercapacitors**

Based on the nature of electrode materials, three main types of electrode materials have been explored extensively for supercapacitor applications: i) EDLC based materials, ii) surface redox based pseudocapacitive materials, and iii) intercalation-type pseudocapacitive materials. Porous carbon has been widely used as the electrode material for EDLCs due to its abundance, high surface area, large power density, and high conductivity. Redox pseudocapacitance occurs when ions are electrochemically adsorbed onto the surface or near surface of a material with a concomitant faradaic charge-transfer. Transition metal oxides and conductive polymers have advantages of good mechanical properties, fast charge/ion transport, and high conductivity. These advantages make them attractive for applications in SCs. However, the easy deterioration of material structure caused during charge/discharge process normally leads to poor cycling stability. Transition metal based materials such as transition metal oxides/hydroxides [80], sulfides, selenides, phosphides, and MXenes are advantageous in that they can store much more energy than carbon materials due to the faradaic electron transfer involved in the electrochemical process [58, 81]. Thus, currently there are numerous investigations in making use of this materials specially the transition metal oxides. In intercalation pseudocapacitance, charge storage occurs in the bulk of a redox active material.
accompanied by faradic charge transfer. The kinetics are not diffusion-limited and instead are limited by surface processes so that the overall behaviour seems capacitive.

2.5.2. Carbon-based electrode materials

Because of the unique properties of carbon nanomaterials such as large surface area, high conductivity, high thermal stability, low cost and exceptional chemical inertness carbon is the most commonly explored electrode material used in a wide range of energy storage technologies [32]. The existence of different allotropic forms of carbon such as fullerenes, graphite and nanotubes with different nanostructures [37] and its ease of production with different porous structure, have made it as the most suited electrode material for supercapacitors. Carbon nanomaterials like activated carbon (AC), carbon nanotubes (CNTs), graphene, and carbon nanofibers (CNFs) are the most widely studied categories [82].

Activated carbons (ACs) are the first reported electrode materials for EDLCs. They are porous carbon materials with a high surface area up to 3000 m² g⁻¹, good electrical properties and low cost. They are produced from carbonaceous source materials through a mild oxidation process [83]. Although they have high surface area and various pore structures, activated carbons have low specific capacitance in the range of 94 - 413 F g⁻¹, which is not proportional to the surface area [84]. ACs have been commercially employed as supercapacitor electrode materials. However, their applications are still constrained due to the limited energy storage and rate capability.

Carbon nanotubes (CNTs) are another class of carbon material with a narrow pore size distribution, high surface area, low resistivity, and high stability [85]. They are composed of mesopores and exhibit surface areas of about 10² m² g⁻¹. These features of CNTs has led to their investigation as electrode materials for EDLCs and specific capacitances of 15-300 F g⁻¹ have been reported [86].

Other carbon materials such as activated carbon fibers (ACFs), carbon aerogels (CAGs), graphene and carbon onions have also been studied for supercapacitor applications. However, the performance of carbon materials as electrodes is still not sufficient for the high-performance
applications and needs improvement. Therefore, pseudocapacitive materials are preferred in this case as they provide higher specific capacitance than capacitive type carbon materials as they combine both EDLC and pseudo capacitive behavior.

2.5.3. Mixed transition metal oxide-based electrodes (MTMOs)

Pseudocapacitors based on the faradic-type active materials have been demonstrated to produce much higher specific capacitance and energy density than purely carbon based EDLCs [87, 88]. Electrochemically active materials suitable for Faradaic supercapacitors should have characteristics including being stable without structural change, having two or more oxidation states allowing multielectron transfer, and being conductive to both electrons and ions. Metal oxides can have such characteristics and are now explored extensively as electrochemically active materials for the next generation of supercapacitors.

Transition metal oxides are regarded as an attractive electrode materials because of their high specific capacitance, low resistance and high energy density making it easier to construct high performance supercapacitors [67]. Among the transition metal oxides RuO₂ is the first reported and most studied because of its exceptionally high theoretical capacitance of 1200–2200 F g⁻¹, very high electrical conductivity and excellent chemical stability [89]. However, its high cost has limited the practical application and prompted to look for other transition metal oxides. In the recent decades, single-component metal oxides such as MnO₂, NiO, Co₃O₄, Fe₂O₃, have been extensively investigated as potential electrode materials [58, 90-92]. But, the performance of these single-component transition metal oxides is restricted by their poor electrical conductivity and low specific capacitances. Therefore, many studies have focused recently on the development of new electrode materials that comprise of multicomponent mixed transition metal oxides (MTMOs), rather than a single metal component [93]. The mixed transition metal oxides (MTMOs) display higher specific capacitances, better rate capabilities, and long-term cycling stability owing to their multiple oxidation states and multi-metal component system, which leads to rich electroactive sites and high electrical conductivity [94-97].
2.5.3.1. Ternary mixed transition metal oxides

Mixed transition metal oxides (MTMOs) based on spinel structure are fascinating class of electrode materials exhibiting specific capacitances 10-100 times higher than the electric double layer type electrodes [98, 99]. In this context, binary mixed transition metal oxides of AB$_2$O$_4$-type, specifically those based on cobalt such as NiCo$_2$O$_4$, ZnCo$_2$O$_4$, CuCo$_2$O$_4$, MnCo$_2$O$_4$, and FeCo$_2$O$_4$ have been explored as high-performance electrode materials for supercapacitors and superior to single transition metal oxides [100-106]. Due to the promising performances of binary systems, there is a current endeavor to further investigate more complex ternary transition metal oxides, which have been an attractive area of exploration recently due their superior performance [107, 108]. Incorporating more metal ions into the spinel structures leads to improved charge transfer kinetics and ion diffusion, thereby allowing for enhanced supercapacitive properties making ternary systems more attractive electrode materials.

The spinel structures of transition metal oxides are described by the general formula of AB$_2$O$_4$, where A and B are the divalent and trivalent metal cations, respectively [109]. Their structure is characterized by a face centered cubic close-packing type and belongs to a Fd3m space group consisting of divalent A (M$^{2+}$) and trivalent B (M$^{3+}$) cations distributed among the tetrahedral (8a) and the octahedral (16d) interstitials and the oxygen atoms are assigned in the cubic close-packed structure as shown in Figure 2.7. The distribution of the cations between these two sites depends mainly on the nature of the cations incorporated into the structure. Usually, the tetrahedral interstices are smaller than the octahedral interstices and, therefore, cations with smaller radii prefer to occupy the A sites, while larger cations prefer to occupy the B sites [110]. This cation distribution is important as it will result in the corresponding change of the two structural parameters a and u, lattice parameter and oxygen parameter, respectively. Hence, based on cation distribution spinels can be categorized to normal and inverse [111]. Intermediate distributions can also occur between the normal and inverse spinels. In normal spinels, the divalent A and trivalent B cations occupy the tetrahedral and octahedral sites, respectively. In inverse spinels, on the other hand, half of the trivalent B cations reside on the tetrahedral sites, and the remaining trivalent B and divalent A cations occupy the octahedral sites.
Ternary mixed transition metal oxides that are based on spinel cobaltites (MCo$_2$O$_4$) have been recently reported as high-performance electrode materials for supercapacitors [113-117]. Tamboli et al. [118] reported the preparation of hierarchical Ni substituted Mn$_{1-x}$Ni$_x$Co$_2$O$_4$ metal oxides with a good control over morphology with varying composition and offering outstanding supercapacitive performance as electrode materials for a supercapacitor. The highest specific capacitance of 1762 F g$^{-1}$ was achieved for Mn$_{0.4}$Ni$_{0.6}$Co$_2$O$_4$ with high cycling stability, which is much higher than the binary MnCo$_2$O$_4$ and NiCo$_2$O$_4$ oxides. It also exhibited high energy density of 35.2 Wh kg$^{-1}$ in an asymmetric capacitor device as a positive electrode. Similarly, Chang et al.[119] synthesized ternary Mn-Ni-Co mixed oxides NiMn$_x$Co$_{2-x}$O$_{4-y}$, manganese substituted nickel cobaltite, by a co-precipitation method. The structural properties and electrochemical performances were highly affected by the substitution of Mn for Co and a specific capacitance of 110 F g$^{-1}$ was obtained for NiMn$_{0.5}$Co$_{1.5}$O$_4$ (x = 0.5). Mariappan et al. [120] have obtained monodispersed Mn$_{0.8}$Ni$_{0.2}$Co$_2$O$_4$ mesoporous microspheres through ammonium bicarbonate-assisted solvothermal method and displayed a specific capacitances of 1822 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$, which is higher than that of the undoped MnCo$_2$O$_4$ oxide.

Figure 2.8. The spinel crystal structure. Small red spheres are the oxygen positions. Light yellow tetrahedrons and light blue octahedrons represent the tetrahedral and octahedral sites, respectively. The figure is generated using VESTA [112].
Other than the Mn-Ni-Co ternary systems, Zn-Mn-Co and Zn-Ni-Co oxides have also been identified as potential electrode materials due to the enhancement of the electrical conductivity and electrochemical performance by Zn [108, 117]. Recently, Hussain et al. [116] synthesized binder free Zn-Mn-Co ternary oxide nanoneedles with a high specific capacity of 849 C g\(^{-1}\) at a current density of 1 A g\(^{-1}\). Besides, it exhibited an exceptional cycling stability with a very high coulombic efficiency after 8000 cycles. Mary et al. [121] reported Mn-doped ZnCo\(_2\)O\(_4\) synthesized by a hydrothermal method with a 10 wt% Mn-doped electrode materials having a maximum capacitance of 707.4 F g\(^{-1}\). This study has also demonstrated the important role of Mn doping on the structural and electrochemical performances of ZnCo\(_2\)O\(_4\). Mariappan and co-workers [122] have investigated the structural properties and electrochemical performances of spinel-type porous Zn\(_{0.2}\)Ni\(_{0.8}\)Co\(_2\)O\(_4\) microspheres prepared by a hydrothermal method for electrochemical energy storage applications in LIBs and supercapacitors. The mesoporous microspheres were found to exhibit a high specific capacitance of 2081 F g\(^{-1}\) at 2.5 A g\(^{-1}\) and good cycling performance as electrode materials for supercapacitors. Another study on ternary Zn-Ni-Co oxides for applications in supercapacitors was reported by Wu and his group [117]. They reported mesoporous cobalt-nickel-zinc ternary oxide nanosheets prepared hydrothermally on nickel foam and displaying a high specific capacity of 1172.2 C g\(^{-1}\) at 1 A g\(^{-1}\) making them suitable materials for applications in high-performance supercapacitors. Hu et al. [123] have fabricated flower-like nickel-zinc-cobalt mixed metal oxide nanowire arrays hydrothermally on nickel foam and found that the mixed metal oxides manifested high specific capacitance of 776 F g\(^{-1}\) at a current density of 2 A g\(^{-1}\). They also displayed extended cycling stability with 88.9% capacitance retention after 10,000 cycles.

In addition to the above-mentioned ternary oxides, there are also some reports on systems prepared by substituting elements like Mo, Fe, Cu, and V owing to their good capacitive performance, low cost and environmentally friendliness [124, 125]. For instance, Vijayakumar et al. [126] have prepared Cu-Zn-Co oxide nanoflakes for applications as a binder free electrode for energy storage. They displayed a specific capacitance of 178 C g\(^{-1}\) at a current density of 1 A g\(^{-1}\) as electrode materials for supercapacitors. In another study, mesoporous Fe–Ni–Co ternary oxide nanoflakes were prepared by Sahoo et al. [127] and showed a specific capacitance of 867 F g\(^{-1}\) at a current density of 3 A g\(^{-1}\). She et al. [124] manufactured nickel-cobalt-molybdenum metal oxide nanosheets, which possessed high specific capacitance of 1366 F g\(^{-1}\) at the current density of 2 A g\(^{-1}\) and demonstrated an excellent cycling stability.
2.5.3.2. Ternary mixed transition metal oxides/carbon composites

Pseudocapacitive electrode materials are of enormous interest in the advancement of supercapacitors with improved energy storage capacity. However, the poor electrical conductivity and slow ion diffusion of mixed transition metal oxides (MTMOs) lead to low specific capacitance and/or very poor cycling performance hindering their practical applications [128]. Therefore, fabrication of composites of carbon and MTMOs, which can benefit from the EDLC and faradaic characteristics of the active material, is an effective strategy to improve the electrical conductivity and hence the electrochemical performance forming hybrid electrodes [89]. The hybridization of MTMOs with carbonaceous materials develop synergistic effect by providing large accessible surface area to the active material and enhancing the kinetics of ions and electron diffusion at the electrode/electrolyte interface [129]. In hybrid electrodes, the requirements for the carbon materials include a high specific surface area, suitable pore structure that provides easy access for electrolyte ions, and a graphitic structure that provides high electrical conductivity [130].

Metal oxide/carbon composites can be prepared by either loading metal oxides on to an already fabricated carbon or through in situ cooperative formation [131]. Fabricating hybrid electrode materials by loading of metal oxides onto a carbon support is a very appealing technique to exploit the surface area of the hybrid material and obtain nanoscale mixing of the two components. There are very few reports made on composites of ternary transition metal oxides and carbon structures. In this context, Wu et al. [132] prepared reduced graphene oxide nanosheet supported Mn–Ni–Co ternary oxides via a simple coprecipitation route followed by calcination. They found that the hybrid electrode exhibited remarkably high specific capacitance of 646.1 C g\(^{-1}\) at 1 A g\(^{-1}\) demonstrating the capacitive enhancement effect of the reduced graphene oxide nanosheets. Similarly, Sanchez et al. [133] have reported porous NiCoMn ternary metal oxide/graphene nanocomposites as electrode materials for hybrid energy storage devices. The composite electrode material showed better capacity and rate performance than the bare NiCoMn ternary oxide due to the synergistic effect.
2.5.4. Typical synthesis methods of mixed transition metal oxides

Several methods for the preparation of nanostructured mixed transition metal oxide materials with various morphologies have been employed widely. The main techniques include sol-gel, co-precipitation, hydrothermal, molten salt method, electrospinning, reverse micelle method and sacrificial template methods.

2.5.4.1. Sol-gel technique

Sol-gel is a multistep wet-chemical method and is based on the formation of a sol from precursors and its transformation into a network structure known as a gel [134]. It has many advantages over traditional synthetic methods such as simplicity, high-yield, low operation temperature, and low cost. In addition, it allows for a formation of highly pure, controlled composition and homogeneous multi-component metal oxide nanostructures instead of a mixture of simple oxides [135, 136]. Metal salts are the typical precursors used in this method together with common chelating agents such as citric acid [137], EDTA (ethylenediaminetetraacetic acid) [138], and propylene oxide [139, 140]. This method involves four key processes; preparation of sol, the transformation of sol into a gel, drying of the gels to form xerogels, and the final calcinations [141]. In this process, control of the different parameters such as temperature, pH, type of chelating agent, and reaction time are key factors in the formation and final morphology (particle size, shape, pore size) of the obtained powders and their electrochemical performance as well.

So far, numerous MTMOs prepared by sol-gel technique have been reported for supercapacitor applications [137, 142]. For example, Liu et al. [142] fabricated mesoporous NiO/NiCo2O4/Co3O4 composite by sol-gel process by employing citric acid as a complexing agent. The composite material exhibited a high specific capacitance of 1717 F g⁻¹, outstanding rate performance and cycling stability with capacitance retention of 94.9% after 1000 cycles. Bhujun et al. [137] also reported mixed ternary transition metal ferrite nanocrystallites prepared by the sol–gel method using citric acid and achieved a specific capacitance of 221 F g⁻¹ at 5 mV s⁻¹.
2.5.4.2. Coprecipitation

Coprecipitation is a simple and common method that involves mixing of more than one component in solution and simultaneous precipitation on the addition of precipitants [143, 144]. It occurs only if the concentration of one solid is more than the equilibrium solubility of the host solid [145]. This method offers advantage of the large-scale powder production due to its exceptional stoichiometric control and high degree of homogeneity. Besides, relative rates of nucleation and growth during the synthesis process are the contributing factors in obtaining desired size and size distribution of the products.

2.5.4.3. Hydrothermal method

Hydrothermal method, also known as solvothermal method is an extensively employed technique for the preparation of nanostructured mixed transition metal oxides with a precise size and morphology. It is a solution method of formation and growth of crystals carried out in a closed system above ambient temperature and pressure [146, 147]. It should be mentioned that the hydrothermal method can also be extended to non-aqueous systems using organic solvent like ethanol and ethylene glycol also known as solvothermal synthesis [98]. One of the peculiar benefits of this technique is its capability in precisely controlling the synthetic conditions, which is a key in control of morphologies and particle size distribution and it produces highly pure products as well [148]. A wide range of MTMOs with various oxidation states and phases are synthesized by a hydrothermal approach and reported as supercapacitor electrode materials [116, 117, 126, 149]. Furthermore, it does not involve toxic chemicals, injurious surfactants or templates and is environmentally benign.

2.5.4.4. Microwave-assisted synthesis

Hydrothermal technique is convenient for the synthesis of MTMOs with controllable composition and nanostructure. Nevertheless, it requires long duration of reaction and is therefore a time-consuming process. Thus, microwave assisted synthetic technique is
considered as a simple and rapid method for the preparation of nanostructured mixed transition metal oxides [63]. Compared to the conventional heating, microwave heating can provide a more controlled heating and benefit of efficient growth of nanomaterial and reduced reaction time to minutes or seconds [145, 150]. In addition, this method can suppress side reactions and speed up the crystallization process, resulting in the formation of highly pure nanostructures and improved yield [151]. Microwave-assisted routes have been employed for synthesis of a great variety of binary and ternary transition metal oxide nanoparticles and nanostructures [152] such as 3D Ni-Co-Mn oxide nanoflakes [153], CoO nanoparticles [154], NiCo2O4 microspheres [155].

2.5.4.5. Template method

Sacrificial template method has been largely explored for the synthesis of hollow metal oxides based on templates. This route of synthesis for nanostructured hollow metal oxides involves template preparation, assembling of the targeted materials over the template, and removal of the template [156, 157]. This method is considered as a facile and versatile route for the fabrication of various mixed transition metal oxides and carbonaceous materials with hollow structures for energy storage applications [158-160]. The common templates used include carbonaceous spheres, silica, and polymer spheres, which are used to produce porous mixed metal oxides with a high specific surface area. Self-sacrificial templates, in which the precursor plays the roles of both the template and the reactant, are also being used as an alternative type of templates which includes metal-organic frameworks (MOFs) [161, 162], oxalates [163], and carbonates [164]. Among these templates, metal-organic frameworks (MOFs) are nowadays regarded as perfect self-sacrificial templates for the synthesis of mixed transition metal oxides and their composites with carbon in situ for energy storage applications.

2.5.4.6. Electrodeposition

Electrodeposition is another simple method used in the synthesis of MTMOs and exhibiting the advantage of one-pot synthesis. The working principle of electrodeposition is based on the
electrochemical redox reactions, which involves the deposition of metal on the electrode by allowing an electric current to pass through the metal salt solution [93]. There are various factors such as the type of anion, pH of metal solution and deposition potential, which are crucial for the effective deposition of MTMOs on an electrode [98]. This method allows for preparation of mixed metal oxides directly on conductive substrates, which results in higher energy density and enhanced electrical contact as electrode materials for energy storage applications [165].

In addition to the synthetic methods mentioned above, there are other techniques that can be used for the synthesis of ternary mixed transition metal oxides and their composites, such as spray pyrolysis method and reverse micelle method. Spray pyrolysis is an efficient technique to prepare well-crystallized and fine powders of nanophase metal oxides with homogeneous composition and is based on the generation of droplets in a continuous way from a solution containing metal precursors [166]. It is beneficial in the fabrication of powders of multicomponent mixed metal oxides with a uniform yolk-shell structures, which have potential applications in the energy storage fields [167, 168].

Table 2.2 below summarizes the recently reported ternary mixed cobaltite-based electrode materials for supercapacitor application with their respective synthesis method and electrochemical performance.
Table 2.2. Summary of the recently reported ternary spinel cobaltite-based electrode materials for supercapacitors

<table>
<thead>
<tr>
<th>Materials</th>
<th>Synthesis methods</th>
<th>Specific Capacitance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{0.8}$Ni$</em>{0.2}$Co$<em>{2}$O$</em>{4}$ mesoporous microspheres</td>
<td>Solvothermal</td>
<td>620 F g$^{-1}$ (2 A g$^{-1}$)</td>
<td>[120]</td>
</tr>
<tr>
<td>NiCoMnO$_{4}$ nanoparticles</td>
<td>Hydrothermal</td>
<td>510 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>[169]</td>
</tr>
<tr>
<td>Ni substituted Mn$<em>{1-x}$Ni$</em>{x}$Co$<em>{2}$O$</em>{4}$</td>
<td>Hydrothermal</td>
<td>1762 F g$^{-1}$ (1 mA cm$^{-2}$)</td>
<td>[118]</td>
</tr>
<tr>
<td>Ni–Co–Mn metal oxides</td>
<td>Hydrothermal</td>
<td>1434.2 F g$^{-1}$ (2 mA cm$^{-2}$)</td>
<td>[170]</td>
</tr>
<tr>
<td>NiMn$<em>{x}$Co$</em>{2-x}$O$_{4-y}$ (x ≤ 1.0)</td>
<td>Coprecipitation</td>
<td>110 F g$^{-1}$ (4 mV s$^{-1}$)</td>
<td>[119]</td>
</tr>
<tr>
<td>Zinc–Nickel–Cobalt Ternary Oxide Nanowire</td>
<td>Hydrothermal</td>
<td>2481.8 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>[115]</td>
</tr>
<tr>
<td>flower-like Ni-Zn-Co oxide nanowire arrays</td>
<td>Hydrothermal</td>
<td>776 F g$^{-1}$ (2 A g$^{-1}$)</td>
<td>[123]</td>
</tr>
<tr>
<td>Zn$<em>{0.2}$Ni$</em>{0.8}$Co$<em>{2}$O$</em>{4}$ microspheres</td>
<td>Hydrothermal</td>
<td>2081 F g$^{-1}$ (2.5 A g$^{-1}$)</td>
<td>[122]</td>
</tr>
<tr>
<td>Mn-doped ZnCo$<em>{2}$O$</em>{4}$</td>
<td>Hydrothermal</td>
<td>707.4 F g$^{-1}$ (0.5 A g$^{-1}$)</td>
<td>[121]</td>
</tr>
<tr>
<td>Cu-Zn-Co oxide nanoflakes</td>
<td>Hydrothermal</td>
<td>178 C g$^{-1}$ (1 A g$^{-1}$)</td>
<td>[126]</td>
</tr>
<tr>
<td>sheet-like Ni$<em>{x}$Co$</em>{2}$Mo$_{3}$O</td>
<td>Hydrothermal</td>
<td>2.94 F cm$^{-2}$ (5 mA cm$^{-2}$)</td>
<td>[125]</td>
</tr>
<tr>
<td>Zn-Mn-Co ternary oxide nanoneedles</td>
<td>Hydrothermal</td>
<td>849 C g$^{-1}$ (1 A g$^{-1}$)</td>
<td>[116]</td>
</tr>
<tr>
<td>Mesoporous Fe–Ni–Co ternary oxide nanoflake</td>
<td>Hydrothermal</td>
<td>867 F g$^{-1}$ (1 A g$^{-1}$)</td>
<td>[127]</td>
</tr>
<tr>
<td>Nickel-cobalt-molybdenum oxide nanosheets</td>
<td>Hydrothermal</td>
<td>1366 F g$^{-1}$ (2 A g$^{-1}$)</td>
<td>[124]</td>
</tr>
<tr>
<td>3D Ni-Co-Mn oxide nanoflakes</td>
<td>Microwave assisted</td>
<td>2536 F g$^{-1}$ (6.49 A g$^{-1}$)</td>
<td>[153]</td>
</tr>
<tr>
<td>Porous NiCoMn ternary metal oxide/graphene</td>
<td>Hydrothermal</td>
<td>115 mAhg$^{-1}$ (1 A g$^{-1}$)</td>
<td>[133]</td>
</tr>
<tr>
<td>RGO Nanosheet Supported Mn–Ni–Co Ternary Oxides</td>
<td>Coprecipitation</td>
<td>646.1 C g$^{-1}$ (1 A g$^{-1}$)</td>
<td>[132]</td>
</tr>
</tbody>
</table>
2.6. Chapter summary

Nowadays, supercapacitors are recognized as one of the promising candidates for electrochemical storage system. The typical features of supercapacitors include high power density, long cycle life, and fast charge-discharge kinetics, which enables them to bridge the gap between dielectric capacitors and rechargeable batteries. Despite the above attractive features, supercapacitors still need to improve to meet the demands for practical applications. Generally, the improvement can be made by designing high performance electrode materials which involve pseudo-capacitive type hybrid materials as they combine both EDLC and pseudocapacitive behavior. In this regard, electrode materials based on ternary mixed transition metals are promising due to the synergistic effect arising from the multicomponent metal centers and increased electrical conductivity. Additionally, fabricating composite materials with carbon is another strategy to improve the supercapacitive performance of the ternary mixed transition metal oxides in a bid to boost the practical applications of supercapacitors.
2.7. References


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CHAPTER 3

Experimental Methodology

This chapter gives a detailed explanation of the materials, synthesis methods, characterization tools and the electrochemical performance techniques utilized in this study.

3.1. Reagents and Materials

Most of the reagents and materials used were of analytical reagent grade, obtained from Sigma Aldrich (South Africa), ACE Chemical (South Africa), Merck Millipore (South Africa) and were used as received. The materials and reagents were used in this study are given in Table 3.1.

3.2. Materials synthesis techniques

3.2.1. Sol-gel method

Sol-gel is a facile method and widely employed in preparing spinel-type transition metal oxides with different nanostructures. Typically, metal salts are used as precursors and common chelating agents such as citric acid, ethylenediamine tetraacetic acid (EDTA), propionic acid, or ethylene glycol are usually applied to form a complex with metal ions [1]. Glucose is often used as a pore-former and carbon resource.

This method is used here in the study to prepare the mixed ternary spinel-type Mn-Ni-Co oxides as powders using the metal acetate precursors and citric acid and ethylene glycol as a chelating agent and enhancer, respectively as shown in scheme 3.1.
3.2.2. Coprecipitation method

The precipitation method usually mixes different contents in solution. After adding the precipitant, the precursor is obtained after filtering. Then, the precursors usually require calcination at high temperature to decompose and produce the transition metal oxides. The common precipitants used include NaOH, KOH, Na₂CO₃, H₂C₂O₄, ammonia, NaHCO₃, sodium dodecyl sulfate, (NH₄)₂CO₃ or NH₄HCO₃, and urea. Carbonate and oxalate precipitants

Table 3.1. Materials or chemicals used in the thesis

<table>
<thead>
<tr>
<th>Reagents/Materials</th>
<th>Purity</th>
<th>Manufacturer</th>
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</thead>
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<tr>
<td>Cobalt acetate tetrahydrate</td>
<td>AR grade</td>
<td>Sigma Aldrich</td>
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<tr>
<td>Manganese acetate tetrahydrate</td>
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<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Nickel acetate tetrahydrate</td>
<td>98%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Zinc acetate dihydrate</td>
<td>99.99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Citric acid monohydrate</td>
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<tr>
<td>Ammonia</td>
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<td>ACE Chemical</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>37%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>≥99%</td>
<td>VWR Chemical BDH, USA</td>
</tr>
<tr>
<td>Ammonium bicarbonate</td>
<td>≥99%</td>
<td>Merck Millipore</td>
</tr>
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<td>Absolute ethanol</td>
<td>≥99.8%</td>
<td>Merck Millipore</td>
</tr>
<tr>
<td>Glucose</td>
<td>≥97%</td>
<td>Merck Millipore</td>
</tr>
<tr>
<td>Conductive carbon (carbon black)</td>
<td>99.9%</td>
<td>Alfa Aesar, UK</td>
</tr>
<tr>
<td>Polyvinyl pyrrolidone (PVDF)</td>
<td>&gt; 99.5%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>N-methyl pyrrolidone (NMP)</td>
<td>99%</td>
<td>Merck Millipore</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>≥85%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>≥97.0%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>99%</td>
<td>Alfa Aesar, UK</td>
</tr>
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<td>Sodium sulphate</td>
<td>Anhydrous, ≥99%</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Nickel foam</td>
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<td>MTI Corporation, USA</td>
</tr>
<tr>
<td>Carbon fibre paper</td>
<td>-</td>
<td>Alfa Aesar, UK</td>
</tr>
</tbody>
</table>
Scheme 3.1. Processes involved in the sol-gel preparation of transition metal oxides

usually form porous structures because of the generation of CO₂ in the calcination process.

In this study, the coprecipitation technique is used for the synthesis of Mn-Zn-Co oxides employing NH₄HCO₃ as a precipitant in a water and ethanol solvent mixture to produce porous microspheres.

3.3. Materials Characterization Techniques

3.3.1. Microscopy Methods

3.3.1.1. Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is considered as one of the most powerful techniques for characterizing the surface morphology of nanomaterials. The working principle of SEM is based on scanning a small diameter electron probe with a focused primary electron over the sample. Then, secondary electrons from each atom on the specimen are emitted, detected, amplified and forming an image of the scanned area.

A FEI XL40 SEM equipped with two EDS detectors is employed to test the surface morphology and structure of the materials prepared. Prior to imaging, the samples were stabilized by carbon tapes on the aluminum sample holder and coated with ~10-15 nm of carbon rods using a sputtering coater (JEOL JFC-1600).
3.3.1.2. Transmission Electron Microscope (TEM)

To have a better understanding of the nanostructured features of synthesized samples, characterization was done using the TEM microscope (JEOL 2100F, USA) to obtain the morphological and crystallographic information. HRTEM images were captured by interfering with the thin crystals within the samples and resulting in an electron interference patterns at an appropriate defect-of-focus, which can be directly interpreted as projected potential of the crystal structure operated at 200 kV. Lattice-fringe fingerprinting is a novel method of identifying nanocrystals on the basis of the Fourier transforms of high-resolution transmission electron microscopy (HRTEM) images. The spacings between lattice fringes and the interfringe angles, measured when nanocrystals show crossed lattice fringes in HRTEM images, are used to initially "fingerprint" the nanocrystal. By measuring the distance between the fringes, it is possible to determine the type of crystal planes and d-spacing, which corresponds to the XRD measured one.

3.3.2. Diffraction Methods
3.3.2.1. X-Ray Powder Diffraction (XRD)

X-ray diffraction (XRD) is considered as one of the fundamental techniques to characterize the crystal structure. The physical fundamental of XRD is based on the path difference between the X-ray waves scattered by atoms from adjacent lattice planes (hkl) of spacing d \[2\]. The resultant intensity peaks on XRD pattern at each measured angle shows the condition of the constructive interference according to Bragg’s law:

\[ n\lambda = 2d\sin\theta \]  

(3.1)

where \( n \) is an integer represents the order of diffraction, \( \lambda \) is the wavelength of the X-ray source, and \( \theta \) is the angle between the incidence and diffraction to the lattice planes.

The structural information was characterized by D2 Phaser XRD (Bruker Corporation, USA) equipped with Co-K\(\alpha \) radiation (\( \lambda = 1.78060 \) Å) and STOE STADI/P Diffractometer (XRD;
Mo Kα1 radiation, \( \lambda = 0.709321 \, \text{Å} \). The XRD measurement that was used is theta/2theta scan measurement where the X-ray source and detector are coupled to move simultaneously while the sample location is fixed. As each crystal structure and phase have characteristic XRD patterns, our resultant patterns were compared to database sheets in order to determine the crystal structure and the phases present in our samples.

3.3.2.2. Rietveld Method

To have a complete structural analysis of a material, a structure refinement is often required in order to assess how well the collected diffraction data agrees with a structural model. A structural analysis based on the Rietveld method is usually used to fit powder X-ray and neutron diffraction data. Rietveld analysis is a sophisticated form of crystallographic modeling that consists on fitting a structural model (or known crystal structure) to a powder diffraction data using a least squares minimization algorithm. The method considers the entire powder X-ray diffraction pattern and by varying an array of refinable parameters aims to deliver a fitted structure. This process requires determining the structural parameters (unit cell, atom positions and displacement/thermal parameters, etc.) for all crystalline phases present, as well as different instrumental and sample parameters that describe the experimental and sample conditions: scale factor, the background, peak broadening, atomic positions, thermal factors, preferred orientation, etc. In most cases, Rietveld analysis is mainly performed to determine the lattice parameters, but increasingly, the method is also employed to estimate relative amounts of the crystallographic phases, the amount and type of peak broadening, the preferred orientation or similar types of sample characterization.

Rietveld refinement was performed in thesis using fundamental parameters peak shape profile implemented in TOPAS 4.2 package [3]. A five coefficient Chebychev polynomial background, a zero error, sample displacement, unit cell parameters, scale factor and crystallite sizes were sequentially refined.
3.3.2.3. Selected Area Electron Diffraction (SAED)

The principle of electron diffraction in this technique is similar with XRD by adhering to Bragg’s law. Due to the extremely short wavelength of highly coherent electron beam in TEM chamber, the wave-like electron passes through the lattice plane within the crystal which serve as diffraction grating, eventually resulting in diffraction. This technique provides information of crystal orientation relationships between grains, and it can identify the lattice metrics of the crystals. Samples for SAED were prepared by sonicating under ethanol and drops of the resulting suspension was deposited on holey-carbon coated copper-grids and fitted with a low background Gatan double tilt holder.

3.3.3. Spectroscopy Methods
3.3.3.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy detects the molecular absorption and transmission characteristics of a material when exposed to infrared (IR) radiation. Fourier transform infrared spectra (FTIR) was recorded in the range of 400–4000 cm\(^{-1}\) using a Shimadzu 8400 FTIR. An appropriate amount of the calcined powder was mixed with potassium bromide (mass ratio KBr: Sample of 10: 1) and then pelletized at room temperature, and then used to measure the various FTIR spectra.

3.3.3.2. Raman Spectroscopy

Raman spectroscopy technique is widely used in order to characterize the molecular structure of the materials. The physical principal of Raman spectroscopy is based on the inelastic scattering of the electromagnetic radiation of a source by the molecules of a sample. Raman spectrum records the frequency changes between radiation and scattering frequency which is called Raman Shifts.
Raman spectra were acquired on DXR2 SmartRaman spectrometer (Thermo Fisher Scientific) using a Diode-pumped, solid state (DPSS) laser (532 nm).

### 3.3.3.3. Energy Dispersive X-Ray Spectroscopy (EDS)

Elemental compositions of the samples were analyzed by EDS equipped to SEM or TEM. For EDS-SEM, working distance of 15 cm and accelerating voltage of 20 kV were selected and scanned to obtain the spectrum. After irradiated by a focused electron beam, ground state electrons in energy level bounded to nucleus absorb the incident energy and escape away from the orbital, leaving behind empty holes. Energy-dispersive spectrometer analyzes the amount and energy values of characteristic x-ray and reveals the elemental composition of a sample.

### 3.3.3.4. X-Ray Photoelectron Spectroscopy (XPS)

By irradiating the samples with x-ray beam at known energy values, the electrons within the samples absorb energy and escape from the top surface (~10 nm). By measuring the kinetic energy of escaped electrons, the characteristic binding energy values of each element on the top surface layer can be identified. This characteristic binding energy peaks can be correlated to the specific orbitals in the atoms, for instance 1s, 2s, 2p. Hence, XPS provides useful information of elemental composition, chemical states of element, and quantitative amount of each element.

Herein, X-ray photoemission spectroscopy (XPS) was performed using a SPECS PHOIBOS 150 hemispherical electron energy analyser, Germany and a monochromatised Al Kα photon source (\(h\nu = 1486.71\) eV). The overall energy resolution was set to 0.7 eV for survey spectra and 0.55 eV for all other high-resolution core level spectra.
3.3.4. **Porosity Measurement**

The Brunauer-Emmett-Teller (BET) surface area and pore size distribution of the samples were measured on ASAP 2020 surface area analyzer (Micrometrics instrument, USA) by using the N$_2$ adsorption-desorption isotherms at 77 K. Before the measurement, the samples were degassed at 393 K under nitrogen flow.

3.3.5. **Thermal Analysis**

Thermogravimetric analysis (TGA) and Differential calorimetric studies (DSC) were performed by using Thermogravimetry/Differential Thermal Analyzer (Hitachi-STA7200RV, California, USA) by heating the samples (~10-20 mg) from room temperature to target temperature under air at a ramp rate of 10 °C min$^{-1}$, with 40% air as sample gas and 60% nitrogen as balance gas.

3.3.6. **Magnetic Studies**

Magnetic properties of the metal oxide samples were studied to obtain some information on the structural details of the samples. Magnetic measurements were performed using a Cryogenic measurement platform equipped with a vibrating sample magnetometer (VSM) insert. VSM measurements were done in zero field cooled (ZFC) and field cooled (FC) modus of measurement in a temperature range of 2 to 300 K. Hysteresis loops were performed in a field range of +2.5T to -2.5T.

3.4. **Electrochemical Studies**

3.4.1. **Electrode Preparation**

Most electrodes of batteries or supercapacitors are composites of powders composed of the active material, a conductive additive, and a polymer binder to hold the mix together and bond
the mix to a conductive current collector. In a typical procedure for preparation of electrodes, 70-80 wt% active material, 10-20 wt% conductive carbon, and ~10 wt% PVDF binder are mixed together with few drops of N-methyl pyrrolidone (NMP) to make a homogenous slurry and coated on a substrate using a doctor blade technique. Then, the electrode is heated in a vacuum oven at 120 °C overnight to remove the organic solvent.

3.4.2. Cyclic Voltammetry

Cyclic voltammetry (CV) is usually used to study the redox reaction reversibility and determine the voltage window of electrodes or devices. The principle of CV is to measure the resulting current simultaneously when applying a linear voltage to an electrode or a device between two preset voltage limits.

The specific capacitance can be calculated from the cyclic voltammetry in a given potential window. Based on the CV curves, the specific capacitances (Cs) of the as fabricated electrodes calculated using the following equation:

\[ C = \frac{\int IdV}{mv\Delta V} \]

where \( \int IdV \) is the integral area under the CV curve (A), \( \nu \) is the scan rate (mV s\(^{-1}\)), \( m \) is the mass of the electroactive material (g), and \( \Delta V \) is the potential window (V).

In this dissertation, Gamry Interface 1000 E potentiostat/galvanostat/ZRA (Gamry Instruments, Inc.) was used for CV experiments. CV experiments were carried out at different scan rates selected from 5 mV s\(^{-1}\) to 100 mV s\(^{-1}\).

3.4.3. Galvanostatic Cycling (Chronopotentiometry)

Galvanostatic charge-discharge cycling (GCD) is a widely used technique to calculate the capacitance and cycling stability of electrodes or devices. The principle of GCD is to measure
the resulting voltage simultaneously when applying a constant current to an electrode or a device between two predetermined voltage limits.

The specific capacitance from the galvanostatic charge discharge curves can be calculated according to the following equation:

\[
C_m = \frac{I \times \Delta t}{\Delta V \times m}
\]

where, \(C_m\) (F g\(^{-1}\)) is the specific capacitance, \(I\) (A) is discharge current, \(\Delta t\) (s) is the discharging time, \(\Delta V\) (V) represents the potential drop during discharge process, and \(m\) (g) is the mass of the active material within the electrode.

Gamry Interface 1000 E potentiostat/galvanostat/ZRA (Gamry Instruments, Inc.) was used for our GCD experiments. GCD experiments were carried out at different current densities selected for each series of samples.

3.4.4. Electrochemical Impedance Spectroscopy (EIS)

The equivalent series resistance (ESR), charge transfer resistance (CT) and diffusion impedance of electrochemical devices can be studied by electrochemical impedance spectroscopy (EIS). The main difference between EIS and CV that in EIS a low amplitude (≤ 10 mV) sinusoidal voltage signal is imposed at a range of frequencies and the resulting current is measured, while a linear voltage is applied in CV. The electrode resistance, electrolyte resistance, and the equilibrium differential capacitance can be identified from Nyquist plot (Fig. 3.1).

Electrochemical impedance spectroscopy (EIS) experiments were performed on the Gamry potentiostat/galvanostat over a frequency range of 0.1Hz-100KHz at open circuit potential and at an AC amplitude of 10 mV. All electrochemical measurements were carried out at room temperature in KOH aqueous electrolyte.
Figure 3.1. Nyquist profiles under controlled by charge transfer and diffusion
3.5. References


CHAPTER 4

Sol-gel synthesis of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ spinel phase materials: structural, electronic, and magnetic properties

Abstract

A series of spinel-type Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ (x = 0, 0.3, 0.5, 0.7, 1) oxides were synthesized by using a citrate sol-gel technique. The structural, magnetic and electronic properties of the oxides with different Mn content were investigated using X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), vibrating sample magnetometer (VSM) and X-ray photoelectron spectroscopy (XPS). The XRD and FTIR studies revealed that Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ formed in a cubic structure for all the compositions synthesized. Transmission electron microscopy (TEM) studies show cubic nano-plates for x = 0 and on increasing Mn concentration, agglomerated nanoparticles with sphere-like shape are observed with a particle size in the range of 11.7 nm to 22.1 nm. This is in close agreement with the results of XRD analysis. The Mn 2p, Ni 2p, and Co 2p XPS spectra reveal the coexistence of Mn$^{2+}$, Mn$^{3+}$, Ni$^{2+}$, Ni$^{3+}$, Co$^{2+}$, and Co$^{3+}$ species on the surface of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ samples in differing proportions. The measurements of magnetic properties at room temperature show that the samples have some ferromagnetic behaviour. The saturation magnetization, remnant magnetization, and coercivity of the nanoparticles vary significantly with a concentration of Mn, which tends to be distributed in both tetrahedral and octahedral positions of the spinel lattice.
4.1. Introduction

Spinel oxides based on transition metals of the form $\text{AB}_2\text{O}_4$, (where $\text{A, B} = \text{Mn, Fe, Co, Ni, Cu, Zn, A} \neq \text{B}$) are an important class of materials having diverse practical applications because of their thermal, electronic, magnetic, and optical properties [1]. Among the spinel oxides, cobaltites of Mn and Ni have been extensively investigated as thermistors [2-6], while the optical and electrical properties have been studied [7-9] and applied in microbolometers [10]. Mn-Ni-Co mixed metal oxides have also shown interesting physical-chemical properties, especially when processed as nanomaterials, including unique humidity and thermal sensing properties when controlling the nano-structural morphology of the material [11]. In addition, Mn-Ni-Co metal oxide nanoparticles were applied as thermocatalysts for the degradation of methylene blue [12]. In the field of energy storage and conversion, Mn-Ni-Co ternary oxide nanowire arrays have shown promise as electrochemical capacitors [13] and as cathode material in batteries when processed as a nano-powder [14].

The structural, electrical, optical, magnetic and chemical properties of the metal oxide particles are strongly influenced by the choice of synthesis methods. There are various chemical methods that have been used to prepare Mn-Ni-Co based spinel oxides; these include hydrothermal [15], sol-gel method [16], co-precipitation [2], and combustion synthesis [17]. Different compositions of Mn-Ni-Co ternary oxides have been prepared by doping of binary cobaltites in order to improve and tailor electrical, magnetic and chemical properties of these ternary spinel oxides. This is possible due to their variable oxidation states, better electronic conductivity and synergistic effect arising from the constituent metal ions [16, 18-20].

The citrate sol-gel method is a common wet-chemical method used to synthesize binary, ternary and quaternary metal oxides [21]. It has the advantage of mixing ions on the atomic scale to obtain high-purity, homogeneous, and ultrafine powders making it easier to control the stoichiometry of metal oxides. Citric acid, a commonly used chelating agent, combines with metal ions to form citrate complexes in the reaction solution and decomposes at relatively lower temperatures to form oxide powders [21]. Ternary spinel-type oxides of Mn-Ni-Co have been prepared so far using this method. Duran et al. [22] were able to prepare pure phase $\text{Co}_x\text{NiMn}_{2-x}\text{O}_4$ ($0.2 \leq x \leq 1.2$) spinel-type powders by auto-combustion of ethylene glycol–metal nitrate polymerized gel precursors and then by subsequent calcination at 600–700 °C.
They showed that agglomerated nanoparticles are formed with a cubic crystal structure in which the size and morphology were dependent on the chemical composition. Wang et al. [23] also synthesized nanocrystalline Ni$_1$Co$_{0.2}$Mn$_{1.8}$O$_4$ powders via a gel auto-combustion process of nitrate–citrate gels and were able to get single spinel phase at 500 °C. The majority of work reported on the citrate sol-gel method uses metal nitrate precursors because of the role of the counter nitrate ion as an oxidant during the combustion. Nevertheless, other types of metal precursors like acetates can also be used. For example, Zhang et al. [16] reported the synthesis of Mn$_{1.5-x}$Co$_{1.5}$Ni$_x$O$_4$ nanoparticles by the sol-gel method using citric acid and metal acetate precursors; pH played a major role during the formation of cation-citrate complex and the Ni ions were observed to occupy both the tetrahedral and octahedral positions.

At present, the magnetic properties of the Mn-Ni-Co-O systems attract particular interest owing to their unusual and interesting behaviour in the nano-crystalline form and as thin films. At a nanoscale, these materials transition from the antiferromagnetic to ferromagnetic state attributed to the surface and finite size effects or the existence of net magnetic moment due to uncompensated spins [24-26]. Nickel cobaltite NiCo$_2$O$_4$, possessing inverse spinel structure demonstrates ferrimagnetism, produced by magnetic exchange interactions between the Co ions in the tetrahedral and the Ni and Co ions in the octahedral positions [27]. Magnetic parameters, such as saturation magnetization and coercive force can be changed by doping nickel cobaltite with other transition metals.

In this study, a series of spinel-type oxides with a new composition of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) were obtained by adopting a citrate sol-gel route making use of citric acid and ethylene glycol as cation chelating agents and metal acetate precursors. The ternary mixed spinel-type oxides of the composition Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) prepared here have not been reported previously. The prepared oxides were characterized and investigated for their structural, magnetic and electronic properties.
4.2. Experimental

4.2.1. Synthesis of spinel oxides

Spinel oxides of MnₓNi₁₋ₓCo₂O₄ (x = 0, 0.3, 0.5, 0.7, 1) were prepared by adopting a citrate sol-gel method. The metal precursors were purchased from Sigma Aldrich (South Africa), in the form of Co(CH₃COO)₂.4H₂O (AR grade), Ni(CH₃COO)₂.4H₂O (98% purity) and Mn(CH₃COO)₂.4H₂O (≥99% purity). Citric acid monohydrate, C₆H₈O₇.H₂O (SAR-CHEM) was used as a chelating agent. A stoichiometric amount of Co(CH₃COO)₂.4H₂O, Ni(CH₃COO)₂.4H₂O and Mn(CH₃COO)₂.4H₂O was dissolved in 40 ml of distilled water and continuously stirred until a homogenous metal acetate solution was formed. During stirring, the citric acid monohydrate was slowly added to the metal acetate solution with a target molar ratio of citric acid to metal ions of 1.5:1. The pH value of the solution was adjusted to about 7 by adding ammonia solution (25%, purchased from ACE Chemical South Africa) and then 40 mL of ethylene glycol (VWR) was added to the mixture to assist the gelation process. The solution was continuously stirred while heating on a hot plate to 80-90 °C. This was done for 6 hours until a gel was obtained. The gel was dried overnight at 100 °C. Finally, the dried gel was calcined in air at a temperature of 450 °C with a ramp rate of 2 °C min⁻¹ for 5 hours in a tube furnace to produce a black powder.

4.2.2. Characterization

The crystal structure of the spinel oxides was characterized by powder X-ray diffraction (XRD; Bruker D2 Phaser, Co-Kα radiation, λ=1.78060 Å) with a step size of 0.026° over the 2θ range of 15 to 110°. Rietveld structural refinements of the calcined powders were performed using the TOPAS 4.2 package [28]. Thermogravimetric analysis (TGA) was carried out on an SDT Q600 (V20.9 Build 20) instrument (Universal V4.5A TA Instruments, USA) in the temperature range between 27 °C and 1000 °C at a heating rate of 10 °C min⁻¹ in a flowing air atmosphere. Fourier transform infrared spectra (FTIR) was recorded in the range of 400–4000 cm⁻¹ using a Shimadzu 8400 FTIR. An appropriate amount of the calcined powder was mixed with potassium bromide (mass ratio KBr: Sample of 10: 1) and then pelletized at room temperature, and then used to measure the various FTIR spectra. The morphology and chemical composition were obtained by scanning electron microscope (SEM; S-4800 operated at 20 kV) and energy-
disperse X-ray spectroscope (EDS). Transmission electron microscope (TEM) images were obtained on a JEM-2010 instrument, USA. Magnetic measurements were performed using a Cryogenic measurement platform equipped with a vibrating sample magnetometer (VSM) insert (Lake Shore Cryotronics, Inc., USA). VSM measurements were done in zero field cooled (ZFC) and field cooled (FC) modus of measurement in a temperature range of 2 to 300 K. Hysteresis loops were performed in a field range of +2.5 to -2.5T at 300 K. X-ray photoemission spectroscopy (XPS) was performed using a SPECS PHOIBOS 150 hemispherical electron energy analyser and a monochromatised Al Kα photon source (hν = 1486.71 eV). The overall energy resolution was set to 0.5 eV for all the spectra shown in this contribution.

4.3. Results and discussion
4.3.1. Formation of the spinel oxides and thermal analysis

The spinel-type MnₓNi₁₋ₓCo₂O₄ oxides were synthesized by using a citrate sol-gel route using metal acetate precursors in a mixture of water and ethylene glycol. The key issue in the formation of the single-phase ternary spinel oxides using this method is the presence of the chelating agent. In this method, the citric acid works as an effective chelating agent for all three metal ions. The reaction mixture initially contains the metal acetate salt, and once the citric acid was added, the metal cations are coordinated to the citrate anions forming a metal–citrate complex [16, 29]. Song et al. [30] have demonstrated the effectiveness of citric acid as a chelating agent for the synthesis of Ni-Co-Mn precursor for LiNi₀.₅Co₀.₂Mn₀.₃O₂ systems. In the current MnₓNi₁₋ₓCo₂O₄ spinel system, the citric acid shows a similar effectiveness. Ammonia solution was added in order to adjust the pH of the solution to about 7. It was discovered experimentally that this pH is optimum for a complete complexation of the metal ions in the current system, and thus the formation of the required gels.

The thermal decomposition properties of Mn-Ni-Co citrate precursor were investigated by means of thermogravimetric and derivative thermogravimetric (TG/DTG) techniques. The dried gels of the Mn-Ni-Co citrate precursor were heated from 27 to 1000 °C at a rate of 10 °C min⁻¹ in a flowing air atmosphere. The TG/DTG curves of Mn-Ni-Co citrate (x = 0.5) are shown in Fig. 4.1. From Fig. 4.1, it is clear that the decomposition of Mn-Ni-Co citrate precursor
occurs in three stages. The first stage had a maximum rate of decomposition at 90 °C, and small mass loss of about 2%, which can be ascribed to the loss of physisorbed water from the gel. The second stage had a maximum rate of decomposition at 290 °C and a mass loss of about 13%. The mass loss in the second stage could be attributed to the loss of water of crystallization from the Mn-Ni-Co citrate precursor and the partial decomposition of the citrate precursor. In the third stage, a maximum rate of decomposition was observed at 375 °C with a significant weight loss of about 48%, which can be attributed to the complete decomposition of the citrate precursors and the formation of pure Mn-Ni-Co oxide [17]. On increasing the temperature further, no significant weight loss was observed above 600 °C. The maximum peak in the DTG curve at around 375 °C signifies that for the synthesis of pure Mn-Ni-Co oxides, a temperature above 400 °C can be used for calcination.

![TG and DTG curves of the Mn-Ni-Co citrate precursor](image)

**Figure 4.1.** TG and DTG curves of the Mn-Ni-Co citrate precursor

### 4.3.2. Structural characterization

Figure 4.2(a) shows the XRD patterns for the spinel oxides of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ prepared by using citrate sol-gel route and calcined at 450 °C in air with different values of $x$. Figure 4.2(b) shows a magnified view of the (311) diffraction peaks. The dotted line in Figure 4.2(b) is placed
at the peak of the sample with $x = 0$ so that the relative shift in the 2θ of the (311) peaks can be observed with increasing $x$.

Considering Figure 4.2(a), it is evident that for all the compositions single-phase cubic spinel oxides were obtained. The (111), (220), (222), (311), (400), (422), (511) and (440) major lattice planes in the XRD patterns confirm the formation of spinel cubic structure with the $Fd3m$ space group (JCPDS card no. 73-1702). In addition, a trace amount of secondary NiO impurity phase begins to appear with increasing Ni concentration ($0 \leq x < 0.5$) marked by an asterisk in Figure 4.2(a). This could be due to the partial decomposition of the spinel Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ oxides occurring above 400-500 °C [31, 32]. The amount of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ and NiO were obtained from the Rietveld refinement and are listed in Table 4.1. The NiO phase could be indexed to the (200) and (220) reflections in the cubic structure of NiO (JCPDS card no. 47-1049). Figure 4.2(b) shows the magnified view of a relative shift in the (311) diffraction peaks.

![Figure 4.2](image)

**Figure 4.2.** (a) XRD pattern for the spinel oxides of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ ($x = 0, 0.3, 0.5, 0.7$ and $1$) prepared by using citrate sol-gel route and calcined at 450 °C in air. (b) magnified view of the (311) diffraction peaks as a function of $x$.

As the Mn concentration decreases, the (311) diffraction peak shifts towards a smaller 2θ angles for a sample with $0 \geq x \geq 0.5$ and then shifts again towards higher 2θ angles for the
samples with $x > 0.5$. This behaviour will be explained based on the variation of lattice parameter, below. In addition, the intensity of the diffraction peaks increases and the FWHM decreases with decreasing Mn concentration indicating an increase in the size of the $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ nanoparticles. The $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4$ nanoparticles were also prepared by calcining at 350 °C and 700 °C and the cubic spinel phase remained unchanged as shown in Fig.S-2.

Rietveld refinements of the XRD patterns were carried out assuming a structural model with a spinel cubic lattice and space group symmetry $Fd3m$ using the TOPAS 4.2 software. In the refinement process, scale, atomic coordinates, site occupancies, atomic displacement parameters, background parameters, lattice constants and peak profile analysis were refined as part of the process. Besides these factors, the reliability R-factors; expected $R_{\text{exp}}$, profile $R_p$, and weighted profile $R_{\text{wp}}$, and the goodness of fit ($\text{GoF} = R_{\text{wp}} / R_{\text{exp}}$) were analyzed in order to indicate the best fit of the obtained XRD data to the theoretical model. The average crystallite sizes were estimated from the Scherrer’s equation and refined using the TOPAS software. It decreased from 19.5 nm for $x = 0$ to 9.7 nm for $x = 0.7$, and then increased to 15.5 nm for $x = 1$. The observed, calculated, and difference curves for the Rietveld refined XRD patterns are shown in Fig. 4.3. The Rietveld refined patterns for the other samples are provided in Fig.S-3. The GoF values improve with increasing Mn and decreasing NiO impurity from $x = 0$ to $x = 1$, approaching a value of 1. Moreover, the crystallographic data of the samples obtained from the Rietveld refinement are summarized in Table 4.1. According to the Rietveld refined XRD patterns and R-factors summarized in Table 4.1, the calculated curve (red) matches reasonably well with the experimental curve (blue).
Table 4.1. Structural parameters obtained after the Rietveld refinement of the XRD patterns of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$

<table>
<thead>
<tr>
<th>Composition</th>
<th>x = 0</th>
<th>x = 0.3</th>
<th>x = 0.5</th>
<th>x = 0.7</th>
<th>x = 1</th>
</tr>
</thead>
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<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>Fd3m</td>
<td>Fd3m</td>
<td>Fd3m</td>
<td>Fd3m</td>
<td>Fd3m</td>
</tr>
<tr>
<td>Lattice parameter a (Å)</td>
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<td>8.1357</td>
<td>8.1480</td>
<td>8.1402</td>
<td>8.1281</td>
</tr>
<tr>
<td>Cell volumes/Å$^3$</td>
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<td>538.3</td>
<td>543.3</td>
<td>539.6</td>
<td>535.4</td>
</tr>
<tr>
<td>$R_{exp}$</td>
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<td>1.95</td>
<td>1.80</td>
<td>1.65</td>
<td>1.54</td>
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<td>$R_{wp}$</td>
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<td>2.55</td>
<td>1.99</td>
<td>1.85</td>
<td>1.63</td>
</tr>
<tr>
<td>$R_p$</td>
<td>2.60</td>
<td>1.99</td>
<td>1.59</td>
<td>1.48</td>
<td>1.31</td>
</tr>
<tr>
<td>GoF</td>
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<td>1.31</td>
<td>1.11</td>
<td>1.13</td>
<td>1.06</td>
</tr>
<tr>
<td>Crystallite size (nm)</td>
<td>19.5</td>
<td>14.6</td>
<td>15.1</td>
<td>9.7</td>
<td>15.5</td>
</tr>
<tr>
<td>wt % Mn$<em>x$Ni$</em>{1-x}$Co$_2$O$_4$</td>
<td>89.98</td>
<td>96.59</td>
<td>98.63</td>
<td>99.72</td>
<td>100</td>
</tr>
<tr>
<td>wt % NiO</td>
<td>10.02</td>
<td>3.41</td>
<td>1.37</td>
<td>0.28</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 4.3. Rietveld refined XRD pattern of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ (x = 0.5). The blue, red and gray lines represent experimental (observed) patterns, calculated patterns, and difference curves, respectively.
The lattice parameter values (a), obtained with the Rietveld refinement are in good agreement with NiCo$_2$O$_4$ (JCPDS card no. 73-1702) and MnCo$_2$O$_4$ (JCPDS card no. 23-1237). The variation of the lattice parameter with a concentration of Mn obtained from the Rietveld refinement are shown in Figure 4.4, and the values are presented in Table 4.1. The lattice parameter increases continuously from 8.1084 Å for $x = 0$ to reach a maximum value of 8.1480 Å for $x = 0.5$. However, it starts to decrease from $x = 0.5$ onwards with the further substitution of Mn ions and reaches to a value of 8.1281 Å for $x = 1$. This can be explained based on the cation distribution assuming an inverse spinel-type NiCo$_2$O$_4$, which could be represented as Co$_2$$^{2+}$Co$_{2-x}^{3+}$[Co$^{3+}$Ni$_{1-x}^{2+}$Ni$^3_+$$]_4$ $(0 < x < 1)$ [27]. The Ni ions occupy the octahedral sites and the Co ions occupy both the octahedral and tetrahedral sites. The increase in the unit cell parameter with increasing Mn content up to $x = 0.5$ could be due to the substitution of smaller Ni$^{2+}$/Ni$^{3+}$ions (0.69 Å/0.56 Å) by the bigger Mn$^{2+}$ ions (0.83 Å) in the octahedral position [33]. With increasing Mn concentration above $x = 0.5$, the Mn (and/or Ni) cations might be forced to move from octahedral (B) sites to tetrahedral (A) sites, which might cause the migration of Co$^{2+}$ ions from B to A sites. In this case, the Mn and Ni ions might partially reside in both the tetrahedral and octahedral sites forming a partial inverse spinel-type structure. A similar behaviour was observed in Zn$_x$Mn$_{1-x}$Fe$_2$O$_4$ nanoferrites produced by the hydrothermal method [34].

![Graph showing the variation of lattice parameter, a, as function of Mn concentration, x, for Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ oxides.](image)
The FTIR spectra of the dried Mn-Ni-Co citrate gel and Mn-Ni-Co oxide (x = 0.5) and Mn_xNi_{1-x}Co_2O_4 (x = 0, 0.3, 0.5, 0.7, 1) oxides prepared by calcining at 450 °C are shown in Figure 4.5. As shown in Figure 5(a), two absorption peaks are observed around 1630 cm\(^{-1}\) and 1400 cm\(^{-1}\) for both the dried Mn-Ni-Co gel and calcined sample. These correspond to asymmetric and symmetric stretching of the carboxyl group (C=O) [35], indicating the presence of trace organic precursors that have remained undecomposed in the calcined sample. The bands at 1300–1100 cm\(^{-1}\) correspond to vibration of C-O from the -COOH groups of the citric acid [36]. The two strong peaks observed in the calcined sample (Fig. 4.5(a)) corresponding to the main absorption bands of the M-O bonds are not present in the uncalcined sample indicating the formation of the spinel oxides [37]. The absorption peaks observed between 2355 cm\(^{-1}\) and 2404 cm\(^{-1}\) are ascribed to the surface sorption of CO\(_2\) molecule from the atmosphere [38]. The absorption band at 2854–2924 cm\(^{-1}\) is attributed to the stretching vibration mode of the CH\(_2\) groups from organic precursors. Figure 4.5(b) shows the FTIR spectra for Mn_xNi_{1-x}Co_2O_4 spinel oxides with different compositions. Generally, spinel oxides show two absorption bands in the wave number ranging between 400 and 700 cm\(^{-1}\) [37]. The strong peaks at ~560-563 cm\(^{-1}\) and ~653-655 cm\(^{-1}\) correspond to the M-O vibration frequency of metals (M = Ni, Mn or Co) at the octahedral and tetrahedral sites, respectively. This FTIR

**Figure 4.5.** FTIR spectra of (a) the dried Mn-Ni-Co gel (x = 0.5) before calcination and Mn-Ni-Co oxide (x = 0.5) obtained after calcining at 450 °C respectively. (b) Mn_xNi_{1-x}Co_2O_4 (x = 0, 0.3, 0.5, 0.7, 1) spinel oxides obtained after calcination at 450 °C.
absorption data confirms the successful formation of spinel Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ oxides in agreement with the XRD studies.

4.3.3. Morphological characterization

The morphology and microstructure of the as-synthesized Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ were examined with Transmission electron microscope (TEM) and Scanning electron microscope (SEM) equipped with EDS. The TEM, HRTEM and particle size distribution of the Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ nanoparticles are shown in Figure 4.6. From the TEM images, it was observed that the morphological features of the particles changed from large cubic shaped nano-plates towards smaller sized sphere-like particles with increasing concentration of Mn. The results indicate that the Mn content plays an important role on surface morphologies of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ microstructure and control of the particle size. From the size distribution the average particle size of 22 ± 1, 13 ± 2, 12 ± 2, 12 ± 2, and 12 ± 3 nm were obtained for x = 0, x = 0.3, x = 0.5, x = 0.7, and x = 1 samples, respectively. The sizes are in a good agreement with the crystallite sizes obtained from XRD data. The particle size decreased gradually with increasing Mn concentration. Furthermore, high-resolution TEM images (b, e, h, k, n) were taken and showed well-developed lattice fringes, which correlate well with the d-spacing from XRD results of the different planes indicating the polycrystalline nature of the samples.

To assess the bulk morphology of the nanoparticles and their composition, SEM studies and EDS analysis were done for the sample Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ as indicated in Figure 4.7. The morphology from SEM shows agglomerates of nanoparticles, consistent with what was observed in the TEM images. EDS analysis confirmed the presence of only Mn, Ni, Co and O atoms.
Figure 4.6. TEM images, HRTEM images and particle size distribution of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ prepared by calcining at 450 °C with different compositions (a) to (c) $x = 0$, (d) to (f) $x = 0.3$, (g) to (i) $x = 0.5$, (j) to (l) $x = 0.7$, and (m) to (o) $x = 1$. 
XPS measurements were performed in order to gain insight into the electronic structure of the Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ series. Figure 4.8(a) shows the comparison of the wide scans for all samples. Spectra show all the expected peaks and are dominated by the O 1s and the Co 2p core levels. The Ni 2p core level decreases in intensity from the top to the bottom of the figure (as expected from the fact that the Ni concentration decreases accordingly), while the Mn 2p core level behaves in the opposite way. Figure 4.8(b) shows the comparison of the Co 2p core level for the Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ series. The Co 2p binding energy region is dominated by two peaks located at 780.1 eV and 795.2 eV in binding energy, corresponding to the Co 2p3/2 and Co 2p1/2 spin-orbit components, respectively. In addition to these, two satellite peaks are detected at about 8 eV towards higher binding energy from the main peaks. The line shape of the two main peaks, as shown in the bottom of Figure 4.8 (b), can be decomposed into two components, which are due to Co$^{3+}$ (at lower binding energy) and Co$^{2+}$ (at higher binding energy) oxidation states, respectively. Each doublet is separated by a spin-orbit splitting of approximately 15.1 eV. The overall fit to the experimental data (thick line) shows good agreement with the raw data. The area ratio of the two components shows that 60% of the Co ions are in the 2$^+$ ionization state. This is consistent with previous studies [39]. The line shape of the Co 2p core level is consistent throughout the series, so only the fit for MnCo$_2$O$_4$ has been reported in Figure 4.8(b).

Comparison of the Mn 2p core level XPS spectrum is reported in Figure 4.8(c). The Mn 2p line shape for MnCo$_2$O$_4$ (at the bottom of the figure) is composed of two main peaks whose centroids are located at 642.1 eV and 653.7 eV binding energy, corresponding to Mn 2p3/2 and 2p1/2 levels respectively. For Ni-doped samples, the raw data (dashed lines in Figure 4.8(c))
Figure 4.8. XPS spectrum (a) and peaks of Co 2p (b), Mn 2p (c), Ni 2p (d) and O 1s (e) for Mn$_x$Ni$_{1-x}$Co$_2$O$_4$.

show a shoulder developing on the lower binding energy side of the Mn 2p3/2 peak. This is because the Mn 2p3/2 peak partially overlaps with the Ni LMM Auger peak. In order to extract the bare Mn 2p line shape, the Ni LMM Auger (measured for the x = 0 sample and shown as a dotted line at the top of Figure 4.8(a) has been subtracted from the Mn 2p spectrum after proper renormalization and is shown in Figure 4.8(c). The Mn core-level line shape can be deconvoluted into the sum of two spin-orbit doublets representing Mn$^{2+}$ (at lower binding energy) and Mn$^{3+}$ (at higher binding energy) respectively, separated by a spin-orbit splitting of 11.2 eV. The area ratio of these two doublets shows that 50% of the Mn ions have a 2+ ionization state and 50% have a 3+ ionization state. It is important to note that the line-shape
of the Mn 2p core level does not change with Ni substitution, so only the fit for MnCo$_2$O$_4$ has been reported in Figure 4.8(c).

In Figure 4.8(d) the comparison of the fitted Ni 2p XPS core level spectra are shown. The centroids of the main peaks are located at 855 eV for the 2p3/2 level and 872.5 eV for the 2p1/2 level. Two broad satellites are also observed at about 861 eV and 880 eV. The two main peaks can be deconvoluted into two sub-components, ascribed to Ni$^{2+}$ (at 854 eV and 871.3 eV) and Ni$^{3+}$ (at 855.8 eV and 873.3 eV) oxidation states. As opposed to the Mn 2p and Co 2p core levels discussed above, the line shape of the Ni 2p core level does change with x. In particular, it is the relative percentage area of Ni$^{2+}$ and Ni$^{3+}$ that varies, as reported in Table 4.2. The x = 0.5 sample is found to have the largest amount of Ni$^{2+}$.

**Table 4.2.** Relative percentage area of Ni$^{2+}$ and Ni$^{3+}$ components extracted from the fit of Ni 2p core level.

<table>
<thead>
<tr>
<th>x</th>
<th>% area Ni$^{2+}$</th>
<th>% area Ni$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>34</td>
<td>66</td>
</tr>
<tr>
<td>0.3</td>
<td>31</td>
<td>69</td>
</tr>
<tr>
<td>0.5</td>
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<td>59</td>
</tr>
<tr>
<td>0.7</td>
<td>32</td>
<td>68</td>
</tr>
</tbody>
</table>

The O 1s XPS fitted spectra for the series is shown in Figure 4.8(e). Each spectrum has been fitted using three components, consistently with that published in the literature [39]. The fitted binding energies of the three components are reported in Table 4.3, together with their relative percentage areas. The binding energy of the main component shifts upwards by around 0.6 eV going from x = 0 to x = 1. The main peak at the lower binding energy side (or component 1) is attributed to stoichiometric oxygen in the oxides, while the peak at 531.1 eV can be attributed to defects and/or oxygen vacancies [40, 41]. The third component at 533 eV can be ascribed to chemisorbed oxygen [42]. The percentage weight of the oxygen vacancy component increases with Ni doping, which may suggest that MnCo$_2$O$_4$ has the best crystal lattice quality within the series.
Table 4.3. Binding energies and relative percentage areas of the three components of the O 1s core level.

<table>
<thead>
<tr>
<th>X</th>
<th>BE comp1 (eV)</th>
<th>BE comp2 (eV)</th>
<th>BE comp3 (eV)</th>
<th>% area comp.1</th>
<th>% area comp.2</th>
<th>% area comp.3</th>
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<td>79</td>
<td>16</td>
<td>5</td>
</tr>
</tbody>
</table>

4.3.4. Magnetic properties

Temperature-dependent magnetization in ZFC and FC modes for the Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ (x = 0, 0.3, 0.5, 0.7, 1) samples prepared by calcining at 450 °C and measured in a magnetic field of 500 Oe are shown in Figure 4.9. The samples were initially cooled from 300 K to 2 K, without any external magnetic field (ZFC), and the magnetization was recorded while warming the sample in the applied field of 500 Oe. With the measured temperature decreasing from 300 K to 2 K, all the ZFC curves dramatically rise and reach a maximum peak at a certain temperature, $T_{\text{max}}$, except for $x = 0.5$, which shows anomalous behaviour. The ZFC curves finally begin to drop and deviate from the FC magnetization curve. The bifurcation between ZFC and FC magnetization curves is due to the existence and distribution of energy barriers of the magnetic anisotropy and the slow relaxation of the nanoparticles below $T_{\text{max}}$ [43]. The bifurcation between the ZFC and FC magnetization starts at a temperature known as irreversible temperature ($T_{\text{irr}}$), which is related to the blocking of the largest particles [43]. The $T_{\text{max}}$ obtained from the ZFC maximum is generally assumed to be directly proportional to the average blocking temperature ($T_B$) for non-interacting particles that depends upon the type of particle size distribution [44].

As seen from Figure 4.9, all the FC curves continuously decreased with increasing temperature indicating the relatively large magnetic anisotropy of the samples except for $x = 0.5$. A broad
maximum in the ZFC magnetization curve for $x = 0$ and $x = 0.3$ samples occur at $T_{\text{max}} \sim 66.58$ K and 84 K, respectively. However, for $x = 0.5$ sample, the ZFC magnetization curve shows anomalous behaviour in which the magnetization initially increases slowly, reaches the temperature at $\sim 46.85$ K, and then seems to decrease until $\sim 192.23$ K. Nevertheless, it starts to increase afterward and no clear coincidence of the FC and ZFC curves was observed up to 300 K. This indicates that the irreversibility temperature ($T_{\text{irr}}$) for this sample may be larger than 300 K suggesting a blocking temperature above room temperature and a broader distribution of the effective energy barriers. Therefore, it appears that the blocking temperature increases from $x = 0$ to $x = 0.3$. The cause for this could be the presence of precipitated NiO phase and simultaneous formation of off-stoichiometric cobalt-rich $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ nanoparticles in these samples as it is given on table 1. In the cobalt-rich phase, a lattice distortion can result in the lowering of effective magnetocrystalline anisotropy, which in turn can cause lowering of blocking temperature $T_B$ [32]. Therefore, with increasing Mn concentration from $x = 0$ to $x = 0.5$, the amount of NiO phase decreases and hence an increase in the blocking temperature $T_B$ was observed. On further increasing the Mn concentration above $x = 0.5$, the blocking temperature starts to decrease, and a shoulder develops towards the higher temperature end forming a second maxima.

In order to better elucidate the emergence of more than one blocking temperatures, the corresponding differential curves of ZFC for the $x = 0.7$ and $x = 1$ samples are shown as an inset in Figure 4.9(d) and (e). The arrows mark three maximums representing the blocking temperatures. The $T_{\text{max}1}$, $T_{\text{max}2}$, and $T_{\text{max}3}$ observed for $x = 0.7$ is found to be at 21, 97, and 142 K, respectively and 16, 99, and 126 K for $x = 1$. It is noticeable that there is a bifurcation between field-cooled (FC) and zero-field cooled (ZFC) magnetization curves below the second maxima and the sample is in a paramagnetic state above this temperature. Such multiple maxima observed in the ZFC magnetization may be due to the presence of ferromagnetic and antiferromagnetic sublattices, their superposition and competition, and different temperature dependencies of magnetization in the sublattices [45]. The observed multiple maxima may be assigned as (a) $T_{\text{max}1}$-long-range antiferromagnetic transition, (b) $T_{\text{max}2}$-antiferromagnetic-type transition, and (c) $T_{\text{max}3}$-onset of the magnetic transition (ferromagnetic-like transition) [46]. Similar features were observed for MnCo$_2$O$_4$ nanocrystallites synthesized by a sol-gel process where two maxima are observed in $\chi_{\text{ZFC}}$. This could be due to a contribution from either core-shell arrangement of spins or disordered spins from different size distribution [47]. Mixed
Figure 4.9. Temperature dependence of magnetization in field cooled (FC) and zero field cooled (ZFC) regimes for $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$; (a) $x = 0$, (b) $x = 0.3$, (c) $x = 0.5$, (d) $x = 0.7$, and (e) $x = 1$ measured in a magnetic field of 500 Oe. Insets in the Fig. (d) and (e) show the corresponding ZFC differential curves.
ternary spinels (Co, Ni, Mn)$_3$O$_4$ and NiMn$_{2-x}$Co$_x$O$_4$ also exhibited similar behaviour and is explained based on the existence of a paramagnetic-ferrimagnetic state and two magnetic sublattices [24, 48].

The room temperature (T = 300 K) magnetic properties for Mn$_{x}$Ni$_{1-x}$Co$_2$O$_4$ were investigated by applying a magnetic field of ± 25 kOe. Magnetic hysteresis loops of Mn$_{x}$Ni$_{1-x}$Co$_2$O$_4$ are shown in Figure 4.10. A hysteresis loop is observed in all the samples, except for the x = 1 sample. It can be seen from Figure 4.10 that there was no saturation magnetization observed even in the presence of relatively strong magnetic field (H$_{app}$ = 25 kOe). This might be due to the magnetic surface disorder effects often observed at reduced dimensions and the presence of an antiferromagnetic component together with the ferromagnetic phase [26]. In the hysteresis loop for the sample x = 1, the magnetization increased linearly with the applied fields, typical of antiferromagnetic materials with almost close to zero coercivity and remnant.

Figure 4.10. Magnetic hysteresis loops for Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ (x = 0, 0.3, 0.5, 0.7, 1) measured at 300 K. The inset shows the magnified portion of the hysteresis loop.
magnetization. From the M-H curve, the values for coercivity, remnant magnetization, and saturation magnetization were extracted and reported in Table 4.2. The estimates of the room-temperature saturation magnetization ($M_s$) value for the samples were obtained by the extrapolation of $M$ versus $1/H$ curves to zero. The coercive field $H_c$ increases with increasing Mn concentration and reaches a maximum at $x = 0.5$. It then decreases with further increase in Mn concentration from $x = 0.5$ to reach a minimum at $x = 1$.

The magnetic moment ($\mu_B$) of $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ per formula unit can be calculated using [49]:

$$\mu_B = \frac{M \times M_S}{5585}$$  \hspace{1cm} (4.1)

where $M$ is the molecular weight, and $M_S$ is the saturation magnetization in emu g$^{-1}$ obtained from hysteresis loop. The value of the magnetic moments calculated were $1.276 \times 10^{-1}$, $0.748 \times 10^{-1}$, $1.953 \times 10^{-1}$, $1.377 \times 10^{-1}$ and $0.502 \times 10^{-1} \mu_B$ with $M_S$ values of $2.963$, $1.745$, $4.569$, $3.232$ and $1.185$ emu g$^{-1}$ for $x = 0$, $0.3$, $0.5$, $0.7$ and $1$ samples, respectively. On increasing Mn concentration from $x = 0$ to $x = 0.5$, the $M_S$ of the samples varies unevenly with a higher value of $2.963$ emu g$^{-1}$ for the NiCo$_2$O$_4$ ($x = 0$) sample than the sample with $x = 0.3$. It could be due to the contribution of the NiO phase and is close to the $M_S$ value of $\sim 2.85$ emu g$^{-1}$ reported by Verma et al. [32]. The NiO system has been described as an exchange-coupled spherical bilayer composed of an inner antiferromagnetic core and an outer shell of uncompensated spins [50].

Looking at the initial ZFC and FC curves, presence of interparticle interactions can be presumed, which can be either ferromagnetic or antiferromagnetic depending upon the orientation of each dipole leading to the frustration. A spin glass type behaviour might have been induced by the NiO due to frustration. This may lead to the presence of a much larger proportion of uncompensated surface spins on the ferrimagnetic core of off-stoichiometric NiCo$_2$O$_4$ lattice, which possibly has enhanced the saturation magnetization. However, with increasing $x$ from $0.3$ to $0.5$, the $M_S$ increases to reach a maximum of $4.569$ emu g$^{-1}$ for the $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ series. On further increasing the Mn concentration beyond $x = 0.5$, the $M_S$ starts to decrease and reaches a minimum value of close to zero for $x = 1$. This variation in magnetic parameters of $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ with Mn concentration can be explained based on the distribution of cations in the tetrahedral (A) and octahedral (B) positions and their exchange interactions. According to the XPS results obtained, it can be seen that all the Mn, Ni and Co ions exist both
in the +2 and +3 oxidation states. Based on the cation distribution in the inverse spinel NiCo$_2$O$_4$, it was shown that the A-site (tetrahedral, Td) is occupied by high spin (HS) Co$^{2+}$ ($^4A_2$, $e^4t_2^6$, $S = 3/2$) and Co$^{3+}$ ($^5E$, $e^3t_2^6$, $S = 2$), while Ni$^{2+}$ ($^3A_2g$, $t_2^6e^2_g$, $S = 1$), low spin (LS) Ni$^{3+}$ ($^2E_g$, $t_2^6e^1_g$, $S = 1/2$) and diamagnetic low spin (LS) Co$^{3+}$ ($^1A_1g$, $t_2^6e^0_g$, $S = 0$) occupy the B-site (octahedral, Oh) [27]. Thus, most of the trivalent Co$^{3+}$ ions at the octahedral site do not contribute to the magnetic behaviour, while the magnetic moment contribution of Co ions is dominated by those present in the tetrahedral sites. According to Néel's two-sublattice model of ferrimagnetism, which states that the cationic spins at the tetrahedral and the octahedral sites are arranged anti-parallel, the net magnetic moment ($n_B$) per formula unit is expressed using [51]:

$$n_B = M_B - M_A$$  \hspace{1cm} (4.2)

where $M_A$ and $M_B$ are the magnetic moments at the A and B sites, respectively.

Table 4.4. Magnetic parameters for Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ measured at room temperature

<table>
<thead>
<tr>
<th>$x$</th>
<th>$M_s$ (emu g$^{-1}$)</th>
<th>$H_c$ (Oe)</th>
<th>$M_r$ (emu g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.963</td>
<td>229</td>
<td>0.163</td>
</tr>
<tr>
<td>0.3</td>
<td>1.745</td>
<td>672.5</td>
<td>0.267</td>
</tr>
<tr>
<td>0.5</td>
<td>4.569</td>
<td>1416.5</td>
<td>1.647</td>
</tr>
<tr>
<td>0.7</td>
<td>3.232</td>
<td>301.95</td>
<td>0.446</td>
</tr>
<tr>
<td>1</td>
<td>1.185</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The variation in saturation magnetization and coercivity as a function of the concentration of manganese is given in Figure 4.11. The increase in $M_s$ values of Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ from $x = 0$ to $x = 0.5$ can be explained on the basis of increasing substitution of Ni ions by the higher magnetic Mn$^{2+}$ ions ($5 \mu_B$) in the octahedral (B) sites of the cobaltite sublattice. This leads to a stronger A-B superexchange interaction rather than A-A and B-B interactions as expected, indicating both Mn and Ni ions occupy octahedral sites and results in an increase in
magnetization in the samples. With increasing Mn concentration from $x = 0.5$, the $M_s$ values start to decrease until $x = 0$. This could be due to the increasing substitution of Ni ions leading to migration of Co$^{2+}$ ions from A to B-sites, which results in the increase of magnetization of B-sublattice ($M_B$) and reduction of magnetization of A-site ($M_A$).

With the continuous substitution of Mn above $x = 0.5$, maximum antiparallelism between the diminishing number of Co$_A$ and Co$_B$ ions cannot be maintained against the increasing antiparallel interaction within the B ions lattice. This destroys ferrimagnetic ordering and leads to magnetic frustration in this system. The reduction in ferrimagnetic ordering causes a reduction in magnetization [52]. This is in good agreement with the result from Rietveld refinement of the XRD patterns. In addition, from the XPS result, it was observed that the $x = 0.5$ sample has the largest concentration of Ni$^{2+}$ compared to other compositions. Thus, considering the larger magnetic moment of Ni$^{2+}$ (2.83 $\mu_B$) and lesser magnetic moment of Ni$^{3+}$ (1.73 $\mu_B$) in the B-site, this observation could explain the maximum $M_s$ and $H_c$ values observed at $x = 0.5$. As these results are new, more detailed studies based on neutron diffraction and magnetic properties measured at various temperatures and applied field are needed to better understand their structural and magnetic properties. This helps in establishing any correlation which may lead to an investigation of important properties such as magnetotransport property which has attracted considerable attention in spinels because it has potential applications in spintronics [53]. Therefore, the existence of room temperature ferromagnetism is imperative for energy systems such as data storage in computers and spintronics.
Conclusions

Single-phase crystalline ternary spinel-type $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) oxides were successfully obtained, from acetate precursors, via a citrate sol-gel method, at a relatively low temperature ($450 \, ^\circ\text{C}$). XRD studies combined with FTIR data confirm a cubic spinel structure with a $\text{Fd}3\text{m}$ space group and a crystallite size between 15.5 and 19.5 nm. These XRD results are in close agreement with the TEM-based particle size estimate, which is between 12 and 22 nm. The lattice parameter increases from $x = 0$ to $x = 0.5$ varying from 8.1084 Å to 8.1480 Å and then starts to decrease to a value of 8.1281 Å when reaching $x = 1$. This could be due to the substitution of Ni ions by the Mn ions in the octahedral position until $x = 0.5$ and the migration of the ions from octahedral position to the tetrahedral position after $x = 0.5$. The XPS spectra confirmed the compositions and oxidation states of Mn, Ni and Co species in the tetrahedral and octahedral sites in the spinel structure. The morphology of the oxides varies slightly with composition. When $x = 0$, cubic nanoplates of $\text{NiCo}_2\text{O}_4$ are formed and on increasing Mn concentration smaller nanoparticles with some agglomeration are formed. In
contradiction with NiCo$_2$O$_4$, Mn$_{0.3}$Ni$_{0.7}$Co$_2$O$_4$, Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ and Mn$_{0.7}$Ni$_{0.3}$Co$_2$O$_4$ nanoparticles that show ferromagnetic behaviour at room temperature, the MnCo$_2$O$_4$ nanoparticles show antiferromagnetic behaviour. The coercive force $H_c$ increased with increasing Mn concentration from a value of $H_c = 229$ Oe for $x = 0$ to $H_c = 1416.5$ Oe for $x = 0.5$, after which it decreases down to $H_c \sim 0$ Oe when $x = 1$. The saturation magnetization $M_s$ and remnant magnetization $M_r$ also vary with varying concentration of Mn. This is due to the variation in the Mn cation distribution in the tetrahedral and octahedral sites, which affects the superexchange interaction.
4.5. References


CHAPTER 5

Electrochemical performance of carbon coated ternary mixed Mn-Ni-Co oxide for supercapacitor applications

Abstract

A ternary mixed Mn-Ni-Co oxide coated with carbon nanosheets was synthesized using a facile and modified citrate sol-gel method, in which citric acid is used as a complexing agent, glucose as the carbon source and NaCl as the template, to make a hybrid nanostructured material. Binary metal oxides of Ni-Co and Mn-Co with carbon nanosheets were also prepared, and all materials were thoroughly characterized using XRD, Raman, FTIR, SEM, TEM, and nitrogen sorption. The metal oxide nanoparticles were observed to be embedded and well dispersed in a carbon matrix, which provides high electrical conductivity for the whole electrode. The ternary Mn-Ni-Co oxide show higher charge storage capacity, as supercapacitor electrodes, exhibiting higher specific capacitance of 322.2 F g\(^{-1}\) at a scan rate of 5 mV s\(^{-1}\) and 308.3 F g\(^{-1}\) at a current density of 1 A g\(^{-1}\) in 1M KOH electrolyte solution compared to the binary oxides. In addition, the carbon coated mixed ternary Mn-Ni-Co oxide hybrid electrode displayed a desirable stability in the alkaline electrolyte during long-term cycles with a specific capacitance of 176 F g\(^{-1}\) after 1000 cycles at a current density of 6 A g\(^{-1}\) with high capacitance retention of 92.6%. The high specific capacitance and excellent cycling stability of ternary Mn-Ni-Co oxide show promise for its application in supercapacitors.
5.1. Introduction

Currently, global demand for clean, renewable, and sustainable energy sources has prompted the need for efficient energy conversion and storage devices [1-4]. This is mainly due to the need to keep pace with the growing global economy, the exhaustion of fossil fuels, and address the rising environmental pollution [5, 6]. In this regard, electrochemical energy storage technologies are considered as the most effective and easier to apply in many areas of energy conversion or storage, which include batteries, fuel cells, and supercapacitors [7]. In terms of energy storage, supercapacitors are an area of rapid and growing research interest globally.

Supercapacitors, are systems that utilize electrochemical processes to store and discharge energy, and although they are used in conjunction with rechargeable battery systems, they may one day replace the currently dominant rechargeable battery technology [3, 4, 7, 8]. They have several advantageous features when compared to batteries; such as, longer lifecycle, environmentally friendly, high power density, excellent shelf life, faster charge/discharge processes, and highly efficient [4, 7, 8]. Supercapacitors are classified as electrochemical double layer capacitors (EDLCs), pseudo-capacitors, or hybrid electrochemical capacitors based on the energy storage mechanism. EDLCs operate based on surface charge storage mechanism at the electrode-electrolyte interface, while in pseudocapacitors charge is stored via a reversible redox reaction at the surface of electrode materials, and hybrid systems use electrode materials that display both EDLC and pseudo-capacitive behavior [3, 4, 7-9]. Recently, tremendous effort has been made in the search for high-performance electrode materials that can be used in supercapacitor systems. The main electrode materials being investigated include carbon-based materials [3, 4, 10], transition metal oxides or hydroxides [3, 4, 11, 12] and conducting polymers [4]. Among these, transition metal oxides are widely explored as electrode materials owing to their higher specific capacitance.

Currently, mixed transition-metal oxides (MTMOs) are observed to display remarkably high specific capacitance and are considered as potential super-capacitive electrodes [12]. Studies have shown that nanostructured MTMOs could deliver richer surface redox reactions and show enhanced electrical conductivity compared to the simple transition metal oxides, and thus significant improvement in super-capacitive behaviors is observed when employed as electrode materials for supercapacitors [11, 13, 14]. In this regard, ternary spinel-type Mn-Ni-Co oxides
are considered as attractive electrode materials with improved super-capacitive properties [15-18]. The improvement in the capacitive properties is attributed to the synergetic effects originating from the multi metals and the variable oxidation states. These mixed metal oxides also display much more electrochemical performance than that of binary Ni-Co and Mn-Co oxides [19].

However, due to their poor electrical conductivity and sluggish ion diffusion, most mixed transition metal oxides are observed to show low electrochemical performance further hindering its real-world applications. One promising way to address these limitations is to fabricate a hybrid structure composed of the MTMOs and conducting materials [20]. The carbon materials serve as a substrate to support the metal oxides and maintain structural integrity of the hybrid materials [20-22]. Despite the numerous research reports on the preparation of hybrid nanostructures, developing simple methods to manufacture such nanostructures still remains a challenging area of research. Recently, Fu et al. [23] have reported spinel MnCo2O4/C hybrid nanostructures consisting of MnCo2O4 nanoparticles dispersed uniformly on a porous carbon nanosheets, prepared by using glucose and NaCl as a carbon source and template, respectively, for the formation of carbon nanosheets. Similar method was reported by Wen et al. [24], in which Co3O4 nanoparticles were homogeneously encapsulated in a porous graphitic carbon prepared by a similar method.

Herein, we report ternary spinel-type Mn-Ni-Co-O/C nanosheet hybrid nanostructure by modifying the citrate sol-gel method reported in our previous study [25]. Making use of a NaCl template, Mn-Ni-Co-O/C nanosheets were prepared in situ using Ni(Ac)2, Mn(Ac)2 and Co(Ac)2 as metal precursors, citric acid as complexing agent and glucose as the carbon source. The electrochemical properties of these materials were tested as electrode materials for supercapacitors.

5.2. Experimental

5.2.1. Synthesis of carbon coated spinel-type Mn-Ni-Co oxide

The carbon coated spinel-type ternary Mn-Ni-Co oxide were prepared by modifying the citrate sol-gel method reported in our previous study [25]. Analytical grade cobaltous acetate,
manganese acetate, nickel acetate, citric acid, sodium chloride and glucose were used for the synthesis. In a typical synthetic procedure, a mixture of 0.245 g of manganese(II) acetate tetrahydrate (Mn(Ac)$_2$·4H$_2$O), 0.249 g of nickel(II) acetate tetrahydrate (Ni(Ac)$_2$·4H$_2$O), 0.996 g of cobalt(II) acetate tetrahydrate (Co(Ac)$_2$·4H$_2$O), and 1.89 g of citric acid monohydrate (C$_6$H$_8$O$_7$·H$_2$O) were dissolved in 50.0 mL of deionized water and the pH was adjusted to 7 by adding ammonia solution (25%) dropwise. Then 16 g of NaCl and 3.6 g of glucose (C$_6$H$_{12}$O$_6$) were ground for 30 min with an agate mortar-pestle set and were then added to the solution mixture of Ni(Ac)$_2$, Mn(Ac)$_2$, Co(Ac)$_2$, and citric acid by stirring for 30 minutes. The mixture was dried at 60 °C for 10 h and then heated at 750 °C for 6 h under N$_2$ atmosphere. The obtained black powder was heated again at 300 °C for 4 h in air to get the final crystalline phase (Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C), a puffy product. It was then cooled down to room temperature and washed with water and absolute alcohol several times to remove the NaCl, and then dried at 60 °C overnight in an oven.

MnCo$_2$O$_4$/C and NiCo$_2$O$_4$/C were also prepared by following the same procedure except taking either the Mn or Ni acetate and Co acetate salts. For comparison purposes, pure Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ was prepared by further annealing the Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C sample at 600 °C for 6 h in air.

5.2.2. Characterization

The crystal structure was investigated by using a Bruker D2 diffractometer (Co Ka radiation, $\lambda = 1.78060$ Å) at a scanning rate of 0.02° s$^{-1}$ in a 2θ range from 10° to 90°. Fourier transform infrared (FTIR) spectra were recorded at room temperature using a Shimadzu 8400 FTIR spectrometer employing potassium bromide (KBr) pellets technique in the range of 4000 - 400 cm$^{-1}$. TEM and SEM images and the composition of the materials were obtained on FEI Nova Nano SEM 450 Scanning Electron Microscope with EDX attached to it and JEOL 2100 Transmission Electron Microscopy. Raman spectra were acquired on a Thermo Scientific DXR2 Smart Raman equipped with a 532 nm laser source at room temperature. The BET surface area was measured N$_2$ adsorption/desorption using an ASAP 2020 (Micrometrics instrument, USA) surface area analyzer and the pore size distribution was evaluated by using the Barrett-Joyner-Halenda (BJH) model.
5.2.3. Preparation of the electrode

A working electrode was prepared by using carbon fiber paper as a substrate and mixing 80% active material, 10% conductive carbon, and 10% PVDF binder using a mortar and pestle and adding few drops of N-methyl pyrrolidone (NMP) to make a homogenous paste. This paste was then coated on to a 1 cm x 1 cm carbon fiber paper substrate, pressed and dried at 80 °C for 6 hours.

5.2.4. Electrochemical measurements

All electrochemical experiments were performed at room temperature on a Gamry interface 1000 potentiostat/galvanostat. The standard three electrode configuration was used where Ag/AgCl electrode was used as a reference electrode and platinum wire was employed as a counter electrode. Initially, cyclic voltammetry (CV) study were performed at different scan rates in four different electrolytes; 1M Na₂SO₄, 1M KCl, 1M KOH, and 1M NaOH to select the best electrolyte and 1M KOH was chosen for the subsequent experiments (Fig. S1). Galvanostatic charge discharge (GCD) test was performed by chronopotentiometry (CP) technique at different current densities. The EIS measurements were performed in the frequency range of 100 kHz to 0.1 Hz (amplitude of 10 mV). The EIS data were analyzed using Nyquist plots.

5.3. Results and discussion

5.3.1. Characterization of the samples

The procedure for the preparation of MnNiCo-O/C nanosheet hybrid nanostructure was adapted from Fu et al. [23] and modifying a citrate sol-gel method from our previous study [25]. In the first step, NaCl was employed as the template for the nanosheets as it has a face-centered cubic crystal structure and citric acid was used as a chelating agent for the metal ions. Then, glucose and metal acetates were selected as carbon source and metal precursors, respectively. The thermal decomposition of the inorganic metal salts forming the metal oxide
followed by glucose carbonization under N₂ gas leads to the formation of the MnNiCo/C hybrid. The MnNiCo/C hybrid is further calcined in air (300 °C) to oxidize MnNiCo/C and form the MnNiCo-O/C hybrid. Finally, the obtained powder is washed with deionized water followed by ethanol to remove the NaCl, and porous MnNiCo-O/C nanosheets are obtained. The presence of NaCl plays an essential role in synthesis process by assisting the formation of nanosheet structure, which agrees with other recent reports [24, 26, 27].

The XRD patterns of the prepared Mn₀.₅Ni₀.₅Co₂O₄/C, NiCo₂O₄/C, and MnCo₂O₄/C hybrid samples are shown Figure 5.1(a). It can be seen that all the samples exhibit similar cubic spinel structure (space group Fd3m (227), JCPDS No. 23-1237) and a carbon peak, which corresponds to the diffraction peak of (002) crystallographic plane of graphitic carbon (JCPDS No. 65-6212) coexist in the obtained product. That means the carbonization of C₆H₁₂O₆ took place at step one, and the carbon remained unaffected after annealing in air at step two. These experimental data confirm the successful formation of MnNiCo-O/C hybrid after thermal treatment at 300 °C in air. For the MnCo₂O₄/C and NiCo₂O₄/C samples, similar XRD patterns were obtained except that NiO phase appeared in the NiCo₂O₄/C sample, which is consistent with our previous report [25]. The Raman spectrum shows the typical D and G bands for the Mn₀.₅Ni₀.₅Co₂O₄/C, NiCo₂O₄/C, and MnCo₂O₄/C hybrids at about 1,343 and 1,581 cm⁻¹, respectively (Fig. 5.1(b)). The ratio of peak intensity between the D and G bands (I_D/I_G) gives a suggestion of the degree of graphitization of carbon materials [28-30]. The calculated I_D/I_G ratio for the Mn₀.₅Ni₀.₅Co₂O₄/C and NiCo₂O₄/C hybrid is 1, suggesting that the carbon has some amorphous characteristics, while for NiCo₂O₄/C hybrid it is 0.87 indicating a relatively well-crystalline graphitic structure, when compared to the ternary oxide hybrid. Moreover, the presence of the characteristic peaks for the Mn-O, Ni-O and Co-O bonds below 800 cm⁻¹ also confirms that high-quality Mn-Ni-Co-O spinel has been successfully synthesized [21, 23]. The formation of the spinel oxides is further confirmed by the FTIR spectra (Fig. 5.1(c)), where the two characteristic absorption bands of metal-oxygen vibrations are observed at 655 and 574 cm⁻¹ [31]. A broad peak at 3426 cm⁻¹ and a weak peak at 1625 cm⁻¹ are observed, which are due to adsorbed water.

The morphology and composition of the MnNiCo-O/C hybrids were initially characterized by SEM. Figure 5.2(a), (b), and (c) show the SEM images of MnCo₂O₄/C, NiCo₂O₄/C and Mn₀.₅Ni₀.₅Co₂O₄/C hybrids with some sheet like structure, which is more clearly shown on the
Figure 5.1. (a) XRD pattern (b) Raman spectra, and (c) FTIR spectra of the Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C, MnCo$_2$O$_4$/C, and MnCo$_2$O$_4$/C hybrids.

TEM image. The elemental mapping and EDS of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C (Fig. 5.2 (d) and (e)) confirm the presence of the elements Mn, Ni, Co, and O only.

TEM, HRTEM, and the corresponding SAED of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C is shown in Figure 5.3. Figure 5.3(a) and (b) show the sheet like structure of carbon and the metal oxide nanoparticles are well-dispersed in the carbon nanosheet. In the highly magnified TEM image (Fig. 5.3(b)), the carbon nanosheets seem transparent under the electron beam, suggesting the formation a thin sheet and the metal oxide nanoparticles are uniformly dispersed. This is clearly shown in
Figure 5.2. Typical SEM images of (a) MnCo$_2$O$_4$/C, (b) NiCo$_2$O$_4$/C, (c) Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C, and (d &e) EDS and elemental mapping of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C.

Figure 5.3(c) where the thickness of the carbon layer is measured to be around 6 nm and it is shown to encapsulate the metal oxide particle well. The HRTEM and SAED in Figure 5.3(d) suggest the polycrystalline nature of the hybrid structures.

The BET surface area and pore size distribution measurement of the samples were performed using nitrogen adsorption/desorption method. Figure 5.4(a, b & c) show the corresponding nitrogen adsorption/desorption isotherms and their BJH pore size distributions. The textural parameters obtained from the isotherms are presented in Table 5.1. A hysteresis loop is
Figure 5.3. (a and b) TEM image of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C nanosheets at different magnifications; (c) High magnification TEM image showing the carbon coating layer; and (d) HRTEM image of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C nanosheets and the inset is the SAED.

observed for all the samples with a typical type IV isotherm and an H3 hysteresis loop (P/P$_0$ > 0.4), indicating a mesoporous structure and a narrow mesopore size distribution. The BET specific surface areas of MnCo$_2$O$_4$/C, Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C and NiCo$_2$O$_4$/C are calculated to be 264.67, 129.93, and 209.52 m$^2$/g, respectively. Despite the relatively lower surface area of ternary spinel Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C hybrid, it has a larger pore volume of 0.537 cm$^3$/g and a multi-modal pore size distribution, with peaks at 2.25 nm, 4.65 nm, and a broad peak at approximately 18.0 nm. Such a pore structure could be advantageous for supercapacitors because of the high surface area, multi-modal pore size distribution, and a large pore volume. This can make the diffusion of electrolyte and charge transfer easier [32]. The variations in the BET surface area, pore volume and pore size distribution of the hybrid structures makes it reasonable to speculate different electrochemical properties. The insets in Fig. 5.4 show pore size distributions. From the PSD curves, it can be observed that the binary metal oxides have similar pore size distributions with peaks around 2 nm, with relatively lower pore volumes and
a narrower pore size distribution when compared to the ternary metal oxide. Thus, the binary metal oxides should be less favorable for rapid ion transport within the electrode surface.
<table>
<thead>
<tr>
<th>Samples</th>
<th>BET specific surface area (m² g⁻¹)</th>
<th>BJH pore volume (cm³ g⁻¹)</th>
<th>BJH pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnCo₂O₄/C</td>
<td>264.67</td>
<td>0.394</td>
<td>6.63</td>
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<tr>
<td>Mn₀.₅Ni₀.₅Co₂O₄/C</td>
<td>129.93</td>
<td>0.537</td>
<td>11.24</td>
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<tr>
<td>NiCo₂O₄/C</td>
<td>209.52</td>
<td>0.256</td>
<td>5.37</td>
</tr>
</tbody>
</table>

5.3.2. Electrochemical performance

5.3.2.1. Cyclic voltammetry studies

Figure 5.5(a) shows the cyclic voltammogram (CV) curves at a scan rate of 50 mV s⁻¹ in 1 M KOH of the binary MnCo₂O₄/C and NiCo₂O₄/C and ternary Mn₀.₅Ni₀.₅Co₂O₄/C hybrid systems in the potential window of 0-0.6 V. The CV curves exhibit some broad redox peaks, except for MnCo₂O₄/C, which resembles the rectangular shape of electric double layer capacitance (EDLC) [22, 33-35]. The MnCo₂O₄/C sample displays an EDLC type behavior with a rectangular type CV curve. Figure 5.5(b-d) shows CV curves of the materials at a different scan rate of 5–100 mV s⁻¹. The CV shapes clearly indicate that the capacitive nature of the hybrid electrode materials is pseudocapacitive. A pair of redox peaks is clearly observed for scan rates 5-50 mV s⁻¹ in each voltammogram for the materials, except for MnCo₂O₄/C. The redox peaks in the CV curves correspond to the reversible redox reactions related to M−O/M−O−OH (M = Co, Ni, and Mn) [36-38]. The redox reactions involved in the electrochemical process can be described as [19];

\[
\text{(Mn, Ni)Co}_2\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow (\text{Mn, Ni})\text{OOH} + 2\text{CoOOH} + 2e^- \quad \text{--------------------} (1)
\]

\[
\text{MOOH} + \text{OH}^- \leftrightarrow \text{MO}_2 + \text{H}_2\text{O} + e^- \quad \text{--------------------} (2)
\]

where M represents Co or Ni and Mn. An interesting aspect of this study is that there is an enhancement in the area under the curve moving from MnCo₂O₄/C to NiCo₂O₄/C and to the ternary Mn₀.₅Ni₀.₅Co₂O₄/C hybrid electrodes and with the highest current response observed
for the ternary Mn_{0.5}Ni_{0.5}Co_{2}O_{4}/C. It is worth mentioning that the current response increases with increasing scan rate for all the electrodes. This shows that the observed current is directly proportional to the scan rate, and hence display capacitive behavior [38]. Comparisons of CV measurement at 50 mV s^{-1} between the bare Mn_{0.5}Ni_{0.5}Co_{2}O_{4} and Mn_{0.5}Ni_{0.5}Co_{2}O_{4}/C electrodes are presented in Fig. S3. The area enclosed by the CV curve of Mn_{0.5}Ni_{0.5}Co_{2}O_{4}/C electrodes is noticeably larger than that of the Mn_{0.5}Ni_{0.5}Co_{2}O_{4} electrode and also show higher redox current, demonstrating the superior capacitive performance of the Mn_{0.5}Ni_{0.5}Co_{2}O_{4}/C electrode. This is attributable to the higher surface area and better electronic conductivity provided by the carbon matrix, which enhances the electrochemical performance of the mixed metal oxide.

Figure 5.5. Cyclic voltammetry (CV) studies. (a) CV curves of MnCo_{2}O_{4}/C, NiCo_{2}O_{4}/C, and Mn_{0.5}Ni_{0.5}Co_{2}O_{4}/C at a scan rate of 50 mV s^{-1} (b) MnCo_{2}O_{4}/C (c) NiCo_{2}O_{4}/C and (d) Mn_{0.5}Ni_{0.5}Co_{2}O_{4}/C at different scan rates.
The specific capacitance values were obtained from the cyclic voltammetry measured in the potential window of 0.0 - 0.6 V. The specific capacitances \( C_s \) of the electrodes is calculated using the following relation [39]:

\[
C_s = \frac{\int IdV}{m\nu \Delta V} \tag{3}
\]

where \( \int IdV \) is the area integrated under the CV curve (A), \( \nu \) is the scan rate (mV s\(^{-1}\)), \( m \) is the mass of the electroactive material (g), and \( \Delta V \) is the potential window (V). The calculated specific capacitance of NiCo\(_2\)O\(_4\)/C, MnCo\(_2\)O\(_4\)/C, and Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C electrodes are 236.9, 273, and 322.2 F g\(^{-1}\) at a scan rate of 5 mV s\(^{-1}\), respectively. The specific capacitances \( C \) of Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C hybrid electrode are found to be 322.2, 227.8, 161.8, 110, and 92.36 F g\(^{-1}\) at scan rate of 5, 10, 20, 50, and 100 mV s\(^{-1}\), respectively. The specific capacitance decreases with the increase of the scan rate as given in Table 2. The variation of the specific capacitance with scan rate is given in Fig. 5.6. The ternary Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C hybrid electrode exhibits enhanced supercapacitance compared to the binary MnCo\(_2\)O\(_4\)/C and NiCo\(_2\)O\(_4\)/C hybrid samples. The improved supercapacitive behaviors of the ternary Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C hybrid electrode systems can be attributed to the synergistic effect of the multicomponent metal oxide and the carbon nanosheet and enhanced conductivity of the hybrid electrode. Similar results were reported earlier emphasizing the synergetic effect of multicomponent systems in mixed metal oxides [15, 19, 22]. The carbon nanosheet in the hybrid nanostructure serves as a conductive matrix supporting the metal oxide and providing large surface area, fully utilizing the electrochemical performance of the ternary metal oxide.
Table 5.2. Variation of specific capacity with a scan rate.

<table>
<thead>
<tr>
<th>Scan rate (mV s(^{-1}))</th>
<th>Specific Capacity (F g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiCo(_2)O(_4)/C</td>
</tr>
<tr>
<td>5</td>
<td>236.9</td>
</tr>
<tr>
<td>10</td>
<td>177.4</td>
</tr>
<tr>
<td>20</td>
<td>137.2</td>
</tr>
<tr>
<td>50</td>
<td>101.5</td>
</tr>
<tr>
<td>100</td>
<td>73.8</td>
</tr>
</tbody>
</table>

Figure 5.6. Variation of the specific capacitance with scan rate.

5.3.2.2. Galvanostatic charge discharge

The galvanostatic charge-discharge (GCD) curves of the Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C electrode materials were recorded at different current densities ranging from 1 A g\(^{-1}\) to 10 A g\(^{-1}\) in 1 M
KOH electrolyte as shown in Figure 5.7(a). The asymmetric shape of the GCD curves indicates the faradaic behavior of the hybrid electrode consistent with the CV curves. The specific capacitance from the galvanostatic charge-discharge curves can be calculated according to the following equation:

\[
C_m = \frac{I \times \Delta t}{\Delta V \times m}
\]

where, \(C_m\) (\(F \, g^{-1}\)) is the specific capacitance, \(I\) (A) is discharge current, \(\Delta t\) (s) is the discharging time, \(\Delta V\) (V) represents the potential difference, and \(m\) (g) is the mass of the active material loaded. The specific capacitance values of the Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C hybrids evaluated from the discharge curves are 308.3, 300, 282.6, 262, 258 and 147.6 \(F \, g^{-1}\) at the current density of 1, 2, 4, 6, 8 and 10 \(A \, g^{-1}\), respectively. The specific capacitance is observed to steadily decrease with the increasing current density. This is due to the fact that the diffusion and migration of electrolyte ions is suppressed at high discharge current density [40]. The specific capacitance \(C_m\) as a function of current density is presented in Figure 5.7(b). It can be seen that a specific capacitance of 147.6 \(F \, g^{-1}\) is obtained even at discharge current density of 10 \(A \, g^{-1}\) indicating a high rate charge-discharge performance of Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C electrode. This may be due to the high surface area and larger pore size, which increase the access of an electrolyte to the electrode surface minimizing the diffusion distance and accelerating the rate of diffusion in the electrode [41].

The long cyclic stability of the Mn\(_{0.5}\)Ni\(_{0.5}\)Co\(_2\)O\(_4\)/C hybrid electrode is evaluated by the galvanostatic charge-discharge performed at a current density of 6 \(A \, g^{-1}\) in the potential range of 0-0.5 V in 1 M KOH solution for 1000 cycles. As shown in Figure 5.7(c), after 1000 cycles specific capacitance of 176 \(F \, g^{-1}\) was observed maintaining 92.6% of its specific capacitance, which is a highly desirable property for high performance energy storage devices.
5.3.3. Electrochemical impedance

In order to get more information about the electrochemical performance and the charge-transfer process of the electrodes, electrochemical impedance spectroscopic (EIS) measurements were carried out before and after GCD measurements. EIS was carried out by using 1 M KOH as an electrolyte, and the data were analyzed by using Nyquist plots. Nyquist plots of the MnCo$_2$O$_4$/C, NiCo$_2$O$_4$/C, and Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C electrodes in the frequency range from 0.1 Hz to 100 kHz are displayed in Figure 5.8(a). In the Nyquist plots, the intercept on the real axis represents the internal resistance in the high frequency region and the semicircles corresponds
to the charge transfer resistance [42]. All the impedance plots are composed of suppressed semicircle in high frequency region followed by a linear line in the low frequency region. An equivalent series resistance (ESR) value of 3.6, 6, and 17.7 Ω were obtained for Mn0.5Ni0.5Co2O4/C, NiCo2O4/C, and MnCo2O4/C electrodes. Thus, Mn0.5Ni0.5Co2O4/C hybrid electrode provides relatively low equivalent series resistance and negligible charge transfer resistance in the electrode during the charge/discharge process. This suggests the low interfacial resistance between the current collector and active material and fast charge transfer kinetics at the interface owing to the high electrical conductivity of the ternary spinel Mn0.5Ni0.5Co2O4/C. The Nyquist plots of Mn0.5Ni0.5Co2O4/C hybrid electrodes before and after 1000 cycles are shown in Figure 5.8(b). The Nyquist plots after 1000 cycles indicates that it has a very low resistance and good capacitive retention without a significant loss. Comparison of the Nyquist plots of bare Mn0.5Ni0.5Co2O4 and carbon coated Mn0.5Ni0.5Co2O4/C is also shown in Fig. S4, indicating the effect of in situ formed carbon nanosheet supporting the metal oxide nanoparticles and enhancing the conductivity of the hybrid electrode.

![Figure 5.8](image)

**Figure 5.8.** Nyquist impedance plots (a) MnCo2O4/C, NiCo2O4/C, and Mn0.5Ni0.5Co2O4/C and (b) Mn0.5Ni0.5Co2O4/C before and after 1000 cycles; insets show the impedance at their respective high frequency region.
5.4. Conclusions

In summary, carbon encapsulated spinel-type MnCo$_2$O$_4$/C, NiCo$_2$O$_4$/C and Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C nanosheet hybrids were successfully prepared by a facile and scalable method by modifying the citric acid assisted sol-gel method and employing a NaCl template-directed pyrolysis and glucose as a carbon source. The prepared ternary spinel-type Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C nanosheets hybrid exhibit higher electrochemical performance as electrode materials for supercapacitors as compared to the binary spinel-type MnCo$_2$O$_4$/C and NiCo$_2$O$_4$/C hybrid electrodes. The porous structure and large surface area of the Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C hybrid electrode provided by the carbon sheets and the synergistic effect of multiple components results in an enhanced electrochemical performance. The hybrid Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C electrode exhibit a specific capacity of 322.2 F g$^{-1}$ at a scan rate of 5 mV s$^{-1}$ and 308.3 F g$^{-1}$ at a current density of 1 A g$^{-1}$ calculated from the charge discharge curve. It also delivers a specific capacitance of 176 F g$^{-1}$ after 1000 cycles at a current density of 6 A g$^{-1}$ with relatively high capacitance retention of 92.6%. Therefore, the good electrochemical properties combined with the facile preparation method will make it an attractive electrode material for promising application in supercapacitors.
5.5. References


CHAPTER 6

Mn substituted Mn₅Zn₇₋₅ₓCo₂O₄ oxides synthesized by co-precipitation; effect of doping on the structural, electronic and magnetic properties

Abstract

Mn substituted MnₓZn₁₋ₓCo₂O₄ (x = 0, 0.3, 0.5, 0.7, 1) oxides were synthesized by a facile co-precipitation method followed by calcination at 600 °C. The presence of manganese ions causes appreciable changes in the structural and magnetic properties of the Mn-substituted ZnCo₂O₄. The morphologies, structures, and electronic properties of Mn-Zn-Co oxide microspheres were characterized using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, Fourier Transform Infrared spectroscopy, and X-ray photoelectron spectroscopy. The X-ray diffraction and Fourier transform infrared spectroscopy results confirmed the formation of spinel MnₓZn₁₋ₓCo₂O₄. It was shown that the Mn-Zn-Co oxide microspheres increase in size and become regular in shape with increasing Mn concentration with the crystal size lying in the range from 19.1 nm to 51.3 nm. Magnetization measurements were carried out using a vibrating sample magnetometer at room temperature and 10 K. The saturation magnetization is observed to increase with increasing Mn concentration from x = 0 to x = 1.
6.1. Introduction

Nano-structured spinel-type transition metal oxides have been investigated intensively for various potential applications including chemical sensors [1, 2], energy storage devices [3], pigments [4], catalysts [5] and spintronics [6]. Among the various transition metal oxides, spinel-type ZnCo$_2$O$_4$ has attracted much attention as an important p-type semiconductor; which has been used as anode material in lithium ion batteries [7], gas sensor [2, 8], organic photovoltaics, electrocatalysis [9], photocatalysis [10, 11], and as a p-type gate in junction field-effect transistors [12].

The magnetic properties of Zn-Co-O systems have been widely investigated, with a number of studies focusing on the thin films and powders, which have exhibited properties ranging from paramagnetic to strong ferromagnetic behaviour [13-16]. Several studies have shown that room temperature ferromagnetism is observed in Zn based transition metal oxide systems such as Zn-Co-O and Zn-Co-Mn-O [17] because of an exchange interaction mechanism such as double-exchange, super-exchange and through dopant electron-delocalized conduction band electron interactions [18, 19]. The ferromagnetism of spinel-type ZnCo$_2$O$_4$ is a continuous debate and its microscopic origins remain poorly understood. Its ferromagnetism is believed to arise due to hole mediated Co-Co interaction while the behaviour turns out to be antiferromagnetic as a result of Co-O-Co super exchange interaction [20], which also exhibits magnetoresistance effect and have application as promising materials for spintronics [21-23]. Kim et al. [20, 24] have investigated the electrical and magnetic properties of spinel-type p-type semiconducting ZnCo$_2$O$_4$ thin films, with results suggesting that departure from stoichiometry in this compound affects its electrical and magnetic properties.

The ZnCo$_2$O$_4$ structure has remarkable features in that it forms a regular spinel structure where Zn$^{2+}$ ions occupy tetrahedral (T$_b$) sites and the Co$^{3+}$ and Co$^{2+}$ ions in octahedral (O$_b$) and some in tetrahedral sites [25, 26]. The variation in the magnetic properties of a ZnCo$_2$O$_4$ can arise when there is a substitution of nonmagnetic ions by magnetic ions. Many studies were conducted on Zn-based spinel oxides to demonstrate the effect of substitution of nonmagnetic ions on their magnetic and structural properties [27-29]. The studies have shown a significant change in the magnetic properties during substitution due to a predominant super-exchange interaction between the cations in the A-site and B-site via oxygen ions.
In the present study, we report the synthesis of Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ (x = 0, 0.3, 0.5, 0.7, and 1) employing a facile coprecipitation method. The structural, electronic and magnetic properties of the nano-crystalline Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ in relation to the concentration of Mn were investigated.

6.2. Experimental

6.2.1. Chemicals

Analytical reagents of Ni(Ac)$_2$·4H$_2$O, Mn(Ac)$_2$·4H$_2$O and Co(Ac)$_2$·4H$_2$O were obtained from Sigma-Aldrich. NH$_4$HCO$_3$ and absolute ethanol (≥99.8%) were purchased from Merck Millipore.

6.2.2. Materials synthesis

Mn substituted Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ was synthesized with a facile co-precipitation method followed by annealing. In a typical synthesis of Mn$_{0.5}$Zn$_{0.5}$Co$_2$O$_4$ (x = 0.5), 0.245g of Mn(Ac)$_2$·4H$_2$O, 0.22g of Zn(Ac)$_2$·4H$_2$O and 0.996g of Co(Ac)$_2$·4H$_2$O were dissolved in a mixture of 7 mL of ethanol and 70 mL of distilled water with vigorous stirring to form solution A. Then, 4.74g of NH$_4$HCO$_3$ was dissolved in 70 mL of distilled water to form solution B, which was then added to solution A drop wise, while stirring. The resulting mixed solution was heated to 45 °C and maintained at this temperature for 9h with vigorous stirring. A pale pink precipitate was obtained, which was collected through filtration, washed thoroughly with distilled water and ethanol and then dried at 60 °C overnight. The obtained carbonate precursor was heat treated in air at 600 °C for 5 h at a temperate ramp of 2 °C min$^{-1}$ to yield a black powder.

6.2.3. Characterization

The phase components and structure of the as-prepared materials were characterized using Bruker D2 Phaser X-Ray Diffractometer (XRD; Co Kα radiation, λ= 1.78060 Å). The XRD data for Rietveld refinement was measured using a D9 X-Ray Diffractometer (XRD; Mo Kα$_1$
radiation, $\lambda = 0.709321$ Å) and was analysed on TOPAS software (version 5). Fourier transform infrared (FTIR) spectra were recorded in the range of 4000–400 cm$^{-1}$ using a Shimadzu 8400 FTIR spectrometer employing potassium bromide (KBr) pellets technique at room temperature. Morphology of the materials was obtained on FEI Nova Nano SEM 450 Scanning Electron Microscope (SEM) and JEOL 2100 Transmission Electron Microscopy (TEM). The composition of the samples was analysed by EDX attached to the SEM instrument. Raman scattering spectra were acquired at room temperature on a Thermo Scientific DXR2 Smart Raman equipped with a 532 nm laser source. The specific surface area was determined using Brunauer-Emmett-Teller (BET) technique and was determined from N$_2$ adsorption/desorption isotherms obtained on an ASAP 2020 (Micrometrics instrument, USA) surface area analyser. Thermogravimetric Analysis (TGA) was carried out under airflow with a temperature ramp of 10 °C min$^{-1}$ using Thermogravimetry/Differential Thermal Analyzer (Hitachi-STA7200RV, California, USA). Magnetic measurements were performed using a Cryogenic measurement platform equipped with a vibrating sample magnetometer (VSM) insert. VSM measurements were done in zero field cooled (ZFC) and field cooled (FC) modus of measurement in a temperature range of 2 to 300 K. Hysteresis loops were performed in a field range of +2.5T to -2.5T at two different temperatures of 10 K and 300 K. X-ray photoemission (XPS) spectra were performed at room temperature using a SPECS PHOIBOS 150 hemispherical electron energy analyser. The photon source used was a SPECS XR 50 M monochromatized X-ray source equipped with an Al K$\alpha$ anode ($h\nu = 1486.71$ eV). The overall energy resolution was set to 0.7 eV for survey spectra and 0.55 eV for all other high-resolution core level spectra shown in this work. High resolution XPS spectra for ZnCo$_2$O$_4$ are not reported here. The reason for this is that the sample was too insulating for charge compensation to take place effectively, even with the aid of a flood gun. The line shape of the XPS spectra for this sample was therefore distorted, making the information extracted from them meaningless. We therefore report high resolution core level spectra only for the other four compounds in the Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ series ($x = 0, 0.3, 0.5$ and 0.7).
6.3. Results and discussions

6.3.1. Formation of the spinel-type oxides

With the starting chemical precursors, the formation reactions of the Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}(CO\textsubscript{3})\textsubscript{2} precursor can be described in the following two steps:

\[
2\text{NH}_4\text{HCO}_3 \rightarrow \text{H}_2\text{CO}_3 + 2\text{NH}_4^+ + \text{CO}_3^{2-} \quad (1)
\]

\[
x\text{Mn}^{2+} + (1-x)\text{Zn}^{2+} + 2\text{Co}^{2+} + 2\text{CO}_3^{2-} \rightarrow \text{Mn}_x\text{Zn}_{1-x}\text{Co}_2(\text{CO}_3)_2 \quad (2)
\]

The ammonium hydrogen carbonate used in the present synthesis mainly serves as a source for the generation of carbonate, as explained in equation (1), while the divalent metal cations are obtained from the acetate precursors.

Thermal analysis allows for determining the precursor decomposition temperature during the heat treatment, which eventually will produce the oxide. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses were performed to characterize the thermal properties and further determine the sintering temperature of the carbonate precursor. Figure 6.1 shows the DSC and TG curves of the as prepared carbonate precursors for the composition \( x = 0.5 \). It can be seen that the carbonate precursor decomposes in two steps. The first step occurs between 120 °C and 190 °C, which is indicated by a small exothermic peak on the DSC curve. It is due to the evaporation of water adsorbed on the surface of the precursor sample. In the second step, a major mass loss of 35% occurs between 196 °C and 430 °C, which can be attributed to the decomposition of the carbonate precursor to a metal oxide. The DSC curve shows a sharp exothermic peak at about 376 °C, corresponding to this dominant mass loss, which indicates that the amorphous carbonate precursor transformed to Zn\textsubscript{0.5}Mn\textsubscript{0.5}Co\textsubscript{2}O\textsubscript{4} at this temperature.

6.3.2. Structural studies

Crystalline nature and phase identity of the prepared materials were precisely determined from X-ray diffraction (XRD) studies. The XRD patterns of the Mn doped ZnCo\textsubscript{2}O\textsubscript{4}, Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4}
(x = 0, 0.3, 0.5, 0.7, 1), oxides prepared by facile coprecipitation route and heat treatment at 600 °C are shown in Figure 6.2 below. The peaks at 2θ values are well matched with the standard cubic spinel structure of ZnCo2O4 (PDF card No. 23-1390) and MnCo2O4 (PDF card No. 23-1237) corresponding to the (111), (220), (311), (222), (400), (422), (511), and (440) lattice planes. This observation demonstrates the formation of a single phase for all the compositions. The intensity of the diffraction peaks of MnₓZn₁₋ₓCo₂O₄ increases and the peak width (full width at half maximum, FWHM) decreases with increasing Zn concentration. The crystallite size was observed to decrease irregularly from 51 to 19 nm with increasing Mn concentration. Rietveld analysis of the XRD pattern of MnₓZn₁₋ₓCo₂O₄ obtained from X-ray diffractometer with Mo-tube is shown in Figure 6.2(b) and Table 6.1 with the reliability factors (Rwp, RB, GOF), lattice parameter and crystal size given. The lattice parameter, a = 8.0874 Å, calculated for ZnCo2O4 is close to the reported values (PDF card No. 23-1390). On substituting Mn ions for Zn²⁺, the lattice parameter increases compared to that of the pure ZnCo2O4 because of the slightly bigger ionic size of Mn ions compared to Zn²⁺ (0.740 Å) [30]. The lattice parameter shows a clear increase and a linear behavior with increase of Mn ion doping which further corroborates successful substitution by the Mn ion.

**Figure 6.1.** Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis curves of the Zn₀.₅Mn₀.₅Co₂CO₃ precursor in an air atmosphere.
Figure 6.2. a) XRD patterns of the Mn substituted Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4} oxide with different Mn concentrations; x = 0, 0.3, 0.5, 0.7 and 1. b) Rietveld refined XRD pattern of Mn\textsubscript{0.5}Zn\textsubscript{0.5}Co\textsubscript{2}O\textsubscript{4}

Table 6.1. Rietveld refined parameters for Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameter (a), Å</th>
<th>R\textsubscript{wp} (%)</th>
<th>R\textsubscript{B} (%)</th>
<th>GOF</th>
<th>Average crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCo\textsubscript{2}O\textsubscript{4}</td>
<td>8.0874</td>
<td>13.90</td>
<td>2.55</td>
<td>1.17</td>
<td>51.3</td>
</tr>
<tr>
<td>Mn\textsubscript{0.3}Zn\textsubscript{0.7}Co\textsubscript{2}O\textsubscript{4}</td>
<td>8.1051</td>
<td>13.06</td>
<td>3.47</td>
<td>1.17</td>
<td>36.8</td>
</tr>
<tr>
<td>Mn\textsubscript{0.5}Zn\textsubscript{0.5}Co\textsubscript{2}O\textsubscript{4}</td>
<td>8.1241</td>
<td>14.29</td>
<td>2.40</td>
<td>1.09</td>
<td>19.9</td>
</tr>
<tr>
<td>Mn\textsubscript{0.7}Zn\textsubscript{0.3}Co\textsubscript{2}O\textsubscript{4}</td>
<td>8.1349</td>
<td>15.48</td>
<td>2.74</td>
<td>1.16</td>
<td>26.7</td>
</tr>
<tr>
<td>MnCo\textsubscript{2}O\textsubscript{4}</td>
<td>8.1508</td>
<td>14.49</td>
<td>2.85</td>
<td>1.11</td>
<td>19.3</td>
</tr>
</tbody>
</table>

The formation of a single-phase cubic structure is also confirmed from the Raman spectra. Raman spectra of all the compositions recorded at room temperature are shown in Figure 6.3. There are prominent broadening peaks observed at three regions like 460-470 cm\textsuperscript{-1}, 600-610 cm\textsuperscript{-1} and 660-670 cm\textsuperscript{-1} in the oxides, corresponding to E\textsubscript{g}, F\textsubscript{2g} and A\textsubscript{1g} modes of spinel oxides [31], which are indicated in the Raman spectra. These characteristics peaks are in agreement
with those reported for crystalline ZnCo$_2$O$_4$ [31, 32], except some of the peaks are shifted by several cm$^{-1}$. This phenomenon can be ascribed to the change in the surface strain or defects owing to the incorporation of Mn into the ZnCo$_2$O$_4$ crystal structure since the defects and strains in the crystal structure can result in the shifts in Raman peaks, which is in accordance with the XRD results.

**Figure 6.3.** Raman spectra of various concentration of Mn doped ZnCo$_2$O$_4$
Figure 6.4. FTIR spectra of the Mn substituted Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4} oxide with different Mn concentrations; x = 0, 0.3, 0.5, 0.7 and 1.

FTIR spectroscopy is an important technique to identify the stretching and bending vibrations of different materials. Figure 6.4 shows FTIR spectra in the range from 1000 to 400 cm\textsuperscript{-1} as signals in this range are generally attributed to the vibration bands of metallic ions in the crystal lattice. Two intense peaks were observed between 700 and 550 cm\textsuperscript{-1} for each Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4} (x = 0, 0.3, 0.5, 0.7 and 1) sample, with a specific shift depending on Mn substitution (x). ZnCo\textsubscript{2}O\textsubscript{4} (x = 0) exhibited absorption peaks centred at 677 and 585 cm\textsuperscript{-1} characteristic of Co-O and Zn-O vibration in the octahedral and tetrahedral sites of the spinel structure, respectively [33]. On doping ZnCo\textsubscript{2}O\textsubscript{4} with Mn, the Mn ions replace Zn\textsuperscript{2+} from the tetrahedral site as it is evident from the change in the lattice parameter shown in the Rietveld refinement of XRD data, and the bands shift to higher wavenumbers, as seen in Figure 4. For MnCo\textsubscript{2}O\textsubscript{4} (x = 1), the peaks shift to 648 and 560 cm\textsuperscript{-1} compared to the undoped ZnCo\textsubscript{2}O\textsubscript{4}. This behavior suggests changes in bonding occurs in the crystal structure, which could be affected by the ratio between Zn and Mn and the lighter atomic mass of Mn compared to that of Zn [28]. These observations further support the formation of cubic spinel crystal structure in the fabricated Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4}.
XPS measurements were performed in order to study the composition and investigate the electronic structure of the Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ series. Figure 6.5(a) shows the full survey spectra for the five investigated samples. The spectra show all the expected peaks and no additional elements were detected. Photoemission and Auger peaks are labelled accordingly in the figure. Zn and Mn core levels vary in intensity according to the sample composition, as expected.

Figure 6.5(b) shows the comparison of Mn 2p XPS core level spectra. Two main peaks with centroids at about 642 eV and 653.5 eV binding energy are visible in this energy region. These correspond to Mn 2p$_{3/2}$ and 2p$_{1/2}$ levels, respectively. The line shape of the main peaks remains identical across the series, indicating that there is no appreciable change in the valence of Mn with substitution by Zn. The only detectable difference is that the centroid of the satellite at the higher binding energy side of the 2p$_{1/2}$ peak shifts by about 1.9 eV towards lower binding energies from $x = 0$ to $x = 0.7$ (the corresponding satellite for the 2p$_{3/2}$ peak is not visible because it overlaps with the 2p$_{1/2}$ peak). This is possibly due to the doping of the samples, as already reported for doped manganites [34]. Because of the fact that the line shape of the main peaks does not change, only the fit of the $x = 0$ sample at the bottom of Figure 6.5(b) is reported. The Mn core level line shape was deconvoluted using two spin orbit doublets representing Mn$^{2+}$ (at lower binding energy) and Mn$^{3+}$ (at higher binding energy) respectively, separated by a spin orbit splitting of 11.2 eV. The area ratio of these two doublets shows that roughly 55% of the Mn ions have a 2+ ionization state and 45% have a 3+ ionization state.

Zn 2p core level spectra for samples $x = 0.3$, $0.5$ and $0.7$ are reported in Figure 6.5(c). The line shape is composed of two peaks at 1021.1 eV and 1044.2 eV, corresponding to Zn 2p$_{3/2}$ and 2p$_{1/2}$ spin orbit components, respectively. The line shape remains the same for the three compositions. This is consistent with Zn ions being found in +2 oxidation state, as reported in previous works [35, 36].

Figure 6.5(d) reports the Co 2p XPS spectra for Mn$_x$Zn$_{1-x}$Co$_2$O$_4$. The Co 2p binding energy region is composed of two main peaks located at 780.2 eV and 795.3 eV, corresponding to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ spin-orbit components, respectively. In addition to these, two satellite peaks are detected on the higher binding energy of the main peaks. The line shape of the Co 2p spectrum shows changes across the series. For this reason, the spectra for MnCo$_2$O$_4$ and Zn$_{0.7}$Mn$_{0.3}$Co$_2$O$_4$ are plotted separately in Figure 6.5(e), together with the overall fit to the data. The spectra have been decomposed into two main doublets corresponding to Co$^{3+}$ (at lower
binding energy) and Co^{2+} (at higher binding energy) oxidation states. The satellite has been fitted with a broad doublet. It is interesting to note that the percentage of Co^{3+} spectral weight increases from 76% in MnCo_2O_4 to 84% in Zn_{0.7}Mn_{0.3}Co_2O_4. This shows that the Co^{3+} content is slightly higher than in similar oxide systems [37, 38]. At the same time, the centroid of the satellite doublet shifts to 4 eV higher binding energy and becomes much narrower when moving from MnCo_2O_4 to Zn_{0.7}Mn_{0.3}Co_2O_4.

The ratio of Co^{3+}/Co^{2+} ions present in the Mn_xZn_{1-x}Co_2O_4 oxides can be determined from the deconvoluted high resolution Co 2p spectrum and is given in Table 6.2. For the prepared samples, with increase in manganese concentration Co^{3+}/Co^{2+} ratio increases, which are consistent with previously reported literatures [39, 40].

Figure 6.5.(f) shows the O 1s XPS spectra for the series. Each spectrum has been fitted with three Voigt-type single components (labeled as “comp1”, “comp2” and “comp3” in the figure) in addition to a Shirley background. This is consistent with what has been published in the literature for similar systems [37, 38]. Component 1, on the lower binding energy side, is ascribed to stoichiometric oxygen in the oxide main matrix, while the second component is attributed to oxygen vacancies or defects in the lattice [38]. The third component at 533 eV can be ascribed to chemisorbed oxygen [41]. The fitted binding energies and relative percentage areas of these three components are reported in Table 3. In general, the fit results show that there is no significant change in the line shape of O 1s spectra across the series.
Figure 6.5. (a) XPS survey scans for the investigated samples. (b) Mn 2p core level spectra for x = 0.3, 0.5, 0.7, and 1 samples (c) Zn 2p spectra for x = 0.3, 0.5 and 0.7 samples (d) Co 2p core level spectra for Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ spinel oxides. (e) Fitted Co2p spectra for MnCo$_2$O$_4$ and Zn$_{0.7}$Mn$_{0.3}$Co$_2$O$_4$ and (f) O 1s core level spectra for Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ spinel oxides.
Table 6.2. Oxidation state ratios obtained by deconvoluting XPS peaks corresponding to Co 2p and Mn 2p core electrons

<table>
<thead>
<tr>
<th>MnₓZn₁₋ₓCo₂O₄</th>
<th>oxidation states ratios obtained from XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co⁴⁺/Co²⁺</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>5.25</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>4.55</td>
</tr>
<tr>
<td>x = 0.7</td>
<td>3.87</td>
</tr>
<tr>
<td>x = 1</td>
<td>3.17</td>
</tr>
</tbody>
</table>

Table 6.3. Fit results for O 1s core level.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BE comp1 (eV)</th>
<th>BE comp2 (eV)</th>
<th>BE comp3 (eV)</th>
<th>% area (comp1)</th>
<th>% area (comp2)</th>
<th>% area (comp3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>529.97</td>
<td>531.61</td>
<td>533.27</td>
<td>74.9</td>
<td>17.8</td>
<td>7.3</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>530.02</td>
<td>531.67</td>
<td>533.31</td>
<td>73.4</td>
<td>18.3</td>
<td>8.3</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>530.01</td>
<td>531.65</td>
<td>533.29</td>
<td>76.7</td>
<td>16.7</td>
<td>6.6</td>
</tr>
<tr>
<td>x = 0.7</td>
<td>530.07</td>
<td>531.58</td>
<td>533.12</td>
<td>81.2</td>
<td>14.6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

6.3.3. Morphological characterization

Figure 6.6(a) through (e) presents the SEM images of the MnₓZn₁₋ₓCo₂O₄ (x = 0, 0.3, 0.5, 0.7, 1) while Figure 6.6(f) is EDS spectrum of the Mn₀.₅Zn₀.₅Co₂O₄ sample. Microspheres of different size with varying concentration of Mn have been obtained as observed from the SEM images. The size of the microspheres tends to increase and become more regular with increasing concentration of Mn from x = 0 to x = 1. The results indicate that Mn content plays an important role in determining the surface morphologies of MnₓZn₁₋ₓCo₂O₄ microstructure.
The EDS analysis of the Mn$_{0.5}$Zn$_{0.5}$Co$_2$O$_4$ sample in Figure 6.6(f) shows that the main elements in the sample are manganese, zinc, cobalt, and oxygen and that the approximate atomic ratio of Mn/Zn/Co is about 1:0.97:2.1.

![SEM images](image)

**Figure 6.6.** SEM images of the MnxZn$_{1-x}$Co$_2$O$_4$ microspheres (x = 0, 0.3, 0.5, 0.7, 1) (a-e), and (f) EDS spectrum of the Mn$_{0.5}$Zn$_{0.5}$Co$_2$O$_4$ (x = 0.5) sample.

Representative TEM, HRTEM, and SAED images of Mn$_{0.5}$Zn$_{0.5}$Co$_2$O$_4$ microspheres are shown in Figure 6.7. The TEM image demonstrates the porous nature of the microspheres and it is made up of small interconnected nanoparticles as shown by the magnified TEM image (Fig. 6.7(c)). Clearly, the corresponding selected-area electron diffraction (SAED) pattern displays the diffraction rings, indicating that the porous Mn$_{0.5}$Zn$_{0.5}$Co$_2$O$_4$ microspheres are polycrystalline (Fig. 6.7(d)). The HRTEM image (Fig. 6.7(b)) further confirms the high crystallinity of the porous Mn$_{0.5}$Zn$_{0.5}$Co$_2$O$_4$ microspheres. The lattice fringe with a spacing of
~ 2.4 Å is assigned to the interplanar spacing between the (311) planes of cubic Mn0.5Zn0.5Co2O4.

Figure 6.7. (a) TEM, (b) HRTEM (c) Magnified TEM and (d) SAED pattern of the Mn0.5Zn0.5Co2O4 (x = 0.5) microsphere.

The specific surface areas and pore size distribution of Mn xZn1-xCo2O4 oxides were characterized by BET analysis using nitrogen adsorption–desorption isotherms. The N2 adsorption-desorption isotherms and pore size distribution data for Mn xZn1-xCo2O4 (x = 0, 0.3, 0.5, 0.7, 1) samples are shown in Figure 6.8. As shown in the Figure 6.8(a), the N2 adsorption-desorption isotherms obtained for the Mn xZn1-xCo2O4 are type IV, according to the IUPAC classification of hysteresis loops [42]. Distinct H3 hysteresis loops were observed at a relative pressure of P/Po = 0.8-1.0 except for ZnCo2O4, indicating the mesoporous structure of Mn xZn1-xCo2O4 microspheres [43]. The textural properties of the samples are given in Table 6.4. It can be seen that the BET surface areas of 17.8, 50.25, 51.47, 56.27, and 51.66 m2g-1 were obtained for ZnCo2O4, Mn0.3Zn0.7Co2O4, Mn0.5Zn0.5Co2O4, Mn0.7Zn0.3Co2O4 and MnCo2O4, respectively. It was observed that the BET surface area increases with substitution
of Zn by Mn. This modification of the surface area correlates with the change in microsphere size as shown on the SEM images. The pore size distributions were mainly centred between 20 and 30 nm with an average pore diameter of 36, 19.4, 20, 17.5, and 18.4 nm, mainly resulting from the aggregation among primary particles as is evident from the TEM image.

![Figure 6.8](image)

**Figure 6.8.** Nitrogen adsorption/desorption isotherms (a) and the corresponding pore size distributions (b) of the Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ (x = 0, 0.3, 0.5, 0.7, 1) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCo$_2$O$_4$</td>
<td>17.80</td>
<td>0.00563</td>
<td>36.0</td>
</tr>
<tr>
<td>Mn$<em>{0.3}$Zn$</em>{0.7}$Co$_2$O$_4$</td>
<td>50.25</td>
<td>0.01280</td>
<td>19.4</td>
</tr>
<tr>
<td>Mn$<em>{0.5}$Zn$</em>{0.5}$Co$_2$O$_4$</td>
<td>51.47</td>
<td>0.01461</td>
<td>20.0</td>
</tr>
<tr>
<td>Mn$<em>{0.7}$Zn$</em>{0.3}$Co$_2$O$_4$</td>
<td>56.27</td>
<td>0.01353</td>
<td>17.5</td>
</tr>
<tr>
<td>MnCo$_2$O$_4$</td>
<td>51.66</td>
<td>0.01171</td>
<td>18.4</td>
</tr>
</tbody>
</table>

**Table 6.4.** Textural properties of Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ samples
6.3.4. Magnetic properties

The magnetic properties of Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ samples were examined using a vibrating sample magnetometer (VSM) at room temperature and 10 K by applying a magnetic field of $\pm 25$ kOe. Magnetic hysteresis loops and the temperature dependent zero-field-cooled (ZFC) and field-cooled (FC) curves are shown in Figures 6.9 and 6.10, respectively.

**Figure 6.9.** Temperature dependent ZFC and FC magnetization of Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ microspheres with different concentration of Mn ($x = 0, 0.3, 0.5, 0.7, 1$) measured at an applied field of 500 Oe.
Temperature dependent magnetization curves $M(T)$ were collected under the zero field cooled (ZFC) and field cooled (FC) conditions and measured in the temperature range 2-300 K at 500 Oe. The magnetization during FC for all samples shows a general increase with decreasing temperature. However, it is noted that as the Mn concentration is increased the FC data tends to level of at low temperatures and an additional inflection similar to the peaks observed in the ZFC $M(T)$ data develops. All the samples exhibit distinct bifurcation between ZFC and FC, except ZnCo$_2$O$_4$ ($x = 0$) for which the zero-field cooled and field cooled (ZFC-FC) curves did not diverge. The bifurcation temperature increases with an increase in Mn doping.

Generally, the presence of a maximum temperature ($T_{\text{max}}$) in the ZFC magnetization curve is directly proportional to the average blocking temperature ($T_{\text{B}}$) that depends upon the type of size distribution. The temperatures associated with the maxima in the ZFC magnetization data for the prepared Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ samples is observed at $T_p = 5.5$ K for $x = 0.3$, $T_p = 25$ K for $x = 0.5$, $T_{p1} = 29$ K and $T_{p2} = 98$ K for $x = 0.7$, and $T_{p1} = 50$ K and $T_{p2} = 153.8$ K for $x = 1$. It is clear from these data that as more of Zn is substituted by Mn, the $T_p$ values increase and eventually more than one $T_p$ values are observed for $x = 0.7$ and 1, which may well be a result of the substitution of nonmagnetic Zn$^{2+}$ by the Mn$^{2+}$/Mn$^{3+}$ ions [44]. On moving form $x = 0.7$ to $x = 1.0$ the magnetization is suppressed to negative values below a temperature of approximately 100 K. This is due to a compensation effect, as the net magnetization is dependent on the sum of the magnetic contributions from the associated sublattices within the spinel structure [45].

Figure 6.10 shows magnetic hysteresis loops of Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) microspheres measured at temperatures of 10 K and 300 K. The magnetization as a function of applied magnetic field, $M$-$H$, curves shows hysteretic behavior in all samples at 10 K, with the exception of the ZnCo$_2$O$_4$ sample. The magnetization is not fully saturated in fields of 25 kOe in all samples measured at 10 K, which represents the weak ferromagnetic ordering of the spins. The saturation magnetization for the samples was determined from extrapolation of $M$ versus $1/H$ curve at $1/H = 0$. The saturation magnetization ($M_s$), remnant magnetization ($M_r$), and coercive field ($H_c$) are summarized in Table 6.5. The $M_s$ gradually increases from 0.01 ($x = 0$) to 1.3 ($x = 1$) emu/g and 1.82 ($x = 0$) to 5.92 ($x = 0.7$) emu/g measured at 300 K and 10 K, respectively with increasing Mn concentrations. The maximum value of $H_c$ is observed for $x = 1$ (MnCo$_2$O$_4$).
Figure 6.10. Magnetic hysteresis loops of Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ microspheres with different concentration of Mn ($x = 0, 0.3, 0.5, 0.7, 1$) measured at (a) 300 K and (b) 10 K.

M-H measurements done at 300 K shown in Figure 6.10 (a) reflects linear behavior associated with paramagnetism for all the samples, with the exception of the MnCo$_2$O$_4$ ($x = 1$) sample. For this sample weak hysteresis is still observed, thus indicating the antiferromagnetic nature of this sample at 300 K [40, 46]. This type of behavior is observed for Cu substituted spinel MnCo$_{2-x}$Cu$_x$O$_4$ ($0 \leq x \leq 0.2$) nanostructures with the samples $x \geq 0.1$ having the coercivity $H_c$ and remanence $M_r$ close to 0 [47].

In the Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ the non-magnetic divalent Zn$^{2+}$ ions tend to occupy tetrahedral (A) sites and thereby force the incoming Mn ions to octahedral (B) sites due to their favoritism by polarization effect [29]. In general, spinel type cobalt-based oxides contain high spin Co$^{2+}$ ($S = 3/2$) in the tetrahedral site and low spin diamagnetic Co$^{3+}$ ($S = 0$) in the octahedral site; magnetic ions in the sub lattices are arranged antiparallel to their four neighbouring ions resulting in antiferromagnetic behavior of the material [48]. In view of the above considerations and the ratio Co$^{3+}$/Co$^{2+}$ given in the Table 6.2 it can be shown that there is an enhancement of weak ferromagnetism of the samples with substitution of Zn with Mn ions. ZnCo$_2$O$_4$ is observed to have a linear M-H curve both at room temperature and 10 K, which is typical of paramagnetic nature and results due to Co-O-Co super exchange interaction [20, 21]. As the content of Mn ions increase and with both Mn$^{2+}$ and Mn$^{3+}$ distributed in the octahedral and tetrahedral sites, the magnetic moment on B-site increases and the magnetic moment on A-
sites decrease and it leads to a stronger superexchange interaction between A and B sites. Thus, the net value of \( M_s \) increases, as expected.

**Table 6.5.** Magnetic parameters for \( \text{Mn}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4 \) samples measured at temperatures of 300 K and 10 K

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_s ) (emu/g)</th>
<th>( M_r ) (emu/g)</th>
<th>( H_c ) (kOe)</th>
<th>( M_s ) (emu/g)</th>
<th>( M_r ) (emu/g)</th>
<th>( H_c ) (kOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{ZnCo}_2\text{O}_4 )</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>1.82</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{Mn}<em>{0.3}\text{Zn}</em>{0.7}\text{Co}_2\text{O}_4 )</td>
<td>0.4</td>
<td>0</td>
<td>0</td>
<td>3.15</td>
<td>0.07</td>
<td>0.3</td>
</tr>
<tr>
<td>( \text{Mn}<em>{0.5}\text{Zn}</em>{0.5}\text{Co}_2\text{O}_4 )</td>
<td>0.55</td>
<td>0</td>
<td>0</td>
<td>3.51</td>
<td>0.25</td>
<td>1.32</td>
</tr>
<tr>
<td>( \text{Mn}<em>{0.7}\text{Zn}</em>{0.3}\text{Co}_2\text{O}_4 )</td>
<td>0.87</td>
<td>0</td>
<td>0</td>
<td>5.92</td>
<td>1.15</td>
<td>1.93</td>
</tr>
<tr>
<td>( \text{MnCo}_2\text{O}_4 )</td>
<td>1.3</td>
<td>0.12</td>
<td>1.2</td>
<td>4.08</td>
<td>1.03</td>
<td>3.02</td>
</tr>
</tbody>
</table>

### 6.4. Conclusions

\( \text{Mn}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4 \) oxide microspheres with a spinel structure were successfully prepared by using a facile coprecipitation method and calcination. It formed porous microspheres with the surface area and morphology being influenced by the composition of Mn. The lattice parameters for the spinel oxides increased linearly with Mn concentration. The results from XPS indicates that the elements Mn, Zn, and Co are observed to have oxidation states of +2 and +3, +2, and +2 and +3, respectively. It was shown that the percentage of Co\(^{3+} \) spectral weight increases from 76\% in \( \text{MnCo}_2\text{O}_4 \) to 84\% in \( \text{Zn}_{0.7}\text{Mn}_{0.3}\text{Co}_2\text{O}_4 \) whereas no appreciable change in the valence of Mn was observed with substitution by Zn. The magnetic properties of the \( \text{Mn}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4 \) microspheres are largely influenced by the concentration of Mn. As the concentration of Mn increases from \( x = 0 \) to \( x = 1 \) the saturation magnetization increases from 0.01 (\( x = 0 \)) to 1.3 (\( x = 1 \)) emu/g and 1.82 (\( x = 0 \)) to 5.92 (\( x = 0.7 \)) emu/g measured at 300 K and 10 K, respectively, which could be due to the substitution of the non-magnetic Zn\(^{2+} \) ion by Mn ions. The \( \text{MnCo}_2\text{O}_4 \) microspheres show maximum \( H_c \) of 1.2 and 3.02 kOe measured at 300 K and 10 K, respectively.
6.5. References


CHAPTER 7

Mn substituted Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ porous microspheres for high performance energy storage application in supercapacitors

Abstract

Mn substituted Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ porous microspheres are synthesized by a simple two-step approach involving a coprecipitation method and subsequent calcination process and utilized for supercapacitive investigation. The Mn$_{0.7}$Zn$_{0.3}$Co$_2$O$_4$ sample displayed the highest Brunauer–Emmett–Teller (BET) specific surface area of 56.27 m$^2$ g$^{-1}$ of all the other compositions. Transmission electron microscopy studies revealed the porous nature of the microspheres and are constituted by well-connected aggregates of nanoparticles. The Mn substitution plays a big role in enhancing the surface area and electrochemical performance of the microspheres. The electrochemical study shows highest specific capacitance of 589.9 F g$^{-1}$ at 1 mA cm$^{-2}$ for Mn$_{0.7}$Zn$_{0.3}$Co$_2$O$_4$ (x = 0.7) with high cycling stability of 92.1% and excellent rate capability at 10 mA cm$^{-2}$, which is much higher than pristine ZnCo$_2$O$_4$ and MnCo$_2$O$_4$. Furthermore, the electrochemical impedance spectroscopy analysis revealed the low resistance and good electrochemical stability of the sample.
7.1. Introduction

High performance and environmentally friendly energy storage devices such as lithium-ion batteries and electrochemical capacitors are important and hot research field because of the power requirement in the daily lives [1]. Among the various energy storage devices, supercapacitors have been widely studied due to their exceptional cycle life, high power density, and fast rate of charge/discharge [2-4]. Specifically, much attention has been given to faradaic capacitors, as they have higher capacitance and larger energy density than that of electrical double-layer capacitors (EDLCs) [5]. Hence, battery-type pseudocapacitive electrodes have attracted a great interest as positive electrode materials in asymmetric supercapacitors offering wide potential window and high specific capacitance required for practical applications [6].

Recently, several studies have been conducted to make use of transition metal oxides such as NiO, CO3O4, NiCo2O4, MnCo2O4, CuCo2O4, ZnCo2O4 as advanced electrode materials [7, 8]. However, there have been only a few reports that are related to ternary transition metal oxides, which are used as supercapacitor electrodes. The coupling of two or more metal species into a single crystal structure could make oxidation-state-rich redox reactions, which are essential for pseudocapacitors [9]. The various combinations of the cations and the tunable stoichiometric/non-stoichiometric compositions of the mixed transition metal oxides could provide great opportunities to manipulate their electrochemical properties. Tamboli et al. [10] have synthesized hierarchical Mn1-xNixCo2O4 (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) metal oxides by hydrothermal method with remarkable electrochemical supercapacitive performance. Among the compositions, Mn0.4Ni0.6Co2O4 (x = 0.6) exhibits high specific capacitance of 1762 F g⁻¹ at 1 mA cm⁻² and good cycling stability with capacitive retention of 89.2% over 2000 cycles. This is mainly attributed to the synergetic effect of morphology and chemical compositions with Ni substituting into Mn sites, which introduces rich redox active center for electrochemical reactions. Mariappan et al.[11] have synthesized Zn-Mn-Co ternary oxide nanoneedles with a superior specific capacitance of 849 C g⁻¹ at a current density of 1 A g⁻¹ compared to Co3O4 and ZnCo2O4 owing to the synergistic effect of Zn, Mn and Co metals enhancing the electrochemical performances. Similar studies have been reported on some other ternary metal oxides such as Zn-Ni-Co ternary oxide nanoneedles, Zn-Ni-Co oxide nanosheets,
Cu-Zn-Co-oxide, mixed ternary transition metal ferrites, and NiₓCoᵧMoₓO nanosheets [12-16].

However, the electrochemical behaviors of these ternary oxides still need to be improved by tuning compositions and morphologies to enhance their performance. Furthermore, until recently, there are very few studies involving varying stochiometric compositions of the different metals in a crystal structure. Compared with Co₃O₄ and binary ZnCo₂O₄ electrode materials, the ZnMnCo-O electrode materials are expected to reduce the cost and possess better safety performance at the same time.

Herein, we report the enhanced supercapacitive performance of Mn substituted MnₓZn₁₋ₓCo₂O₄ porous microspheres synthesized through a simple coprecipitation route. The samples were characterized by means of X-ray diffraction (XRD), nitrogen adsorption with BET analysis, and electron microscopy techniques. The electrochemical performances of Mn substituted MnₓZn₁₋ₓCo₂O₄ porous microspheres electrodes were investigated with a potentiostat/galvanostat in a three-electrode configuration with 2M KOH as electrolyte. The Mn₀.₇Zn₀.₃Co₂O₄ (x = 0.7) porous microspheres exhibit specific capacitances of 589.9 F g⁻¹ at 1 mA/cm², which is higher than the other compositions.

7.2. Experimental

7.2.1. Synthesis of the MnₓZn₁₋ₓCo₂O₄ porous microspheres

All chemical were analytical grade reagents and used without further purification. The materials were prepared using the coprecipitation method previously reported in our group [17] with a slight modification. In this method each sample was prepared by taking the desired amount of metal acetate precursors i.e. zinc acetate, manganese acetate and cobalt acetates dissolved in a mixture of distilled water and ethanol (10:1 ratio) with a total volume of 230 mL. For example, Mn₀.₅Zn₀.₅Co₂O₄ microspheres (x = 0.5) were prepared by taking 1mmole of Mn(Ac)₂·4H₂O, 1mmole of Zn(Ac)₂·2H₂O and 4mmole of Co(Ac)₂·4H₂O and dissolved in a mixture of 21 mL of ethanol and 210 mL of distilled water with vigorous stirring. Then, another solution was prepared by dissolving 60 mmole of NH₄HCO₃ in 230 mL of distilled water and then added to the metal precursor solution drop wise, while stirring. The resulting
mixed solution was heated to 45 °C and maintained at this temperature for 9 h with vigorous stirring. A pale pink precipitate was obtained, which was collected through filtration, washed thoroughly with distilled water and ethanol and then dried at 60 °C overnight. The obtained carbonate precursor was heat treated in air at 600 °C for 5 h at a temperate ramp of 2 °C min⁻¹ to yield a black powder. The MnₓZn₁₋ₓCo₂O₄ (ZMCo) samples with x = 0, 0.3, 0.5, 0.7, and 1 were labelled as ZCo, ZMCo1, ZMCo2, ZMCo3, and MCo, respectively.

7.2.2. Characterization of the samples

The morphology of the samples was investigated by scanning electron microscopy (FEI Nova Nano SEM 450 Scanning Electron Microscope (SEM), USA) and transmission electron microscopy (TEM, JEM-2100). The crystallinity of the samples was examined by D9 X-ray Diffractometer (XRD; Mo Ka₁ radiation, λ = 0.709321 Å). The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method.

7.2.3. Fabrication of electrode and electrochemical performance test

The electrode is fabricated as follows: the active material, activated carbon and polyvinylidene fluoride (PVDF) binder were mixed together in the ratio of 80:10:10 (wt. %). A slurry of the mixture was made using N-Methyl-2-pyrrolidone (NMP), which was coated onto a nickel foil current collector of (1×1 cm) 1.6 mm thickness (produced by MTI corporation) and dried for 4 h to remove the solvent. Cyclic Voltammetry (CV), Chronopotentiometry (CP) and Electrochemical Impedance studies (EIS) were performed using a Gamry potentiostat/Galvanostat employing a standard 3-electrode cell configuration with platinum wire as counter electrode and Ag/AgCl as a reference electrode. The measurements were performed using aqueous 1 M KOH electrolyte at ambient conditions.
7.3. Results and discussion

7.3.1. Structural and morphological studies

Following the previously reported procedure, Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ (ZMCo) microspheres were prepared using the coprecipitation route. The metal acetate precursors were added to the solution of NH$_4$HCO$_3$ in the presence of DI water and ethanol and stirring with heating at 45 ºC forming a pink colored precipitate of ZMCo carbonate microspheres. In this modified procedure, the total volume of the DI water and ethanol used was increased to 460 mL to produce uniform spheres. Subsequent calcination of the dried precipitate at the temperature of 600 ºC yields a black powder sample of ZMCo oxide microspheres. During the calcination process, many pores could be formed due to the constituting of nanoparticles formed and during the removal of H$_2$O and CO$_2$ gaseous components.

Figure 7.1 presents the XRD patterns of Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ samples with x = 0, 0.3, 0.5, 0.7, and 1. All the diffraction peaks can be indexed to be cubic spinel structure (JCPDS Card No. 23-1390) without any impurity phase. According to our previous report [17], the Mn substituted Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ samples have larger lattice parameter than for ZnCo$_2$O$_4$ sample (a = 8.0874 Å) and a slight shift is observed in the peak positions. The intensity of the peaks seems to decrease slightly with increasing Mn concentration.

These Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ microspheres were further characterized by TEM and SEM. The ZMCO spheres of a micron size with a diameter ranging from 200 to 600 nm are obtained and those for ZMCo3 are shown in Figure 7.2. Figure 7.2(a) indicates the SEM image of carbonate microspheres of ZMCo3 obtained from coprecipitation and upon calcination produces the oxide microspheres shown in the TEM image in Figure 7.2(b). The HRTEM image in Figure...
7.2(c) indicates the magnified portion of the edge of the porous microsphere with pores shown, which are formed from the voids between the interconnected nanoparticles. The SAED pattern in the inset of the TEM image further explains the polycrystalline nature of the sample.

The BET specific surface area of ZMCo samples were determined by N₂ adsorption/desorption measurement. Figure 7.3 (a) and (b) shows N₂ adsorption-desorption isotherms of ZCo and ZMCo3 samples and inset of corresponding pore size distributions (nm). The isotherm of ZMCo3 sample shows distinct hysteresis loop starting from P/P₀ ~ 0.75 and demonstrate the presence of mesopores in contrast to the unsubstituted parent ZCo. The corresponding pore size distributions were calculated from the desorption part of the isotherms and given in the insets of Figure 7.3(a) and (b). The ZMCo3 (Zn₀.₃Mn₀.₇Co₂O₄) microspheres exhibit relatively high surface area (56.27 m² g⁻¹) than the other samples. This is probably due to the open pores formed by the nanoparticles in the ZMCo3 microspheres as evident from the TEM results (Fig. 7.2(c)). Moreover, numerous mesopores with size ranging from 10 to 40 nm can be clearly
observed indicating coexistence of structural pores as well as interconnected pores. The BET results indicate that the substitution of Mn into ZnCo$_2$O$_4$ greatly enhances the surface area and therefore improves the capacitive performance of the electrode effectively.

Figure 7.2. (a) SEM image of ZnMCo$_3$ carbonate spheres (on a scale of 5µm) (b,c) TEM and Magnified TEM edge image of the ZnMCo$_3$ spheres and the inset in Figure (c) shows the SAED pattern.
7.3.2. Electrochemical performance

The effect of Mn substitution in ZnCo$_2$O$_4$ crystallites and its suitability for electrochemical performance as electrode materials for supercapacitors was examined by using CV, GCD and EIS techniques. Figure 7.4(a) shows the cyclic voltammetry (CV) curves of the Mn$_x$Zn$_{1-x}$Co$_2$O$_4$ electrodes in a standard 3-electrode configuration at a scan rate of 50 mV/s and in the potential window range of $-0.1$–$0.55$ V. It can be observed that the CV curves of all the samples consists of pairs of well-defined redox peaks, which are associated with the faradaic redox reactions governing the pseudocapacitive behavior [18]. Remarkably, the ZMCo$_3$ (Zn$_{0.3}$Mn$_{0.7}$Co$_2$O$_4$) sample exhibits relatively higher current density and larger area covered under the CV curve than the other samples suggesting the excellent interaction of ZMCo$_3$ microspheres with the electrolyte. Figure 7.4(b) shows the CV curves of the ZMCo$_3$ sample at different scan rates. As scan rate increases, the shape of the CV curves remains unchanged, thus indicating the excellent electrochemical reversibility and outstanding high-rate performance. However, there is a shift in the redox peaks towards lower potential, which may be due to the polarization effect of the electrodes [19]. The different peaks originating from the faradaic redox reactions can be related to M-O/M-O-OH (M = Mn or Co) associated with OH$^-$ anion from KOH electrolyte.
The pair of redox peaks in the CV curves can be explained based on the following equation (M = Mn/Co) [11, 12]:

\[
\text{MO} + \text{OH}^- \leftrightarrow \text{MOOH} + e^- \tag{7.1}
\]

The comparison of discharge curves of ZCo, ZMCo1, ZMCo2, ZMCo3, and MCo electrodes at a current density of 1 mA cm\(^{-2}\) in the voltage range of 0 to 0.45 V are shown in Figure 7.4(c). An obvious discharge voltage plateau can be seen in the discharge curve, which demonstrates that the electrode exhibits typical faradaic battery-like behavior. Significantly, ZMCo3 showed longer discharge time at the same current density and in the same potential window than the other samples suggesting the higher specific capacitance of ZMCo3. The detailed charge/discharge curves of ZMCo3 at a range of current densities 1 – 10 mA cm\(^{-2}\) are displayed in Figure 7.4(d). A plateau can be seen in the discharge process, which indicates the faradaic battery-like behavior of electrodes. The charge/discharge curves exhibit typical deviations from a straight and flat line and display some asymmetry. The specific capacitance of the electrodes can be calculated using the following equation:

\[
C_s = \frac{I \times \Delta t}{m \times \Delta V} \tag{7.2}
\]

where \(I\) (A) is the applied current, \(\Delta t\) (s) is the total discharge time, \(m\) (g) is the mass of the electroactive material, and \(\Delta V\) (V) is the potential window. According to Eq. (7.2), the specific capacitance of ZMCo3 microspheres was calculated to be 589.9 F g\(^{-1}\) at 1 mA cm\(^{-2}\), which was higher than the ZCo (306 F g\(^{-1}\)), ZMCo1 (246.4 F g\(^{-1}\)), ZMCo2 (342.6 F g\(^{-1}\)) and MCo (286.7 F g\(^{-1}\)) samples at same current density. These values are comparable to some literature reported values. For example, Mary et al. [20] reported hydrothermally synthesized Mn-doped ZnCo2O4 nanoparticles with 1, 2, 5, 10 and 15 wt% Mn doping. The 10 wt% Mn-doped ZnCo2O4 sample displayed a maximum capacitance of 707.4 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\). The synergistic effect of Zn, Mn, and Co in the Mn substituted samples enhances the electrochemical performance. The higher specific capacitance of ZMCo3 sample can also be explained based on its high surface area, which enhances the contact between the electrolyte and active electrode material. When the current density was increased from 1 to 10 mA cm\(^{-2}\) (Fig.7.5(b)), the specific capacitance of ZMCo3 decreased to 533.1 F g\(^{-1}\), which indicates a
Figure 7.4. (a) Cyclic voltammetry (CV) curves of ZCo, ZMCo1, ZMCo2, ZMCo3, and MCo at a scan rate of 50 mV s\(^{-1}\) in 1 M KOH electrolyte. (b) CV measurements of ZMCo3 sample at different scan rate from 5 to 100 mV s\(^{-1}\). (c) Galvanostatic charge-discharge curves of ZCo, ZMCo1, ZMCo2, ZMCo3, and MCo samples at a current density of 1 mA cm\(^{-2}\). (d) Galvanostatic charge/discharge curves of ZMCo3 sample at different current densities.

Capacitance loss of only 7.9%. This implies its high rate capability at high current density, a very important feature of electrodes for practical applications.

Cycling stability is an important factor of supercapacitor electrode materials. Stability of ZMCo1, ZMCo2, and ZMCo3 microspheres was measured at a constant current density of 5 mA cm\(^{-2}\) in 1 M KOH solution for 1000 charge discharge cycles and is presented in Figure 7.5(a). As it can be seen from the figure, ZMCo3 sample displays a superior cyclic performance.
compared to ZMCo1 and ZMCo2 samples retaining a specific capacitance of \( \sim 519 \text{ F g}^{-1} \) after 1000 cycles. In the first 450 cycles, the specific capacity seems to increase from the initial value of 383 F g\(^{-1}\) and starts to stabilize onwards reaching a stable 1000 cycles.

EIS measurements were done to further investigate the electrical conductivity and electrochemical behaviors of the electrodes in the region from 100 kHz to 0.1 Hz with amplitude of 10 mV. Figure 7.5(c) and (d) depict the Nyquist plots of the ZCo, ZMCo1, ZMCo2, ZMCo3, and MCo electrodes and the magnified portion of the high frequency region, respectively. The equivalent series resistance ESR (the intercept with the real axis at a high frequency region) is the combination of contact resistance between the active materials on the nickel foam and the current collector, the intrinsic resistance of the active materials, and the ionic resistance of the aqueous electrolyte. All the \( \text{Mn}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4 \) electrodes exhibit similar equivalent series resistance (ESR) 0.96–1.1 \( \Omega \) with ZMCo3 sample providing relatively low overall resistance. The inset in Figure 7.5(c) illustrates the equivalent circuit diagram for electrode materials. The low ESR and charge transfer resistance for ZMCo3 sample (\( \text{Zn}_{0.3}\text{Mn}_{0.7}\text{Co}_2\text{O}_4 \)) reveals its relatively high conductivity.

The excellent electrochemical properties of ZMCo3 sample can be mainly attributed to the synergetic effect of its morphology and multiple chemical compositions. The formation of porous microspheres offers high surface area accessible for the electrolyte ions and enabling faster kinetics and higher utilization of active material. The substitution of Mn into Zn sites can alter the cation distribution over tetrahedral and octahedral sites thereby tuning its electrochemical properties and can offer rich electroactive sites. Owing to the existence of various oxidation states of Mn, it enhances the redox behavior of ZnCo\(_2\)O\(_4\) [12].
Figure 7.5. (a) Variation of specific capacitance with cycle number for ZMCo1, ZMCo2 and ZMCo3 samples over 1000 cycles at a current density of 5 mA cm\(^{-2}\) (b) Specific capacitance of ZMCo3 electrode at different current densities (c) Nyquist plots for ZCo, ZMCo1, ZMCo2, ZMCo3, and MCo samples with amplitude of 10 mV in 0.1 Hz to 100 kHz and the magnified portion of the higher frequency region. The inset in Figure 7.5(c) is the circuit used to fit the data.

7.4. Conclusions

The Mn substituted Mn\(_x\)Zn\(_{1-x}\)Co\(_2\)O\(_4\) microspheres were successfully prepared by a simple coprecipitation method. These microspheres were found to be porous and Mn substitution was observed to enhance the BET surface area with the highest being 56.27 m\(^2\) g\(^{-1}\) obtained for the Mn\(_{0.7}\)Zn\(_{0.3}\)Co\(_2\)O\(_4\) sample. Among the different ratios of manganese to zinc, Mn\(_{0.7}\)Zn\(_{0.3}\)Co\(_2\)O\(_4\) (x
= 0.7) offers excellent electrochemical properties with a high specific capacitance of 589.9 F g\(^{-1}\) at 1 mA cm\(^{-2}\). Electrochemical impedance spectroscopy analysis reveals low equivalent series resistance for the Mn\(_{0.7}\)Zn\(_{0.3}\)Co\(_2\)O\(_4\) (x = 0.7) electrode.

### 7.5. References


17. Dolla, T.H., et al., Mn substituted Mn_{x}Zn_{1-x}Co_{2}O_{4} oxides synthesized by co-precipitation; effect of doping on the structural, electronic and magnetic properties. RSC Advances, 2018. 8(70): p. 39837-39848.


CHAPTER 8

Conclusion and Future Perspectives

8.1. Conclusion

This thesis focuses on the development of mixed transition metal oxides and their composites with carbon materials for their possible application as high performing electrode materials in electrochemical energy storage systems specifically supercapacitors. The several experiments undertaken in this study and the subsequent electrochemical results provided an insight on the ways of developing mixed transition metal oxides by tuning their compositions and forming hybrid nanostructures with carbon materials and their use as promising electrode materials with an improved performance compared to the binary systems.

The experimental investigations carried out and the main findings are as follows:

(1) A modified citrate sol-gel route was developed and optimized for the successful synthesis of $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) spinel mixed ternary oxides at a relatively low temperature. This method allows for the effective control over phase purity, crystallinity and stoichiometry by providing a homogenous mixing of the metal precursors, which is beneficial for an effective electrochemical investigation of materials. It was found that the ratio of citric acid to metal precursors, pH and the calcination temperature played a great role in controlling the phase purity of the ternary oxides. The structural, electronic, and magnetic properties of the oxides were observed to be significantly affected by the substitution of Ni by Mn, which is considered to be distributed in the tetrahedral and octahedral sites of the spinel crystal structure. Based on these results, it can be anticipated that it is important to carefully optimize the conditions for synthesis techniques based on the sol-gel route as it can possibly form mixed phases and if properly controlled, it is a simple, low cost and effective method to fabricate phase pure mixed transition metal oxide powders.
(2) A facile co-precipitation synthetic strategy was designed by using ammonium bicarbonate as a precipitant to fabricate Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4} (x = 0, 0.3, 0.5, 0.7, 1) microspheres comprising interconnected nanoparticles forming a porous structure. The substitution of Zn by Mn has shown to significantly affect morphology by enhancing the growth of bigger microspheres and improving the surface area as it is evident from the BET data, which has shown that the Mn\textsubscript{0.7}Zn\textsubscript{0.3}Co\textsubscript{2}O\textsubscript{4} (x = 0.7) has the highest surface area. The structure, electronic, and magnetic properties are also influenced by Mn substitution as it causes a change in cation distribution in the crystal structure. This synthetic route is advantageous in that it is simple and allows the formation of porous nanostructures by having a control over the formation of different morphologies.

(3) To address the issue of conductivity and uniform dispersion of mixed transition metal oxide nanoparticles as electrode materials, a strategy was designed by coating mixed metal oxides with carbon, which can also help in dispersion of the metal oxide nanoparticles. This was achieved by using a modified citrate sol-gel method followed by a template assisted pyrolysis, in which citric acid is used as a chelating agent, glucose as the carbon source and NaCl as the template assisting the formation of the carbon nanosheets. A hybrid nanostructured material of ternary Mn-Ni-Co oxide coated with carbon nanosheets was successfully prepared and showed an enhanced electrochemical performance as electrode material for supercapacitors compared to the binary metal oxides of Ni-Co and Mn-Co. The metal oxide nanoparticles were observed to be embedded and well dispersed in a carbon matrix, which provides high electrical conductivity for the whole electrode. Furthermore, this method can be used to prepare similar hybrid nanostructures, which are beneficial for energy storage applications.

(4) In addition to the substitution of part of the binary transition metal oxides to form ternary mixed oxides, tuning the optimum composition is another important approach to exploit the high electrochemical performance of mixed transition metal oxides. In connection with this, the porous microspheres of Mn\textsubscript{x}Zn\textsubscript{1-x}Co\textsubscript{2}O\textsubscript{4} (x = 0, 0.3, 0.5, 0.7, 1) were investigated for their performance as electrode materials for supercapacitors. The electrochemical results revealed that the Mn\textsubscript{0.7}Zn\textsubscript{0.3}Co\textsubscript{2}O\textsubscript{4} (x = 0.7) sample displays a superior performance compared to the other compositions. This result is consistent with the BET data emphasizing the advantage of the porous structure, which simplifies the diffusion of
electrolyte ions to access active materials and facilitates rapid electron transport to achieve high-performance.

(5) Comparing the electrode performances of the two types of fabricated ternary mixed metal oxides, Mn-Ni-Co and Zn-Mn-Co, it is can be seen that the Zn-Mn-Co series delivers a promising capacitance owing to its porous morphology and optimized composition of the metals. However, the carbon supported Mn-Ni-Co materials show improved cyclability and hence have significance in the long duration usability.

8.2. Future Perspectives

Mixed transition metal oxides of Mn-Ni-Co and Zn-Mn-Co have shown to be promising electrode materials for energy storage applications. Additional test with two electrode systems can be undertaken to further investigate its practical application. Moreover, development of different morphologies and carbon support can advance these materials for high performance applications. Similar synthetic approaches can be followed to prepare other series of mixed oxides with different types of metals to explore and screen out better electrode materials.
APPENDICES

Supporting information and some data on related experiments (LIBs)

The supporting information included in this section are the data from the additional experiments done and are reported in the papers which have been published, under review, and under preparation for submission. Each appendix is listed based on the paper corresponding to the data reported in it as a supporting information.

Appendix A: Sol-gel synthesis of $\text{Mn}_x\text{Ni}_{1-x}\text{Co}_2\text{O}_4$ spinel phase materials: structural, electronic and magnetic properties

Fig S-1, shows the TGA and DTA curves for the four other compositions synthesized. All of the samples, except for $\text{Mn}_{0.7}\text{Ni}_{0.3}\text{Co}_2\text{O}_4$, show the three stages of decomposition described in the main text for the $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4$. Specifically, loss of physiosorbed water (95-110 °C), loss of water of crystallization (280-340 °C), and complete decomposition of the organic precursors (350 – 400 °C).

The differences in terms of the DTG curves between the various samples can be ascribed to changes in composition and phases during the decomposition process.
Fig. S-1: TG-DTG curves of (a) NiCo$_2$O$_4$ ($x = 0$), (b) Mn$_{0.3}$Ni$_{0.7}$Co$_2$O$_4$ ($x = 0.3$), (c) Mn$_{0.7}$Ni$_{0.3}$Co$_2$O$_4$ ($x = 0.7$), and (d) MnCo$_2$O$_4$ ($x = 1$)

The comparison of XRD patterns for the samples calcined at 350 °C, 450 °C and 700 °C, for the composition with $x = 0.5$, are presented in Fig S-2. The intensity of the diffraction peaks of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ increases and the peak width (FWHM) decreases with increasing calcinations temperatures. This indicates that the crystallinity increases with increasing calcinations temperatures [1,2]. A temperature of 450 °C is selected as an optimum for calcinations based on the decomposition pattern given by the TGA/DTG curve and due to the minimal formation of secondary NiO phase for the Ni rich compositions at this temperature.
Fig. S-2: XRD patterns of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ prepared by calcining at 350, 450 and 700 °C.

Rietveld refinements on the XRD patterns for the Mn$_x$Ni$_{1-x}$Co$_2$O$_4$ ($x = 0$, 0.3, 0.7, and 1) samples were done using the same procedure described in the main text. The observed, calculated, and difference curves for the Rietveld refined XRD patterns are shown in Fig S-3. As discussed in the main text, the calculated curve (red) matches very well with the experimental curve (blue).
Fig. S-3: Rietveld refinement of the XRD patterns for samples (a) NiCo$_2$O$_4$ ($x = 0$), (b) Mn$_{0.3}$Ni$_{0.7}$Co$_2$O$_4$ ($x = 0.3$), (c) Mn$_{0.7}$Ni$_{0.3}$Co$_2$O$_4$ ($x = 0.7$), and (d) MnCo$_2$O$_4$ ($x = 1$)
References


Appendix B: Electrochemical performance of carbon coated ternary mixed Mn-Ni-Co oxide for supercapacitor applications

Figure S1. XRD patterns of $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4$/C and $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4$
Figure S2. CV curves of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C at a scan rate of 50 mV s$^{-1}$ in different electrolytes; 1M KOH, 1M Na$_2$SO$_4$, 1M NaOH, and 1M KCl.

Figure S3. CV curves of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ and Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C at a scan rate of 50 mV s$^{-1}$ in 1M KOH.
Figure S4. Nyquist impedance plots of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$/C and bare Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ compared.
Appendix C: Mn doped Mn_{1-x}Zn_{x}Co_{2}O_{4} oxides synthesized by coprecipitation; effect of doping on the structural, electronic and magnetic properties

Fig. S-1: Rietveld refined XRD patterns for samples (a) ZnCo_{2}O_{4} (x = 0), (b) Mn_{0.3}Zn_{0.7}Co_{2}O_{4} (x = 0.3), (c) Mn_{0.7}Zn_{0.3}Co_{2}O_{4} (x = 0.7), and (d) MnCo_{2}O_{4} (x = 1)
Fig. S-2: A graph of lattice parameter and crystal size vs Mn concentration
Fig. S-3: Full FTIR spectrum of $\text{Mn}_x\text{Zn}_{1-x}\text{Co}_2\text{O}_4$ ($x = 0, 0.3, 0.5, 0.7, 1$) measured in the wavenumber range of 4000 – 400 cm$^{-1}$. 
Appendix D: Some results on the charge-discharge profiles of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ and Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ @C electrodes as anodes for Li-ion batteries (LIBs).

Figure S-1. Charge discharge profiles of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ and Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ @C electrodes as anodes for Li-ion batteries (LIBs).

The ternary Mn-Ni-Co metal oxide was tested for its use as anode material for lithium ion batteries (LIBs) to check its potential in rechargeable battery systems. A galvanostatic charge-discharge experiment was done at a C-rate of 0.1C in a voltage range of 0-3 V on Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ and Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ @C as electrode materials for anodes in LIBs in a PAT-Cell setup (Fig. S-2). A representative charge-discharge profiles are shown in the figure for the two electrodes, which clearly indicates the effect of carbon coating in stabilizing the capacity during cycling. This result implies the possible applications of the carbon supported ternary mixed transition metal oxides as electrode materials in Li-ion batteries. Although our lab set up was not suitable for this kind of study lacking a proper environment free of moisture and air and facilities, with the limited resource we have tried to show the applicability of these class of electrode materials as possible electrode materials for batteries, as well.
Appendix E: Optimization experiments done during synthesis of the ternary Mn-Ni-Co oxide

In addition to the data presented in the main part of the thesis, there are some results not included, which are associated with the vast amount of work done on the optimization of the synthetic methods. In the sol-gel synthesis, different complexing agents were investigated including citric acid (CA), ethylenediaminetetraacetic acid (EDTA), polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), and a surfactant, Pluronic P123 (PEO-PPO-PEO). Figure SS-1 below shows the comparison of XRD patterns of Mn$_{0.5}$Ni$_{0.5}$Co$_2$O$_4$ samples prepared using different complexing agents. Citric acid and EDTA complexing agents have better complexing capability, effectively chelating the metal ions and form a homogenous solid solution and hence a single-phase metal oxide. The other complexing agents form mixed phase of metal oxides and so are not appropriate for preparation of mixed transition metal oxides. The surfactant P123 was also investigated as a possible complexing agent to trap the metal ions and help forming a homogenous gel. As shown in the Figure SS-2, a mixture of phases is formed demonstrating that P123 is unsuitable complexing agent for the multi metal ion systems.
Figure SS-1. XRD patterns of $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4$ sample prepared using different complexing agents and calcined at 500 °C.

Figure SS-2. XRD pattern of $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{Co}_2\text{O}_4$ prepared using the surfactant P123 as a complexing agent and calcined at 500 °C.