

Investigation of Electrochemical Behaviour of Graphene and Manganese Oxide based Catalysts

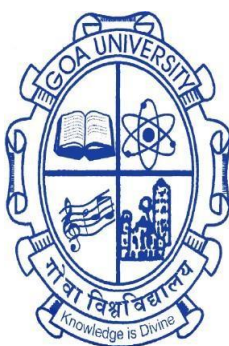
A THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in Chemistry

IN THE SCHOOL OF CHEMICAL SCIENCES

GOA UNIVERSITY



By

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MAY 2026

DECLARATION

I, **Ms. Arti Krishnanand Naik**, hereby declare that this thesis represents work which has been carried out by me and that it has not been submitted, either in part or full, to any other University or Institution for the award of any research degree.

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CERTIFICATE

I hereby certify that the above Declaration of the candidate, **Ms. Arti Krishnanand Naik** is true and the work was carried out under my supervision.

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Acknowledgment

First and foremost, I wish to express my sincere and deepest gratitude to my research supervisor, **Prof. Purnakala V. Samant**, for her invaluable guidance, motivation, insightful comments, unwavering support and immense patience throughout my PhD journey. Her profound knowledge and scientific expertise were instrumental in shaping this research and my development as an independent researcher.

My sincere thanks extend to the members of Departmental Research Committee, **Prof. Julio B. Fernandes**, Rtd. Professor, Goa University and **Prof. Sunder Dhuri**, Registrar, Former Vice-Dean, Goa University, **Prof. Vidhyadatta M. Shet Verenkar**, Dean, School of Chemical Sciences, Goa University, **Dr. Bidhan A. Shinkre**, Vice-Dean (Research), School of Chemical Sciences, Goa University, for their valuable time, insightful questions and constructive suggestions with critical evaluation of my research work during my defense and evaluations.

I am particularly grateful to **Shree. Bhushan K. Savaikar**, Director, Directorate of Higher Education, Porvorim - Goa, and **administrative staff** of Government College of Arts, Science and Commerce, Khandola, Marcela - Goa for the generous grant of two-year study leave from my academic and administrative duties, which provided the necessary time and focus for the completion of this doctoral research. This support was instrumental in achieving this milestone. I also extend my gratitude towards **administrative staff** of Goa University, **Mr. Ashwin Lawande**, Deputy Registrar, **Ms. Siddhi Naik**, Assistant Registrar and **Ms. Aditi** for their administrative support.

I extend my thanks to **Prof. Purnakala Samant**, Principal/Co-ordinator, Cluster Research Centre, Government College of Arts, Science and Commerce, Khandola, Marcela – Goa and **Dr. Dilecta D'Costa**, IQAC Director, for granting permission to work and utilise the research facilities and resources from the institute to accomplish the literature review and investigations.

I would also like to acknowledge **Dr. Atul Kumar Singh**, for providing XPS facility and **Dr. Naminita Gogoi**, IIT Delhi and **SAIF-IIT Madras** for ICP-MS analysis. Thanks are also due to **Dr. Sandip Sabale**, Jaysingpur College, Jaysingpur for BET analysis facility, **CSIF, BITS Pilani, K. K. Birla Goa Campus** for XRD, FE-SEM and CHNS analysis and **School of Chemical Sciences, Goa University** for providing Raman spectral

analysis. **Dr. Beena Vernekar**, PG Co-ordinator, **Government College of Khandola** and **Dr. Shambhu Parab** for rendering necessary help with TG-DTA analysis.

A special thank you to my lab mates **Ms. Firdos Sakli** and **Ms. Pradnya Sawant** for all stimulating scientific discussions, shared frustrations over failed experiments, refreshing chitchats and collective moments of triumph which created a supportive and dynamic environment. Thanks are also due to **Ms. Manisha Mhalsekar** for all her help and necessary suggestions. I am also deeply grateful to all my colleagues in the Department of Chemistry, Government College of Khandola, for their encouragement, timely distractions, necessary advices and belief in me throughout this entire process. I truly valued their thoughtfulness in every shared social event, delicious treats which added much-needed cheer to my routine.

Beyond the professional support, a special note of thanks to my dear friend, **Dr. Anjani P. Nagvenkar**, Assistant Professor, School of Chemical Sciences for her invaluable support since the beginning of my PhD journey and even before.

Thanks are also due to all the non-teaching staff of Department of Chemistry **Ms. Shraddha**, **Mr. Rupesh**, **Mr. Sudhir**, **Mr. Sarvesh**, **Mr. Sunil** and **Mr. Adnesh** for rendering timely assistance during lab work, **Mr. Ajit Faras**, Librarian for his prompt assistance with library resources and all other library staff and office staff of Government College of Khandola for always being very helpful and kind.

Finally, on a personal note, I wish to express my heartfelt appreciation to my family and friends. I am deeply indebted to my parents, **Mr. Krishnanand Naik** and **Mrs. Radha Naik**, my father-in-law, **Mr. Pandharinath Kouthankar**, my dear sister **Ms. Swapna Naik** and my companion, **Mr. Girish Kouthankar**, for their unwavering encouragement and patience. A very special thank you goes to my dear daughter, **Goonj**. Born during the early phase of my research, her resilient spirit and presence served as a constant reminder of why I pursued this goal. Her belief in me, in her own infant way, kept my spirits high and provided the essential moral support needed to complete this challenging endeavour.

Above all, I am thankful to the **Almighty** for His divine guidance and grace, which provided the strength and perseverance necessary to reach this milestone.

Arti K. Naik

Dedicated to my family

For their love, support and sacrifices

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Abbreviations

AEC	Alkaline Electrolysis Cell
AEM	Adsorbate Evolution Mechanism
AEMWE	Anion Exchange Membrane Water Electrolysis
AOS	Average Oxidation State
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CA	Chronoamperometry
C_{dl}	Double-Layer Capacitance
CNT	Carbon Nanotubes
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
DMFC	Direct Methanol Fuel Cell
DTA	Differential Thermal Analysis
ECSA	Electrochemical Active Surface Area
EDAX	Energy Dispersive X-Ray Analysis
EDLC	Electrochemical Double-Layer Capacitor
EIS	Electrochemical Impedance Spectroscopy
ESR	Equivalent Series Resistance
FTIR	Fourier Transform Infra-Red
GCD	Galvanostatic Charge-Discharge
GCE	Glassy Carbon Electrode
GO	Graphene Oxide
HER	Hydrogen Evolution Reaction
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LDH	Layered Double Hydroxide
LIB	Lithium Ion Battery
LOM	Lattice Oxygen Mechanism
LSV	Linear Sweep Voltammetry

MOF	Metal Organic Framework
MOR	Methanol Oxidation Reaction
OER	Oxygen Evolution Reaction
OMS	Octahedral Molecular Sieves
RDS	Rate Determining Step
RGO	Reduced Graphene Oxide
RHE	Reversible Hydrogen Electrode
SC	Supercapacitor
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TMO	Transition Metal Oxide
TOF	Turnover Frequency
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Abstract

The pursuit of efficient and sustainable electrochemical energy storage and conversion technologies is vital for addressing global energy challenges. The research introduces a strategic innovation in dual-heteroatom (N,S) doping of reduced graphene oxide (RGO) and site-selective modification of Cryptomelane-type highly abundant Manganese based Oxide (OMS-2) to address the limitations of conventional electrodes for supercapacitors and fuel cells. The innovation of this work lies in the strategic manipulation of dopant chemistry and site-specific framework modification to engineer defects and active sites that significantly enhance electrochemical kinetics.

Initially, the study focuses on the synthesis of Graphene Oxide (GO) via an improved method (Tour method), followed by a controlled reduction using thiourea to introduce nitrogen (N) and sulphur (S) heteroatoms. By varying the thiourea-to-GO ratio, an optimal ratio of 1:8 was identified; beyond this threshold, the formation of sulphur crystals on the surface was found to hamper charge storage. The resulting dual-doped NS-RGO (TURGO) exhibited a specific capacitance 2.87 times higher than nitrogen-only doped RGO (URGO) and 27.32 times higher than bare GO, demonstrating remarkable stability with 119% capacitance retention after 4,000 cycles. To further explore its electrocatalytic potential, NS-RGO was utilised as a support for Pt nanoparticles for the Methanol Oxidation Reaction (MOR) in acidic media. The Pt/TURGO catalyst, possessing inhibitory effect of S atoms causing incomplete Pt reduction achieved a peak current density (in $\text{mg}_{\text{Pt}}^{-1}$), 22.37 times higher than its URGO counterpart, attributed to the unique Pt-graphene interactions and increased electrochemically active surface area (ECSA) provided by the dual-heteroatom doping.

The research further extends to the modification of Cryptomelane-type Octahedral Molecular Sieves (OMS-2). By incorporating the rare earth element Cerium (1.5 mmol) via a reflux method, the supercapacitance of OMS-2 was increased from 137.34 F.g^{-1} to 216.89 F.g^{-1} in alkaline medium. A durable hybrid composite of Ce-OMS-2 and NS-RGO achieved an optimized capacitance of 275.56 F.g^{-1} at 1 A.g^{-1} in acidic medium. This significant improvement highlights the synergy between the porous tunnel structure of the manganese oxide and the high conductivity of the doped graphene layers. Additionally, a comprehensive evaluation of nickel-modified OMS-2

(Ni_xOMS-2) was conducted using both in-situ (reflux) and ex-situ (wet-impregnation) approaches. The in-situ synthesized Ni_{0.03}OMS-2, calcined at 400°C, emerged as a potent bifunctional catalyst for both MOR and Oxygen Evolution Reaction (OER), showing a 17.34 fold performance increase over bare OMS-2 and an OER overpotential of 461 mV while *ex-situ* variant significantly reduced methanol oxidation onset potentials, representing excellent methanol oxidation selectivity.

All materials were systematically characterized using FTIR, XRD, Raman, TG-DTA, XPS, ICP-MS, CHNS, SEM-EDAX, and BET surface area analysis techniques to correlate structural properties with performance. XPS and ICP-MS analysis were instrumental in defining the location of dopants within the OMS-2 framework (surface, tunnel, or lattice sites) revealing how dopant positioning dictates catalytic activity. Collectively, these findings contribute significant insights into the design of multifunctional materials, providing a scalable pathway toward more efficient and sustainable energy conversion and storage systems.

Outline of thesis

The present work is organized into four comprehensive chapters that systematically detail the progression from fundamental material synthesis to advanced electrochemical performance.

Chapter 1: This chapter establishes the necessity of advanced materials for sustainable energy technologies, specifically supercapacitors, fuel cells, and water electrolyzers. It evaluates the kinetic bottlenecks of the OER and MOR, while identifying the conductivity and stability limitations of pristine manganese oxides. By reviewing the synergy between graphene and octahedral molecular sieves (OMS-2), the chapter outlines a research strategy centered on lattice engineering and heteroatom doping to develop high-performance, non-precious electrocatalysts.

Chapter 2: This chapter focuses on developing a robust carbon support via the simultaneous reduction and co-doping of graphene oxide with nitrogen and sulfur. Using a scalable reflux method with thiourea, the study demonstrates how dual-doping modulates the electronic structure of graphene to enhance charge-transfer kinetics. The resulting N,S-RGO achieved a superior specific capacitance of 488.20 F·g⁻¹ and

significantly outperformed commercial catalysts in methanol oxidation activity, when utilised as a support for platinum nanoparticles,.

Chapter 3: The third chapter explores the structural modification of the manganese oxide lattice through cerium incorporation to create essential oxygen vacancies and enhance redox activity. By anchoring these CeOMS-2 nanostructures onto N,S-RGO, a ternary nanocomposite was engineered with a high surface area of $105.34 \text{ m}^2.\text{g}^{-1}$. The findings reveal a powerful synergistic effect that improves charge storage capacity and provides exceptional durability in acidic environments where most metal oxides fail to sustain.

Chapter 4: This chapter investigates the transition toward bifunctional catalysis through the rational substitution of nickel into the cryptomelane framework. The study analyses the impact of nickel loading and their sites of substitution in driving both the methanol oxidation and oxygen evolution. The results highlight a dual-mechanism (AEM-LOM) that facilitates superior kinetics, effectively lowering onset potentials and offering a viable, earth-abundant alternative to noble metals for industrial hydrogen production and fuel cell applications.

*INVESTIGATION OF ELECTROCHEMICAL
BEHAVIOUR OF GRAPHENE AND MANGANESE
OXIDE BASED CATALYSTS*

CHAPTER I

**INTRODUCTION AND LITERATURE
SURVEY**

Chapter 1

Introduction and Literature Survey

1.1 Introduction to Electrochemical energy technologies

The modern energy sector faces significant challenges: climate crisis, energy unpredictability, and raw material scarcity. These issues mandate a complete energy system overhaul. The Paris Agreement aims for greenhouse gas neutrality between 2040 and 2060, a critical goal given that the current energy system accounts for $\sim 75\%$ of all greenhouse gas emissions [1]. Despite rapid advancements in clean energy, the world remains heavily reliant on fossil fuels. According to the International Energy Agency's (IEA) "Global Energy Review 2025," global energy demand grew by 2.2% in 2024. Renewables now constitute the largest share (38%) of the global energy supply, with fossil fuels and nuclear power making up the rest [2]. However, this continued fossil fuel reliance poses a severe climate risk. A 2025 study warns that the remaining carbon budget for the 1.5 °C warming limit is just 130 billion tons of CO₂, which could be depleted just over three years at current emission rates [3]. To mitigate this, a rapid shift to clean energy production and consumption is essential to achieve net-zero emissions by mid-century.

Addressing both rising energy demands and the need to drastically reduce carbon emissions requires sustainable solutions. While clean energy has prevented 2.6 billion tonnes of annual CO₂ emissions since 2019, this is insufficient to reverse the overall upward trend [4]. Therefore, developing highly efficient and cost-effective electrochemical technologies for both energy storage and conversion is paramount. These innovations are crucial for integrating renewable energy sources and achieving deep decarbonisation. Electrochemical devices, such as secondary batteries and supercapacitors, store and convert energy internally. In contrast, electrolyzers convert electricity into chemical energy (e.g. hydrogen) with $\sim 70\%$ efficiency, and fuel cells reverse this process. This design separation in electrolyzers and fuel cells allows for higher energy output, making them highly attractive for various applications.

1.2 Electrochemical energy storage devices

Energy storage systems (ESS) are devices designed to store energy in various forms like physical, chemical, mechanical, electrical or thermal for future consumption. The pressing need to address environmental concerns and fuel scarcity has made the development of these systems a critical research area. Current efforts are focused on creating advanced ESS that combine high energy density (energy per unit volume) with high power density (speed of energy delivery) and possess tunable architectures for flexible design [5,6]. Compared to fossil fuels, energy storage devices (ESDs) like batteries and supercapacitors are cleaner, more efficient and vital for integrating renewable energy sources. They enable long-term power storage and reliable energy delivery for a wide range of applications, including electric vehicles and broader energy solutions.

1.2.1 Batteries vs. Supercapacitors

Energy storage method is fundamentally divided into chemical (batteries) and electrostatic (capacitors) methods. Batteries rely on faradaic redox reactions, which can be irreversible and reduce their lifespan. Capacitors, on the other hand, store charge electrostatically in a non-faradaic process, providing an exceptionally long cycle life.

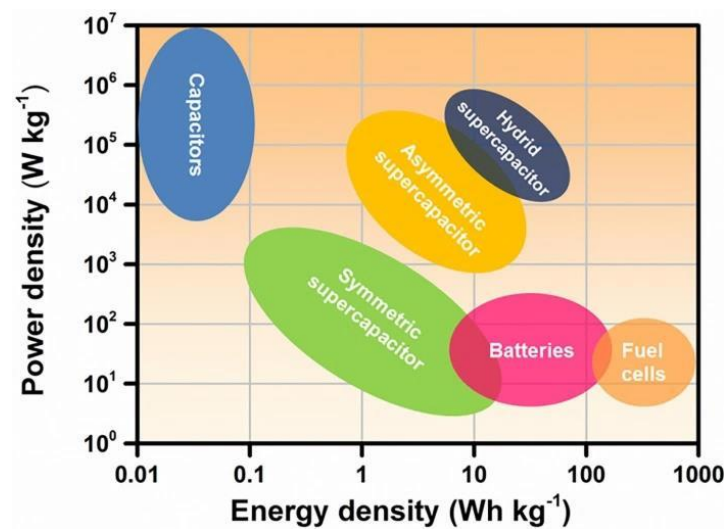


Figure 1.1: Ragone Plot: A Comparative Overview of Electrical Energy Storage (Specific Power density vs. Specific Energy density) Reproduced with permission [7]. Copyright 2022, Elsevier.

The advent of electrochemical supercapacitors (ESCs), which use high-surface-area materials, has significantly increased their energy density, making them a viable

alternative to batteries. While lithium-ion batteries (LIBs) are currently dominant, their future is limited by material supply, slow reaction kinetics and safety concerns. As illustrated by the Ragone plot shown in Fig. 1.1, supercapacitors (SCs) offer superior power density and durability, effectively bridging the performance gap between conventional capacitors and batteries, making them crucial for a range of high-power, long-life applications [5].

Supercapacitors are vital components for high-power applications, including electric vehicles and portable electronics. Valued for their high power density, rapid charge-discharge capabilities, and long cycle life, they also play a crucial role in grid stabilization by balancing fluctuations from renewable energy sources [5]. With researchers seeking alternatives to the limitations of traditional batteries, SCs are emerging as a promising and reliable solution for an electrified, sustainable future.

1.2.2 Structure and functioning of a supercapacitor

A supercapacitor is an energy storage device consisting of two highly porous electrodes (e.g., activated carbon), a porous separator, and an electrolyte as represented in Fig. 1.2. Current collectors enable electrical flow. The energy is stored via a non-faradaic process where electrolyte ions adsorb onto the electrode surfaces, forming an electrical double layer. The device capacitance is directly influenced by the extensive surface area of the electrodes and the thickness of this double layer.

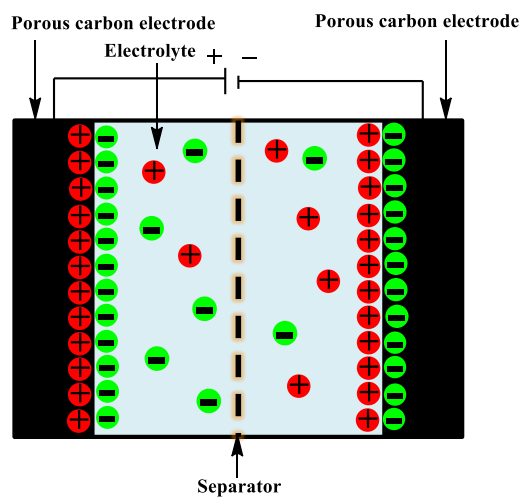


Figure 1.2: Schematic illustration of a supercapacitor

1.2.3 Types of supercapacitors

Supercapacitors are primarily categorized by their charge storage mechanism into three main types: electrochemical double-layer capacitors (EDLCs), pseudocapacitors and hybrid supercapacitors.

Electrochemical Double-Layer Capacitors store charge non-faradaically by accumulating ions at the electrode-electrolyte interface. This mechanism ensures high reversibility and stability, with capacitance directly proportional to electrode surface area. EDLCs offer higher energy density than conventional capacitors and greater power density than batteries. They typically use carbon-based electrodes like graphene, carbon aerogel and activated carbon, chosen for their excellent conductivity and large surface area [7].

Pseudocapacitors store charge via fast, reversible Faradaic reactions, unlike the electrostatic storage of EDLCs. This redox mechanism, which typically uses conducting polymers or metal chalcogenide electrodes, results in higher energy density but slower charge-discharge rates [8,9]. However, because these reactions are surface-based, pseudocapacitors have a shorter cycle life than EDLCs.

Hybrid supercapacitors combine two distinct electrode types: one capacitive (often carbon-based) and the other Faradaic (pseudocapacitive) battery-type, typically metal oxides or conducting polymers) [6]. This synergistic blend utilizes both Faradaic and non-Faradaic energy storage, delivering higher specific capacitance and improved energy density than EDLCs and pseudocapacitors, alongside better cycling stability and affordability compared to the latter.

1.2.4 Material Challenges for High-Performance Supercapacitors

Although supercapacitors offer significant advantages, their commercial potential is currently limited by several key factors. A core challenge is the trade-off between energy and power density, as boosting one often compromises the other despite ongoing research into new materials and designs. High production costs and the difficulty of scaling up manufacturing also limit their competitiveness. Furthermore, ensuring long-term stability and cycling durability in real-world conditions is a major hurdle for widespread adoption, and a similar challenge exists with electrolyte optimization, which forces a trade-off between a wide voltage window and high conductivity.

1.2.5 MnO₂ : A promising material for supercapacitors

Transition Metal Oxides (TMOs) such as RuO₂, MnO₂, Mn₃O₄, WO₃, CO₃O₄, NiO are preferred pseudocapacitor electrode materials due to their unique properties, including variable valency for excellent pseudocapacitance and inherent stability. M. Mayilmurugan et al. [10] have reviewed the important metal oxide and mixed metal oxides with potential supercapacitive properties, representing promising avenues for energy storage. Among the various oxides, manganese dioxide (MnO₂) stands out as an attractive, earth-abundant, cost-effective, and eco-friendly option with high theoretical capacitance (1370 F.g⁻¹). However, practically achievable value for the pristine MnO₂ is far below the predicted value, which hinders its widespread adoption due to poor electrical conductivity and limited cycling stability. To overcome this, researchers are developing MnO₂ composites with materials like carbon and conducting polymers to boost performance. In a study by Li et al. [11], Ni doped MnO₂ nanosheets grown in the internal surface of macroporous carbon (MC) derived from luffa sponge fiber delivered a high specific capacitance of 445 F.g⁻¹ at 1 A.g⁻¹ and energy density of 50 W.h.kg⁻¹, retaining 93% capacity at 1000 cycles. Z. Ma et al. [12] reported that growing NiCo-layered double hydroxide (LDH) nanosheets on MnO₂ nanowires led to an increase in specific capacitance of MnO₂ to 708 C.g⁻¹ at 1 A.g⁻¹. Though achieving both high capacitance and long-term durability remains challenging, however, promising new avenues such as developing composites of MnO₂ with suitable morphologies with other transition metal / metal oxides, hydroxides, layered double hydroxides [13] using supports like graphene, MOFs and COFs can yield improved dispersion, conductivity, ion transport and stability. Ultimately, achieving both excellent performance and cost-effectiveness is crucial for MnO₂ supercapacitors to secure their place as a foundational technology in next-generation energy storage.

1.3 Electrochemical Energy Conversion Devices

1.3.1 Fuel cell

Fuel cell technology offers a promising, eco-friendly energy solution, especially for off-grid rural areas and critical power applications like UPS. They are highly efficient, simple in design, and clean, using hydrogen as fuel. Unlike batteries, fuel cells convert external fuel into continuous electricity electrochemically, with no moving parts and low maintenance. While facing challenges like lifespan, power density, and durability, significant progress is being made, making them a key technology for reducing emissions across diverse applications from transportation to stationary and portable power solutions [14].

Fuel cells convert chemical energy into electrical energy through the electrochemical reaction of a fuel (like hydrogen) at the anode and an oxidant (like oxygen) at the cathode as shown in electrochemical reactions (1) and (2).

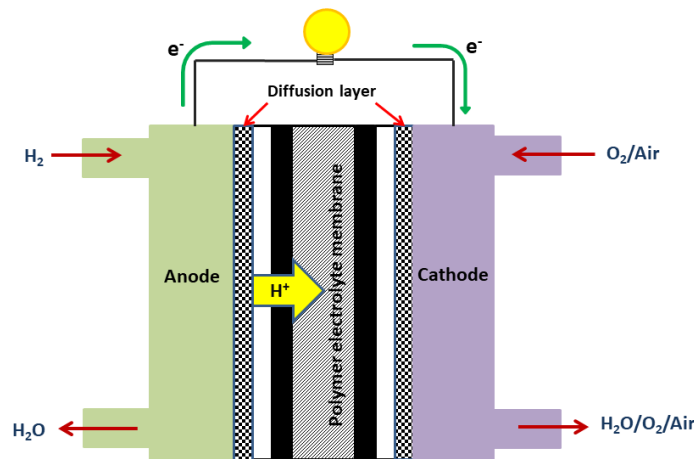
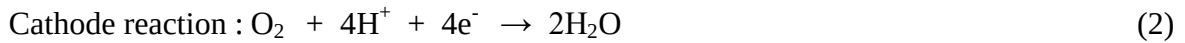


Figure 1.3: Schematic illustration of a Fuel Cell

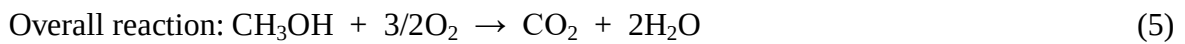
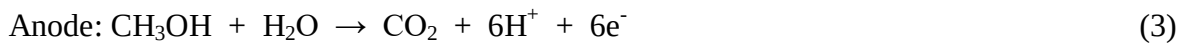
Depending on the electrolyte, either protons or hydroxide ions move through it, while electrons flow through an external circuit, generating electricity as represented in Fig. 1.3.

While hydrogen fuel cells are commercially available for large-scale applications, they are not suitable for small, portable devices. Direct Methanol Fuel Cells (DMFCs), which use

liquid methanol, are a promising alternative. Methanol is easy to store and handle, can be produced sustainably and has a high energy density, making it ideal for portable power. However, the high cost of platinum (Pt) and platinum alloys, which are essential catalysts for both the anode and cathode, is a major barrier to the commercialization of DMFCs [15].

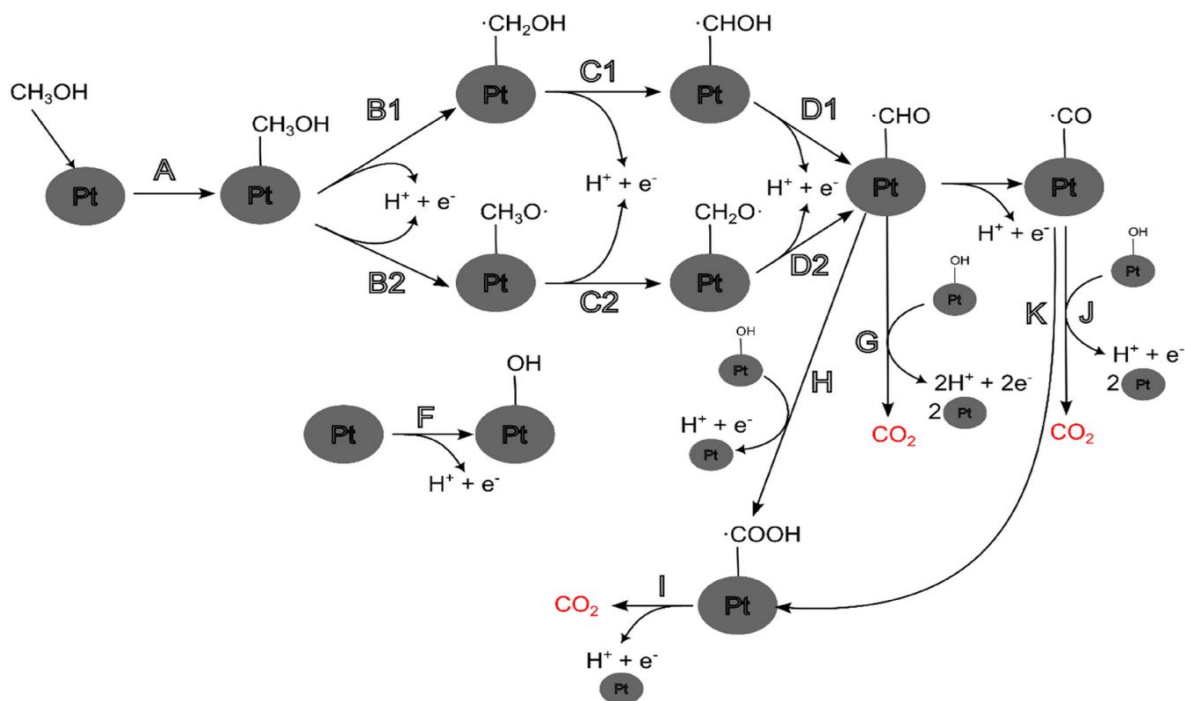
1.3.2 Mechanism of methanol electrooxidation on Pt surface

In DMFC, the oxidation of methanol fuel and oxygen reduction occurs at anode and cathode, respectively, via reactions (3) – (5),



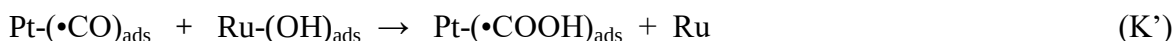
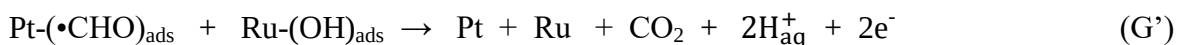
Léger [16] described a complex methanol oxidation mechanism on Pt catalysts forming several adsorbed intermediate species upon dissociation of adsorbed methanol in acidic environment. These intermediates get further converted to strongly adsorbing species which poison the Pt surface leading to sluggish methanol oxidation kinetics as illustrated by E. Berretti et al [17] in the schematic pathway shown in Scheme 1.1.

Methanol first adsorbs onto the Pt surface. This adsorbed methanol then undergoes 3 dehydrogenation steps forming radical species, releasing an electron at each step leading to adsorbed formyl groups ($\text{Pt}(\text{CHO})_{\text{ads}}$) via 2 possible pathways (B1,C1,D1 / B2,C2,D2). This intermediate is further oxidized to adsorbed carbon monoxide ($\text{Pt}(\text{CO})_{\text{ads}}$). This CO strongly binds to Pt, poisoning the catalyst by blocking active sites. Simultaneously, hydroxide (OH^-) groups can adsorb onto the fresh Pt atom. Adsorbed OH can react with the formyl intermediate to directly produce carbon dioxide (CO_2) or form adsorbed carboxyl groups ($\text{Pt}(\text{COOH})_{\text{ads}}$), which subsequently oxidize to CO_2 . However, oxidizing the adsorbed CO ($\text{Pt}(\text{CO})_{\text{ads}}$) to CO_2 requires higher overpotentials, occurring either directly or through an intermediate step. Hence this step is classified as a rate determining step in methanol oxidation on Pt.



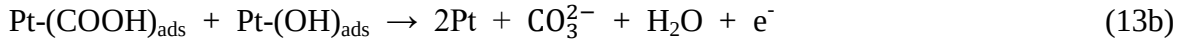
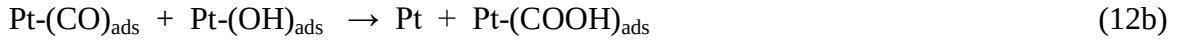
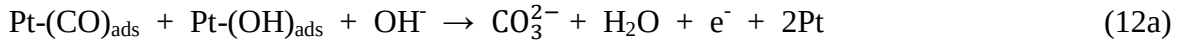
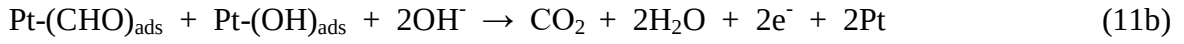
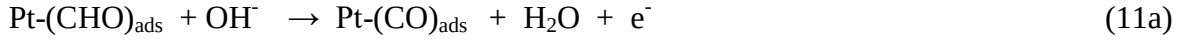
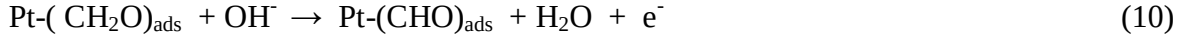
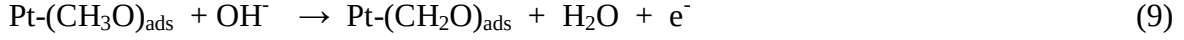
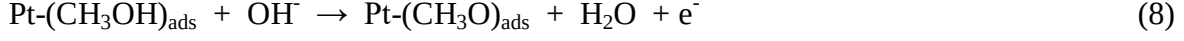
Scheme 1.1: Schematic methanol oxidation pathway in acidic electrolyte. Reproduced from [17] under CC BY 4.0 licence.

To improve the overall kinetics of the reaction, increasing OH_{ads} coverage at lower potentials is necessary which can be attained by adding an oxophilic metal like Ru to Pt in the form of an alloy [18] or core shell architecture [19]. A highest activity was observed over PtRu alloy with 10%Ru for catalysing methanol oxidation at room temperature to 50%Ru at elevated temperatures of 90°C to 130°C [20]. The higher activity in alloy stemmed from the oxidation of adsorbed CHO and CO species occurring at reduced potentials and at faster rate due to bifunctional mechanism between the two metals via alternate reactions F', G' and K'[16] and ligand effects or electronic effects.



On the contrary, in alkaline methanol oxidation, this bifunctional mechanism is believed to show negligible significance due to the ability of Pt itself to adsorb OH^- ions at lower potential similar to Ru. Additionally, the intermediates are weakly chemisorbed on the Pt surface which improves methanol oxidation kinetics in alkaline medium.

The methanol oxidation mechanism over Pt catalysts in alkaline medium occurs via reactions (6) – (13),



Herein, the adsorbed intermediates –CHO and –CO undergo further oxidation to formate or carbonate and is identified as a rate determining step as reported by E. Hao et al. [21] as such carbonate species reduce the pH of electrode and anolyte affecting surface OH coverage. E.D Rus et al. [22] exhibited an increased reaction rate at an optimum concentration of OH[−] ions, as higher OH coverage led to PtO formation reducing the rate of reaction.

1.3.3 Research on catalysts for methanol oxidation

The high cost of Pt-Ru is a significant hurdle for the widespread adoption of DMFCs. To overcome this, researchers are exploring ways to reduce the amount of expensive platinum by combining it with more affordable metals or metal oxides. These alternative materials can help Pt catalysts perform better by creating oxygen-containing compounds on their surface at lower electrical potentials. So far, many different transition metals, including Cu, Fe, Ni, Au, Co, Re, Rh, Sn [23–30] have been tested as binary, ternary alloys with

platinum for the methanol oxidation reaction (MOR). Because platinum-based catalysts are expensive, the key strategies developed to reduce costs and enhance catalyst utilization include designing Pt nanonstructures with active and varying dimensions like nanoworms, nanopetals, nanocubes etc. [31,32] by exposing the active facets of Pt. The other key strategy adopted by researchers is dispersing active Pt nanoparticles over suitable carbon based conductive supports, such as mesoporous carbon [33], multi walled carbon nanotubes [34], cryogel and xerogel carbon [35], graphitic carbon nanosheets [31], graphene [36], boron doped diamond film [37] and non-carbon based materials like zeolites [38], silicon nanocones [32], MXene [39], conducting polymers [40], titanium carbides, nitrides [41], metal oxides like WO_3 [42], VO_x , MoO_x [43], MnO_2 [44] by effectively minimizing the required noble metal content.

For methanol oxidation, platinum catalysts are exclusively used in acidic conditions, but alkaline conditions permit a broader range of materials due to reduced corrosion. Palladium is an excellent alternative to costly platinum in alkaline medium, as it exhibits better tolerance to carbon monoxide poisoning. Alloying palladium with other transition metals, such as rhodium, further enhances its performance. Studies have shown that even a low concentration of rhodium can significantly improve catalytic activity and fuel cell power density [45].

1.3.4 Challenges and scope

The high cost and scarcity of Pt and Pd necessitates a shift towards more earth-abundant catalysts like Ni, Cu. However, these alternatives currently suffer from lower stability and current density. Future research needs to focus on developing advanced catalyst materials and supports to enhance performance and durability. A key strategy is exploring non-Pt/Pd materials in alkaline media, which offers a wider range of selection and greater resistance to CO poisoning.

1.4 Water electrolyzers : Key to sustainable hydrogen

Hydrogen is a compelling alternative fuel due to its exceptional specific energy density (140-142 MJ.kg⁻¹) over twice that of conventional fuels and its environmental friendliness. [46]. Electrochemical water splitting is the most promising route for generating clean, green hydrogen from renewable sources, addressing fossil fuel depletion. This process involving hydrogen evolution reaction (HER) at anode and oxygen evolution reaction (OER) at cathode is conducted in various established and emerging technologies, including alkaline electrolysis cells (AECs) and anion exchange membrane water electrolysis (AEMWE) cells. Although AECs are mature, they have limitations in efficiency and stability. AEMWE offers a promising alternative by enabling the use of abundant, non-noble metal catalysts, though it is still less developed and requires further improvement for widespread adoption [47].

1.4.1 Oxygen Evolution Reaction (OER): The Critical Bottleneck

While HER is a kinetically facile two-electron process, the OER, occurring at the anode ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ in acidic media or $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ in alkaline media), is recognized as the rate-limiting step and primary bottleneck in overall water electrolysis efficiency. This is due to its complex and sluggish four-electron transfer mechanism, which involves multiple intermediate steps and high activation energies. The oxygen evolution reaction is the main hurdle for widespread water electrolysis. While its thermodynamic potential is 1.23 V vs. RHE, a substantial overpotential (η) is needed to drive the reaction at practical industrial rates. This directly inflates energy consumption and diminishes efficiency, severely undermining the economic viability of green hydrogen. Consequently, developing stable, highly active OER electrocatalysts that deliver high current densities at low overpotentials is crucial for mass hydrogen production.

1.4.2. Mechanism of oxygen evolution

In the alkaline and/or neutral environment, OER involves four electron-transfer steps on an active site (*) of catalyst, forming intermediates like *OH, *O, and *OOH, (equation 14-18) similar to acidic environment, and are a prerequisite for an OER electrocatalyst [48].





Standard OER mechanisms fit many hydroxide and oxide catalysts, however perovskites show deviations [49] which were resolved by advanced ^{18}O isotope labeling and DFT studies which revealed the thermodynamics of each step in OER occurring via material specific mechanisms like the traditional Adsorbate Evolution Mechanism (AEM) and Lattice Oxygen Mechanism (LOM) for OER [50] as represented in Fig. 1.4(a).

In AEM electrolysis, water molecules adsorb onto active metal sites (M), leading to a series of steps involving formation of M-OH followed by M-O, and finally M-OOH via O-O bond formation with another water molecule. O_2 is released when M-OOH is oxidized, regenerating the active site. This mechanism is limited by a linear scaling relationship ($\Delta G_{OOH} = \Delta G_{OH} + 3.2 \pm 0.2$ eV), imposing a theoretical overpotential limit of 370 ± 100 mV [51]. However, recent studies showed that this limit can be broken, suggesting alternative OER mechanisms like the Lattice Oxygen Mechanism (LOM) [52], wherein LOM considers the dynamic catalyst surface, where the active site isn't solely the metal center.

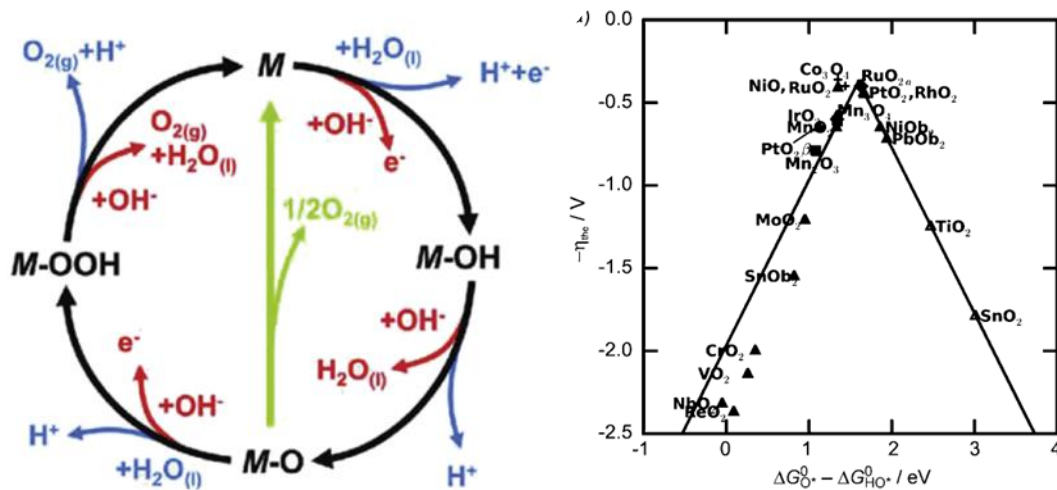


Figure 1.4: (a) OER mechanism showing pathways in acidic (blue) and alkaline (red) media. Note the peroxide (M-OOH) intermediate (black) indicating AEM and direct oxo coupling (M-O, green) routes indicating LOM. Reproduced with permission [53] Copyright 2017, Royal Society of Chemistry (b) Volcano plot showing theoretical OER

overpotential against the free energy difference ($\Delta G^*O - \Delta G^*OH$), highlighting activity trends across various metal oxide catalysts. Reproduced with permission [54] Copyright 2011, John Wiley and Sons

In LOM, M-O formation occurs via steps similar to AEM initial pathway. Further, the M-O couples directly with lattice oxygen to produce O_2 , simultaneously creating oxygen vacancies within the lattice. These vacancies are then refilled by OH^- ions from the solution. The LOM bypasses the M-OOH intermediate, thereby avoiding the AEM's limiting scaling relationship and potentially offering lower overpotentials [51].

The efficiency of OER catalyst is governed by the thermodynamics of binding intermediates and associated reaction kinetics. A high ΔG in the rate-determining step (RDS) directly leads to a high overpotential (η_{OER}) and energy loss. The ΔG_{OER} is determined from the highest ΔG step as follows [55]:

$$\Delta G_{OER} = \max \{ \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \} \quad (19)$$

$$\eta_{OER} = (\Delta G_{OER} / e) - 1.23V \quad (20)$$

For an ideal OER electrocatalyst, $\eta_{OER} = 0$,

i.e. $\Delta G_{OER} = 1.23 \text{ eV}$ and $\Delta G_1 = \Delta G_2 = \Delta G_3 = \Delta G_4$

The $\Delta G^*O - \Delta G^*OH$ free energy difference is a key descriptor, highlighting the need for balanced catalyst-intermediate binding being neither too strong (poisoning) nor too weak (inefficient formation). The volcano plot (Fig. 1.4(b)), based on the Sabatier principle [56], graphically illustrates this optimal balance, with its peak representing the lowest overpotential. This tool is invaluable for rational OER catalyst design and predicting activity while Tafel slope determines the reaction kinetics.

1.4.3 Key electrochemical parameters for evaluation of OER performance of an electrocatalyst

The performance of an OER electrocatalyst is effectively evaluated by several key parameters [55]. Overpotential (η) to achieve a current density of 10 mA.cm^{-2} and Tafel Slope (b) are vital measures of efficiency and reaction kinetics, respectively, with lower values indicating superior performance. The Electrochemical Active Surface Area (ECSA) and Turnover Frequency (TOF) quantify the number of active sites and the intrinsic

activity per site, where higher values are more desirable. For practical application, Mass Activity provides a measure of current per unit catalyst mass, while Exchange Current Density (j_0) reveals the fundamental electron transfer kinetics. The Faradaic Efficiency (FE) assesses the efficiency of electron conversion into the desired oxygen product. Finally, stability of catalyst, evaluated by monitoring performance over time, is paramount for ensuring long-term durability.

1.4.4 Research in oxygen evolution catalysis

Acidic OER faces significant challenges as abundant H^+ intermediates thermodynamically hinder the reaction, and corrosive conditions demand robust catalysts. While ruthenium (Ru) and iridium (Ir) oxides are top acidic OER electrocatalysts lying at the peak of the OER volcano plot due to their favorable binding energies and high electronic conductivity offering higher activity and moderate corrosion resistance (IrO_2 being more stable than RuO_2). However, their scarcity and high cost severely limit large-scale application. Furthermore, both RuO_2 and IrO_2 suffer instability at high anodic potentials through oxidation and dissolution in electrolyte (RuO_2 to RuO_4 or H_2RuO_5 , IrO_2 to IrO_3 or IrO_4^{2-}), despite IrO_2 's superior stability [57]. Efforts were made to improve their stability by modifying their composition and structure. Mayousse et al. [58] showed an improvement in OER performance upon insertion of 50% Ru in IrO_2 lattice while Audichon et al. [59] developed IrO_2 core – RuO_2 shell nanocatalyst with higher OER activity with much improved stability than their individual counterparts. However, given these precious metal limitations, substantial research is now focused on developing earth-abundant transition metal chalcogenides, spinels, inverse spinel oxides, perovskites, layered double hydroxides, including non-metallic materials as also reviewed by Suen et al. [53] with emphasis on synthetic approach, morphology, active sites or redox centres for efficient electron transfer, oxygen vacancies to develop sustainable OER catalysts. In optimising the OER catalysts, the goal should be to shift position of the catalyst on the volcano plot closer to the peak by optimizing the ΔG of their rate-determining step by adjusting overall binding strength of the intermediates.

Earth-abundant transition metals like Ni, Co, and Fe are gaining significant attraction as efficient OER electrocatalysts in alkaline media, often outperforming precious metals [52,60,61]. Their proximity to the top of the Sabatier volcano curves indicates optimal binding strengths with OER intermediates and high active site density. To boost OER

performance, recent efforts have focused on modifying spinel oxides. For instance, Guo et al. [62] hydrothermally doped Co_3O_4 with Ru and Ni, generating numerous active sites and oxygen vacancies, respectively, to improve its OER activity. In a related approach, Chen et al. [63] synthesized a Co-Ni-Fe spinel oxide-carbonitride hybrid using a MOF-derived strategy. This hybrid catalyst exhibited impressive efficiency, delivering $50 \text{ mA}\cdot\text{cm}^{-2}$ at 265 mV overpotential. XPS and DFT studies confirmed that this superior performance stemmed from an optimized electronic environment created by the three metals, which facilitated the adsorption of OER intermediates.

Systematic reviews have demonstrated remarkable OER activity of Ni, Co and Fe, based electrocatalysts often requiring less than 300 mV overpotential for $10 \text{ mA}\cdot\text{cm}^{-2}$ current density [47]. For industrial applications, catalysts need high activity and long-term stability, typically delivering over $500 \text{ mA}\cdot\text{cm}^{-2}$ at less than 300 mV overpotential [64]. Achieving this involves enhancing electrical conductivity (e.g., via mixed oxides or conductive additives) and ECSA through nanostructuring. Importantly, optimizing intrinsic activity by modifying the electronic structure (e.g., through defects, doping, or heteroatom integration) is crucial. In this approach, the lower intrinsic electronic conductivity of spinel oxides have reportedly been found to increase by compositing such oxides with conducting carbon based materials like graphene, CNT etc. [65]. Recent research highlights various effective strategies for enhancing OER catalysts. Reportedly, supporting FeSe_2 - CoSe_2 nanorods on N,S co-doped reduced graphene oxide, achieved a low overpotential of 216 mV @ $10 \text{ mA}\cdot\text{cm}^{-2}$ [66]. Incorporating sulfur heteroatoms by supporting TaO_x on S-doped carbon nanofibers significantly improved stability [67]. Outstanding OER durability (110 hours) and lower overpotential in alkaline conditions were achieved by Xie et al. by growing $\text{Fe}(\text{TCNQ})_2$ nanowires on Fe foil [68]. Furthermore, a novel approach involved fabricating 1D- MnO_2 nanowires in-situ within 2D mesoporous carbon nitride ($\text{MnO}_2@\text{mpg-C}_3\text{N}_4$), resulting in a threefold increase in TOF compared to pristine MnO_2 nanowires due to its open structure, favorable nanowire orientation and abundant transport channels [69]. Another successful strategy involving synergistic interaction between NiSe_2 and MOF-derived CeO_2 as a co-catalyst, led to an enhanced activity and stability in alkaline media [70]. Zhang et al. [71] found that co-doping $\delta\text{-MnO}_2$ with Ni and Ce successfully created oxygen vacancies leading to a defect-rich electronic structure. This in turn generated more active Mn species, significantly improving catalytic performance, while DFT revealed oxidation of O^* to

HOO* as the rate determining step of OER. The NiCe/MnO₂ catalyst achieved a low overpotential (170 mV @ 10 mA.cm⁻²) and excellent stability over 70 h comparable to RuO₂.

1.4.5. Challenges in OER electrocatalyst research

Despite significant research, in transition metal catalysts, their conversion to oxides at high potentials, leads to valence transitions and structural changes during OER. Hence, a notable focus is laid on manganese oxides (MnO_x), particularly MnO₂ [72,73], for their promising electrocatalytic activity and stability. Despite potentially lower activity than Ni, Co or Fe, role of Mn in natural photosynthesis highlights its sustainability. MnO₂ offers advantages like multiple valence states, numerous defect edges for active sites, tunable structures and strong corrosion resistance.

However, the OER field still faces significant challenges in achieving long-term stability and efficiency under demanding conditions, necessitating continued research into catalyst design and optimization to address challenges like high overpotential, durability, cost, and mass transport limitations.

1.5 Graphene : An overview

Carbon exhibits diverse allotropes with exceptional properties. Historically, graphite, glassy carbon, and amorphous carbon are crucial electrode materials due to their stability in various electrochemical environments. Recent decades have seen the emergence of novel forms like fullerenes (0D), carbon nanotubes (CNTs) (1D), and especially graphene (2D), revolutionizing electrochemistry. While other carbon nanomaterials face scalability and quality challenges for electrochemical use, graphene stands out due to its superior performance and potential for high-quality, large-scale synthesis. Its high conductivity, large surface area, and high electron transfer rate make it suitable for applications in high-energy density batteries, fuel cells, supercapacitors, advanced sensors and electrocatalysts [74].

Graphene is a two dimensional monolayer sheet consisting of hexagonally arranged network of sp² hybridised carbon atoms, with strong in-plane σ_{C-C} bonds leading to a delocalized electron network contributed by out of plane π bonds, boosting electrical conductivity and minimizing interfacial resistance with the substrate [75]. A single

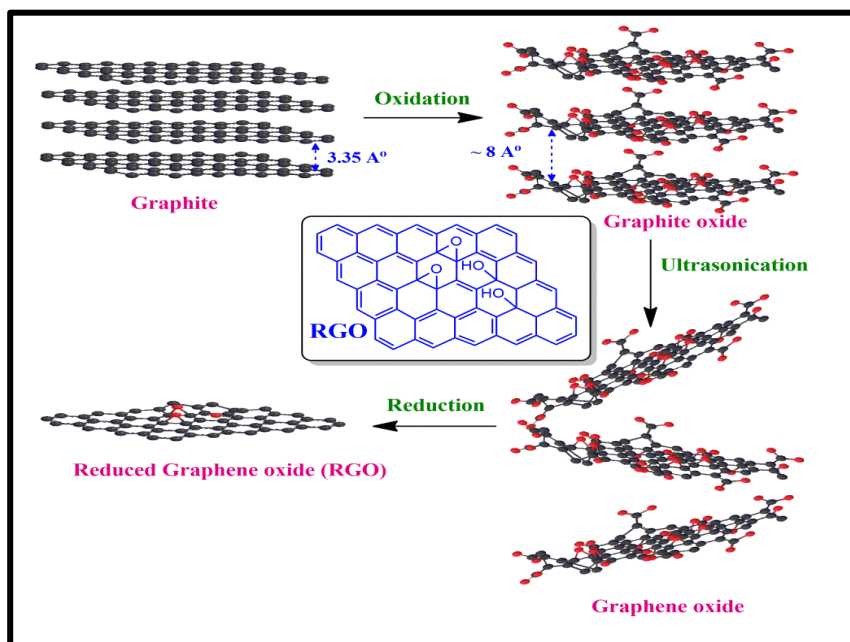
graphene sheet is known as monolayer graphene, while two or three layers are referred to as bilayer and trilayer graphene, respectively. Thicker formations, typically ranging from 5 to 30 layers, are generally classified as multilayer or thick graphene. Local Raman spectroscopy enables precise graphene thickness determination through careful analysis of the G and 2D band characteristics. The 2D-band shape, width and position are particularly sensitive to the number of layers, while the G-band peak position shifts downwards with increasing layer count [76]. Structurally, the carbon-carbon bond distance within a graphene layer is approximately 1.42 Å, and the interlayer spacing is about 3.35 Å. Over the past two decades, graphene has received significant amount of attention owing to its remarkable properties like incredibly large theoretical specific surface area ($2630 \text{ m}^2.\text{g}^{-1}$) and exceptional intrinsic charge carrier mobility (up to $200,000 \text{ cm}^2.\text{V}^{-1}.\text{S}^{-1}$). These qualities give it outstanding electrical conductivity, allowing it to handle high current densities (10^8 A.g^{-1}) and impressive optical transmittance ($\sim 97.7\%$) ideal for transparent conductive applications. Graphene is also incredibly strong, with a high Young's modulus ($\sim 1.0 \text{ TPa}$), and boasts excellent thermal conductivity ($\sim 5000 \text{ W.m}^{-1}.\text{K}^{-1}$) [75]. As a zero-band gap semiconductor, its electronic properties, including the band gap, can be precisely tuned using simple physicochemical processes, adding to its immense versatility for diverse applications. Due to its remarkable properties, graphene and its derivatives have garnered significant attention in materials science and condensed-matter physics. These materials are being widely explored for diverse applications, including nanoelectronics, energy storage (Li-ion batteries, supercapacitors), membranes, and biomedical uses like sensors and drug delivery [77].

1.5.1 Synthesis of Graphene

Early attempts at monolayer graphite synthesis in 1975 were hindered by inconsistent properties and a lack of clear applications [78]. Interest was renewed later, with Ruoff et al. [79] preparing multi-layered graphite via mechanical exfoliation. Graphene's official discovery is credited to Novoselov et al. in 2004, who isolated single layers from highly ordered pyrolytic graphite using simple adhesive tape exfoliation [80]. While this initial top-down method, along with solution exfoliation, demonstrated repeatable synthesis. It faced significant limitations for large-scale production, including defects and poor electrical properties. Consequently, bottom-up approaches like epitaxial growth, CVD, and CNT unzipping emerged to produce high-quality graphene [81,82]. However, these methods are insufficient to meet the projected annual demand exceeding one million tons [77]. This has led to the development of more scalable top-down methods to produce highly reduced graphene oxide (HRG). While initial mechanical exfoliation techniques were not scalable [76], chemical and electrochemical exfoliation proved more promising [83–85]. Of all the methods, the chemical reduction of graphene oxide (GO) has emerged as a particularly cost-effective and scalable approach. This process involves oxidizing natural graphite to GO sheets, which are rich in oxygen-containing functional groups, and then reducing them to reduced graphene oxide (RGO) using chemical, thermal, or microwave treatments. Early methods for synthesizing GO trace back to Brodie (1859) and Staudenmaier (1898), who used hazardous and time-consuming techniques with strong oxidants [86,87]. Hofmann (1937) also used a similar approach [88], but the most notable method was introduced by Hummers and Offeman (1958), who reacted graphite with sulfuric acid, sodium nitrate, and potassium permanganate [89,90]. This method was later refined by Marcano et al. (Tour method), who increased the amount of potassium permanganate and altered the acid ratio to 9:1 ($\text{H}_2\text{SO}_4\text{:H}_3\text{PO}_4$), while importantly omitting sodium nitrate to prevent the formation of toxic gases [91,92]. This modified approach yielded a more highly oxidized GO. Other oxidants, such as Jones' reagent ($\text{H}_2\text{CrO}_4/\text{H}_2\text{SO}_4$), have also been employed to create expanded graphite [90].

Graphite oxide has a stacked structure similar to graphite, but with much wider spacing (6–12 Å) due to water intercalation. It can be exfoliated into single or few-layered sheets using thermal or mechanical methods. As a two-dimensional graphene derivative, GO has a structure with randomly distributed clusters of slightly buckled sp^3 -hybridized carbon atoms, which are decorated with various oxygen-containing functional groups. The

remaining unoxidized areas consist of sp^2 -hybridized carbon atoms. This structure gives GO a high surface area, which is useful for energy storage, catalysis, and sensors while also offering excellent dispersion in solvents for thin films and coatings. Despite structural defects, GO maintains exceptional mechanical strength, making it suitable for robust composites [93].



Scheme 1.2: Schematic top-down chemical synthetic approach for reduced graphene oxide synthesis

The degree of oxidation determines the type and distribution of these functional groups. X-ray Photoelectron Spectroscopy (XPS) is a key technique for identifying these groups and their carbon-oxygen bond states, from deconvoluted C1s spectra showing peaks for sp^2 carbons, hydroxyl, epoxide, carbonyl and carboxyl groups. Raman spectroscopy is used to analyse the oxidation degree and the restoration of sp^2 carbon networks after reduction, with the intensity ratio of the D-band to the G-band directly correlating with these properties. Fourier Transform Infrared (FTIR) spectroscopy confirms the presence of hydroxyl, carbonyl, carboxyl, C=C and ether/epoxide groups through distinct absorption peaks [94]. Additionally, Nuclear Magnetic Resonance (NMR) spectroscopy has identified a broader range of functionalities, including lactols, tertiary alcohols, and edge-bound carboxylic acids and esters [95]. These functional groups are crucial for further functionalizing GO through covalent or non-covalent means, which expands its potential applications. However, this functionalization disrupts the materials conjugated structure,

leading to localized π -electrons and a reduction in both carrier mobility and concentration, thus lowering electrical conductivity. Importantly, electrical properties of GO can be restored through thermal, chemical or electrochemical reduction [96]. This reduction yields reduced graphene oxide, a material that closely mimics pristine graphene in its electrical, thermal, and mechanical properties [90], as well as its surface morphology as shown in schematic representation in Scheme 1.2.

1.5.2 Reduction Strategies for Graphene Oxide

a) Thermal reduction : Thermal reduction is a primary method for producing reduced graphene oxide, where the annealing temperature is a critical parameter that dictates material properties. Increasing the annealing temperature enhances the carbon-to-oxygen (C/O) ratio and improves electrical conductivity. For example, raising the temperature from 500°C to 750°C in an argon atmosphere increased the C/O ratio from 5 to over 13, while further increasing temperature to 1100°C boosted its electrical conductivity tenfold [97,98]. Even more aggressive methods, such as arc discharge at 2000°C, can achieve C/O ratios of 15–18 and conductivities of 2000 S·cm⁻¹ [99]. Temperature control also allows for tuning RGO's electronic properties. Annealing at 300–450°C or 800–1000°C yields n-type RGO due to remaining electron-donating groups, while annealing at 450–800°C results in p-type RGO from residual electron-withdrawing groups [100]. Other rapid thermal reduction methods include microwave reduction, photoreduction, and flame plasma [101–103]. Despite these advancements, challenges remain, such as defect formation at high temperatures, the persistence of residual oxygen groups, and inconsistent initiation temperatures for reduction.

b) Chemical method : Being a cheapest method, this has been extensively used for production of RGO on a large scale. Hydrazine hydrate was initially reported as a reducing agent for GO even before the discovery of graphene, by Stankovich et al. [104]. The product resembled properties close to graphene and also resulted in incorporation of nitrogen heteroatoms which enhanced its electrical conductivity from 1.5×10^{-6} S·m⁻¹ (GO) to $\sim 2 \times 10^2$ S·m⁻¹. However, considering the cons of using hydrazine such as high toxicity, environmentally non-friendliness, increased cost out of more waste generated during reduction process, focus has been laid over less toxic reducing agents.

Agarwal et al. [105] have reviewed numerous chemical reducing agents, plant extracts, microorganisms for successfully reducing GO. To cite a few, Chen et al. [106] reported

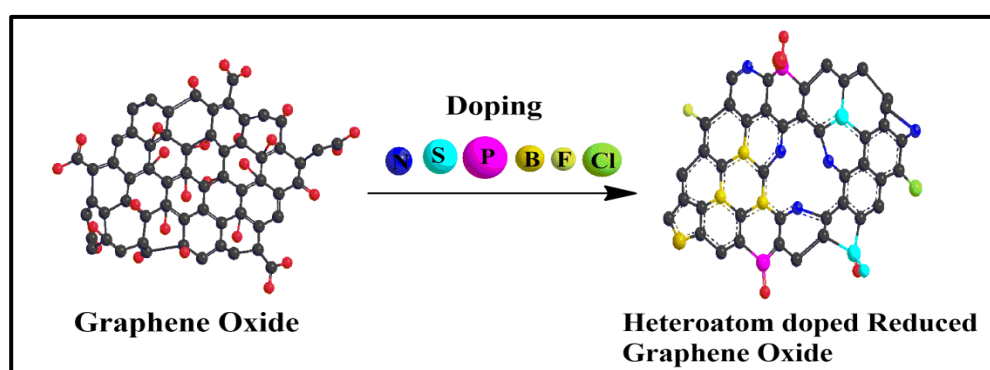
sulfur containing NaHSO_3 , SOCl_2 as less toxic, safer and non-volatile alternatives to hydrazine rendering an electrical conductivity of 6500 S.m^{-1} , much higher than hydrazine reduced graphene oxide. Other safer reducing agents reported include ethylene glycol, sodium sulfide, sodium borohydride, thiourea dioxide, N,N dimethyl hydrazine, hydriodic acid, caffeine, ammonium thiocyanate, urea, ascorbic acid, L-cysteine, thiourea, melamine, boric acid [107–109]. Lin et al. [110] employed thin copper films as catalysts to reduce GO sheets, restoring the graphene lattice. This process, conducted under a diluted hydrogen atmosphere at $700\text{--}900^\circ\text{C}$, yielded p-type RGO sheets with enhanced charge carrier mobility.

c) Electrochemical reduction (ECR) : Electrochemical reduction (ECR) is a "green" and efficient method for synthesizing RGO that utilizes techniques like cyclic or linear sweep voltammetry on GO-coated electrodes [111–113]. This process eliminates the need for harsh chemical reductants by facilitating electron and proton exchange at the electrode surface. For example, Hung et al. demonstrated that ECR significantly improves RGO properties, including an increased C/O ratio and a boost in electrical conductivity from 7.92×10^{-4} to $3.83 \times 10^{-1} \text{ S.cm}^{-1}$ [114]. ECR-produced RGO has also shown higher capacitance compared to hydrothermally produced nitrogen-doped RGO [115]. Compared to chemical reduction, ECR is fast, economical and eco-friendly. It allows for morphological control at mild temperatures and requires no post-purification steps. ECR's in-situ coating capability makes it ideal for sensing and electrocatalysis. Additionally, it can achieve homogeneous reduction in polymer/GO composites, which is a challenge for traditional chemical reductants [105,109].

1.5.3 Heteroatom-Doped Graphene in Supercapacitors and Electrocatalysis

Graphene's zero-bandgap and feeble defect structure limits its use in catalysis and energy storage by hindering charge separation and ion transport. While RGO is an improvement, it still suffers from defects and low conductivity. To expand its utility, graphene must be functionalized to create a porous, conductive network [116]. This is achieved through methods like surface transfer doping and substitutional doping into the carbon lattice. Surface transfer doping method non-covalently adsorbs dopants like metals, metal compounds, and heavy halogens onto graphene's surface, causing charge transfer via hydrogen bonding, electrostatic, π -stacking or van der Waals interactions [117,118]. This

creates p-type or n-type semiconductors with minimal structural defects, preserving high surface area and active sites for electrocatalysis [119]. A key limitation, however, is the instability of these adsorbates at high temperatures. Substitutional doping method replaces carbon atoms in the graphene lattice with heteroatoms (e.g., B, Si, N, P, S) to form covalent bonds (Scheme 1.3). The number of valence electrons determines the type of doping. Boron (B) creates p-type doping, while nitrogen (N) and phosphorus (P) create n-type doping [116]. Dopant electronegativity and atomic size influences the degree of lattice distortion and the formation of active sites. Atoms similar in size to carbon (B, N, F) integrate with minimal distortion, while larger atoms (Si, P, S, Cl) induce more defects and create longer C-dopant bonds. This process also creates polarization, which significantly impacts the electrical and photocatalytic properties of the material.



Scheme 1.3: Substitutional doping of heteroatoms with simultaneous reduction of graphene oxide

Thus chemical doping with foreign atoms is a powerful way to tailor graphene's electronic and chemical properties. Recent research highlights the promise of heteroatom-doped graphene as metal-free electrocatalyst and also as catalyst support in oxygen reduction, methanol oxidation, water splitting [120–122], fuel cells [123], metal free sensors [124], supercapacitors [125], batteries [126]. The most common methods for preparing such doped graphene include chemical vapour deposition [127], hydrothermal method [128], solvothermal [66], thermal annealing [120], plasma treatment [129], microwave assisted synthesis [107] electrochemical synthesis [130], pyrolysis [123].

Integrating nitrogen into RGO, particularly as pyridinic-N and pyrrolic-N, (with minor contributions from nitrilic-N, graphitic-N, and oxidized-N), significantly boosts the conductivity of RGO by increasing charge density through p-orbital electron contributions. For example, Yadav et al. [131] achieved a high charge storage capacity of 514 F.g⁻¹ with

5% nitrogen content. Similarly, Zhu et al. [132] co-doped RGO with sulfur and nitrogen in a 3D hydrogel, yielding a capacitance of 346 F.g^{-1} . This performance was an outcome of a high surface area and a polarized, defective structure due to sulfur dopant (in sulfide and thiophenic sulfur form), alongside nitrogen, which tuned the electronic properties. Another study demonstrated that co-doping RGO with (1.41 at.%) boron and (2.69 at.%) nitrogen significantly boosted its charge storage capacity to 350 F.g^{-1} at 0.5 A.g^{-1} [129] by leveraging the synergistic effect of borons electron-deficient holes and nitrogens electron-donating nature.

Multiple heteroatom doping further expands the utility of RGO. Shi et al. [123] developed a 3D porous graphene (NPS G2) simultaneously doped with nitrogen (5.57 at.%), phosphorus (3.38 at.%) and sulfur (0.83 at.%), which showed bifunctional electrocatalytic activity for fuel cells. The oxygen reduction reaction (ORR) activity of the material was comparable to commercial platinum-carbon (Pt/C), and also supporting platinum nanoparticles on it improved catalyst stability. Sun et al. [108] loaded platinum nanoparticles onto boron and nitrogen co-doped graphene via thermal annealing, with (3.7 at.%) B and (2.4 at.%) N primarily incorporated as B-N-C and B-C-O bonds, resulting in methanol oxidation activity that was 3.0 to 3.6 times higher than other catalysts. This was attributed to boron, increasing electron density and lowering the d-band center of platinum, which accelerated methanol dehydrogenation and reduced carbon monoxide (CO) poisoning. Kale et al. [66] also showed that supporting $\text{FeSe}_2\text{-CoSe}_2$ nanorods on N,S co-doped RGO, prevented agglomeration due to intrinsic defects and provided abundant active sites, leading to a low overpotential during oxygen evolution. These examples, along with other studies on doped graphene with various metals, metal oxides and polymers [117,122,128,133–135], highlight the potential of this approach. Optimizing doped graphene for energy applications requires balancing the bandgap and electron mobility for efficient catalysis. A key strategy is dual-doping with n-type and p-type elements to create p–n heterojunctions, which enhances electron–hole separation and electrical conductivity, ultimately improving catalytic efficiency.

1.6 Manganese oxides : A versatile platform for electrocatalysis and energy storage

1.6.1 Introduction to Manganese oxides

Transition metal oxide nanomaterials, particularly those with varied mixed valencies, are crucial for smart materials research. In recent decades, TMO nanomaterials have gained significant interest due to their shape and size-dependent properties, which has led to a focus on simple, low-cost preparation methods.

Among TMOs, Manganese oxides (MnO_x) stand out for their abundance, low cost, and environmental compatibility. They possess exceptional properties, including a high theoretical specific capacitance (up to 1370 F.g^{-1}) and large specific surface area [136]. These characteristics make them promising for applications in rechargeable batteries, catalysis, sensors and energy storage [137]. The wide range of redox states of manganese (from +2 to +7) allows for diverse stoichiometric oxides, hydroxides and oxyhydroxides. Common manganese oxides such as MnO , Mn_2O_3 , Mn_3O_4 , and MnO_2 are used in various fields including wastewater treatment [138], catalysis [139], and energy storage [103]. Wang et al. [140] have reviewed the use of MnO_x -based heterogeneous catalysts, highlighting the potential of vacancy, facet and crystal-phase engineering.

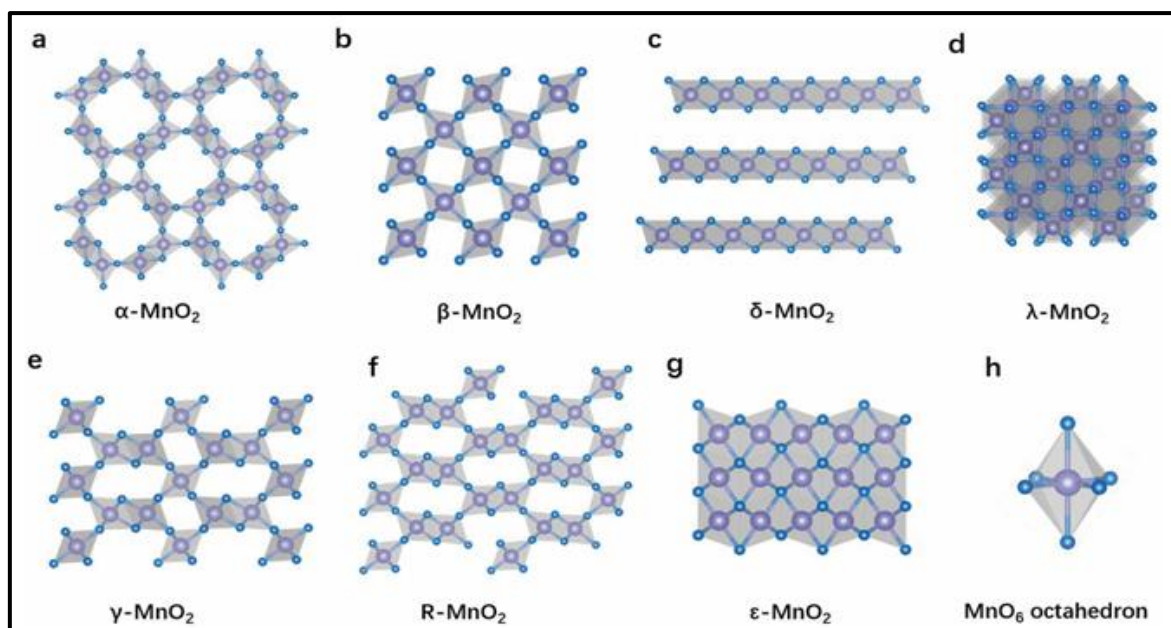


Figure 1.5 : Crystal structures of various MnO_2 polymorphs. Reproduced with permission [141]. Copyright 2023 John Wiley and Sons.

Among the various Mn oxides, MnO₂ is a highly researched material due to its low cost, environmental compatibility and exceptional physicochemical properties, including easily changeable oxidation states, thermal stability and catalytic stability in acidic environments [137]. Its customizable morphology, redox properties, and abundant defect sites allows wide range of applications. MnO₂ has several polymorphs, each based on distinct arrangements of its core [MnO₆] octahedral units [184]. These units link to form tunnel structures (α -, β -, and γ -MnO₂), layered structures (δ -MnO₂), or 3D frameworks (λ -MnO₂). The tunnel polymorphs are differentiated by their unique tunnel dimensions as shown in Fig. 1.5. For instance, β - and λ -MnO₂ (pyrolusite and spinel) have small 1.89 Å (1×1) tunnels, while α -MnO₂ (hollandite/cryptomelane) features larger 4.6 Å (2×2) tunnels, rendering it higher catalytic and electrochemical activity over other MnO₂ polymorphs. γ -MnO₂ (Nsutite) combines (1×1) and (1×2) tunnels with 1.89 Å and 2.3 Å size voids, respectively and offers abundant defects within the structure. The 2D layered δ -MnO₂ (birnessite), with its 7 Å interlayer spacing, is notable for its high capacitance due to efficient K⁺ cation accumulation [142]. Yang et al. [143] demonstrated that various MnO₂ polymorphs could be synthesized hydrothermally by simply adjusting the reaction temperature and duration, without altering the precursors. Such porous structure classifies them as Octahedral Molecular Seives (OMS – X), where, X essentially refers to the number of [MnO₆] octahedra along one side of the square tunnel opening.

1.6.2 Cryptomelane type Octahedral Molecular Seives (OMS-2)

Among the various octahedral molecular seive structures, OMS-2 (α -MnO₂) with cryptomelane type structure, has gained much importance due to its ability to reversibly intercalate various ions, high redox activity and structural tunability through doping. This makes it ideal for electrocatalysis and pseudocapacitive energy storage.

Characterized by the formula A[Mn₈O₁₆].nH₂O, OMS-2 exhibits an average Mn oxidation state of around +3.8, primarily due to Mn(IV). Its inherent charge imbalance is compensated by tunnel-bound cations such as K⁺, which stabilize the structure and are exchangeable. Strategic replacement of these K⁺ ions with other mono- or divalent cations leads to beneficial changes in surface area and volume, thereby boosting pseudocapacitance and catalytic activity. Various researchers have adopted different synthetic approaches for developing OMS-2 such as hydrothermal [144], reflux [145] one-step redox reaction [146], co-precipitation [147], sol-gel [148], low-temperature solvent

free method [149], air oxidation [150] exhibiting nanorods type morphology in many studies along with nanofibres, nanoneedles, microspheres, nanowires, nanotubes depending upon the synthesis method and precursors used. Slight synthetic modifications lead to notable changes in OMS-2 morphology, reactivity, and textural properties. This inherent structural versatility allows for easy optimization of catalytic activity for diverse applications, tailored to specific reaction and morphological needs. Studies highlight key approaches to optimizing manganese oxide catalysts. Wang et al. [151] reported that 1D α -MnO₂ nanorods, synthesized hydrothermally, showed promising catalytic activity for toluene oxidation, outperforming other morphologies. To boost OMS-2's electrical conductivity for ORR, Sun et al. [152] specifically manipulated oxygen vacancy content through NaBH₄ surface reduction, effectively creating adequate active sites that promoted the reaction.

1.6.3 Doped OMS-2 for electrochemical applications

OMS-2, a widely utilized mesoporous material for environmental remediation (serving as an oxidation catalyst and adsorbent), is frequently modified through doping [139,150,153–155]. This strategy aims to boost its activity, selectivity and unlock new applications. Doping is achieved by replacing tunnel K⁺ ions, framework Mn or occupying interstitial sites with various metal ions like Sr²⁺, Mg²⁺, Ca²⁺, Ag⁺, Nb⁵⁺, Mo⁶⁺, Fe³⁺, Ni²⁺, and Cu²⁺ [146,147,156–159].

I. Doped OMS-2 based materials for supercapacitors

Substituting metal ions into the K-OMS-2 framework allows for precise tuning of its properties, affecting aspects like rod morphology (L/D ratio), aggregation, thermal stability, Mn³⁺/Mn⁴⁺ redox balance, conductivity, and catalytic activity [159]. Despite manganese dioxide's inherent advantages of high theoretical capacitance and fast kinetics, its electrochemical efficiency is often hampered by low electrical conductivity (10⁻⁵ to 10⁻⁶ S.cm⁻¹) and structural changes during redox reactions. To overcome these limitations, doping has proven to be a highly effective method for improving both its conductivity and charge storage performance. Enhancements in electrochemical capabilities of α -MnO₂ is realized through targeted doping and composite formation. Doping with 0.15M Cu prompts a phase change to the stable β -MnO₂, improving charge storage and lowering resistance [9]. Similarly, 0.25 mM Ni doping in α -MnO₂ increases specific capacitance by 1.72 times, as ionic compatibility of Ni optimizes the crystal and electronic structure,

creating beneficial defects and oxygen vacancies [160]. Additionally, integrating α -MnO₂ with carbon or non-carbon supports in hybrid capacitors exploits synergistic pseudocapacitive and EDLC effects, resulting in higher surface area and superior structural stability [161,162]. Significant advancements in MnO₂-based supercapacitors have been achieved through diverse modification strategies. Comparative doping studies with Fe, V, Co and Ni doped MnO₂ nanosheets (MONSs) grown on macroporous carbon derived from luffa sponge fibre by Li et al. [11], showed that 2.36% Ni doping in MnO₂ nanosheets can yield a remarkable 445 F.g⁻¹ specific capacitance and 93% retention after 1000 cycles, surpassing other metal dopants. Broader composite approaches, reviewed by Patil et al. [163], integrate MnO₂ with various materials like transition metals, graphene, and MXenes to address its intrinsic limitations. For instance, decorating MnO₂ nanowires with NiCo-LDH nanosheets via a simple liquid phase reaction boosts specific capacitance to 708 C.g⁻¹ with good cyclic stability (82.3% over 2000 cycles) and favorable asymmetric supercapacitor performance [12]. Other effective methods include inducing oxygen vacancies via Na⁺ intercalation in MnO₂ via electrodeposition, which, when paired with a MXene anode in a flexible asymmetric supercapacitor, delivers high energy density (25.7 W.h.Kg⁻¹) and exceptional retention (98.8% after 10,000 cycles) [136]. Additionally, binder-free Ag-doped MnO₂/GO composite thin films deposited by a facile and binder-free successive ionic layer adsorption and reaction (SILAR) method, have achieved an impressive 192 m².g⁻¹ surface area and a solid-state symmetric supercapacitor with 164 F.g⁻¹ specific capacitance and 94% retention over 10,000 cycles [164].

II. Cerium-Enhanced Metal Oxide Supercapacitors

Cerium (Ce) doping has significantly enhanced the pseudocapacitive properties of various metal oxides due to its high redox activity, low cost and environmental friendliness. For instance, Saranya et al. [165] showed that 1% Ce doping in mesoporous NiO doubled its BET surface area. The substitution of large Ce³⁺ ions for smaller Ni²⁺ ions caused lattice strain and unit cell expansion, boosting specific capacitance to 2444 F.g⁻¹ (from 721 F.g⁻¹ for pristine NiO) and lowering resistance to 1.5 Ω . A similar improvement was seen in hydrothermally synthesized cobalt spinel ferrite, where 0.5 mole Ce doping yielded a high specific capacitance of 937.50 F.g⁻¹ with 82.3% retention after 4000 cycles [166]. Similarly, ultrasonically substituting Ce⁴⁺ ions into the V₂O₅ crystal structure resulted in a superior specific capacitance of 321.9 F.g⁻¹ compared to 190.9 F.g⁻¹ for V₂O₅ nanoparticles, with a stability of 95.2% after 5000 cycles [167]. Li et al. [168] improved

WO₃ nanowire arrays by Ce doping, which induced oxygen vacancies and increased lattice spacing which enhanced its conductivity, ion transport and stability while boosting specific capacitance from 416 F.g⁻¹ to 493 F.g⁻¹. The doped material also showed superior cycling stability, with 90.4% capacitance retention after 5000 cycles (versus 80.3% for undoped WO₃). Ce doping caused beneficial lattice distortion and denser nanowires, and its positive impact has been observed in other metal oxides as well [169–171]. Incorporating CeO₂ into a CeO₂@MnO₂/MXene electrode also had a significant impact, showing an improved specific capacitance of 1370 F.g⁻¹ (CV) and 1520 F.g⁻¹ (GCD) at 0.5 A.g⁻¹, with 73.5% cyclic stability after 10,000 cycles [172]. This composite addresses drawbacks of standalone CeO₂ like weak conductivity and agglomeration by leveraging the synergistic alliance with the highly conductive MXene. These findings collectively highlight potential of cerium to transform metal oxide electrodes through its redox activity and beneficial structural changes, creating advanced, efficient and durable supercapacitors.

III. Doped OMS-2 based materials for MOR and OER electrocatalysis

MnO₂ is a highly effective electro-catalyst for alcohol oxidation due to its high redox activity from the Mn⁴⁺/Mn³⁺ couple, labile oxygen, large surface area, and specific crystal structure [173]. As a hybrid support with carbon black, for Pt nanoparticles, it surpasses activity beyond commercial Pt/C catalysts by improving CO tolerance and promoting CO stripping through a synergistic effect between hydroxyl (OH_{ads}) groups on MnO₂ and adsorbed carbon monoxide (CO_{ads}) on Pt [44]. Similarly, supporting Ni nanoparticles on MnO₂/C yields a 1.43 times greater current density for methanol oxidation than Ni/C, as MnO₂ lowers the charge transfer coefficient and increases the diffusion coefficient [174]. Pd/MnO₂-RGO catalysts also benefit from improved Pd dispersion and an expanded ECSA, with MnO₂ facilitating the adsorption of hydroxyl groups to promote CO desorption from the Pd surface [175]. Furthermore, Mardani et al. [176] found that α -MnO₂ significantly boosted the performance of a bimetallic Ni-Cu sulfide catalyst for alkaline methanol oxidation by acting as a promoter and modifier. This led to a lower MOR onset potential of 0.38 V and a current density of approximately 70 mA.cm⁻², enhancing catalyst stability and resistance to poisoning.

Beyond its role as a direct support, doped OMS-2 is effective at oxidizing CO, a common intermediate of MOR. Doping OMS-2 with approximately 4 wt% Cu enables 100% CO conversion for over 50 hours, even in the presence of water [177]. Similarly, incorporating

2% Ag ions into OMS-2 micropores results in 100% selective CO oxidation for 250 hours [178]. The overall performance of MnO₂-based catalysts is further enhanced by loading them onto highly conductive supports like RGO, MWCNT or conducting polymers, which increase the ECSA and electrical conductivity [175,179–181]. For example, Baruah et al. [118] fabricated highly active MOR catalysts by coating MnO₂ nanorods with a porous PEDOT:PSS composite supported on RGO. The resulting catalyst achieved an anodic current density of 56.38 mA.cm⁻² at lower onset potential of 0.32 V, attaining 83% cyclic stability. Similarly, in a Pd nanocomposite supported on a PANI/MnO₂ base, MnO₂ supplied active oxygen atoms to Pd via the reversible redox transformation of MnOOH to MnO₂, improving CO tolerance [182].

α -MnO₂ and γ -MnO₂ are ideal carriers for OER catalysts due to their large tunnel structures, numerous defects and variable oxidation states. The catalytic activity of MnO₂ is highly dependent on its crystalline phase and the electrolytes pH, with activity following the order α -MnO₂ > β -MnO₂ > δ -MnO₂ [183]. OER performance is highest in alkaline conditions, where the overpotential is low. Below pH 9, overpotential increases due to the disproportionation of the Mn³⁺ precursor into Mn²⁺ and Mn⁴⁺. Conversely, at higher pH, the comproportionation of Mn²⁺ and Mn⁴⁺ back to Mn³⁺ facilitates efficient electrocatalysis [184]. A compelling strategy to improve OER is combining MnO₂ with precious metals. For example, doping MnO₂ with 0.87 at.% single-site Ir enhanced acidic OER, achieving 42 times the mass activity of commercial IrO₂ with over 650 hours of stability [185]. Similarly, introducing single Ru atoms into MnO₂ cation vacancies increased alkaline OER activity 44-fold, reaching 10 mA.cm⁻² at a low 240 mV overpotential [186]. While these single-atom catalysts show excellent stability at low current densities, a critical challenge remains at high current densities used in industrial water electrolysis wherein, the leaching of the precious metal single atoms, compromises long-term stability and is a key issue for practical application.

Methanol oxidation in acidic media, though kinetically easier, requires noble metals due to the poor stability of non-noble metals. Conversely, alkaline MOR is advantageous for its reduced toxicity, lower overpotential polarization, and superior oxidation kinetics [187]. This has led to a focus on coupling non-precious transition metals with MnO₂ to boost their catalytic activity [71,188]. Coupling MnO₂ with non-precious metals is a key strategy, particularly for the alkaline OER, as acidic OER is hindered by high proton concentrations, energy barriers and slow kinetics [51]. These metals enhance catalytic

activity by improving MnO_2 morphology, increasing surface area and controlling oxygen vacancy formation. For instance, dispersing Ag single atoms in $\alpha\text{-MnO}_2$ increased electrical conductivity and created charged oxygen vacancies that acted as active sites [189]. In a comparative study, Lu et al. [190] found that intercalating Fe^{3+} into MnO_2 significantly increased the concentration of Mn^{3+} and oxygen vacancies. This synergy enhanced hydroxyl (OH^-) adsorption, resulting in a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ at a lower overpotential of 330 mV compared to doping with Co^{2+} or Ni^{2+} . Similarly, low dopant concentrations of $6\times 10^{-4} \text{ mol}\cdot\text{g}^{-1}$ in Fe^{2+} and Co^{2+} doped hollandite ($\alpha\text{-MnO}_2$) electrodeposited with NH_4^+ ions acting as template, reduced OER overpotential and increased Mn^{3+} content, enhancing OER current density [191]. This highlights the importance of optimizing doping and phase composition for superior OER electrocatalysis.

IV. Synergistic Nickel-Manganese Oxide based MOR and OER Electrocatalysts

Supported by manganese dioxide (MnO_2), non-precious metal catalysts are improving but remain less effective than precious metals. While MnO_2 is effective for the alkaline OER, acidic conditions create a high energy barrier. The strong synergy between Ni and MnO_2 has positioned Ni modified MnO_2 as a promising catalyst [192,193]. Ni-based materials are widely studied for MOR, ORR and water splitting due to their affordability, high activity, and stability in basic solutions. Its similarity to platinum also makes it a subject of great interest [72]. Various Ni-based materials, including hydroxides, sulfides, selenides, nitrides, carbides have been successfully used as electrocatalysts [55,187,194].

Research by Zhu et al. [195] demonstrated that Ni-Mn hydroxide is superior to Ni-Fe hydroxide for the methanol-to-formate electro-oxidation reaction. They proposed a bifunctional mechanism involving $\text{Ni}^{\text{II}}\text{-(OH)}_2/\text{Ni}^{\text{III}}\text{-OOH}$ redox transitions, where combined active sites on $\text{Ni}^{\text{III}}\text{-OOH}$ (Ni^{III} and nearby electrophilic oxygen) drive MOR, and Mn synergistically boosts catalytic activity of nickel. Subbaraman et al. [196] demonstrated that Ni hydr(oxy)oxides outperform Co, Fe, and Mn counterparts for HER, OER, and CO oxidation in alkaline media, attributing this to optimal $\text{OH-M}^{\text{n+}}$ bond strength. In $\text{NiO/MnO}_2\text{@PANI}$ systems, Ni boosts the activity of MnO_2 to levels comparable with noble metals due to its superior water oxidation potential [192]. A microwave-irradiated $\text{Ni-MnO}_x/\text{C}$ catalyst also showed improved MOR activity, as MnO_x created hydrophilic sites that favored $\text{Ni(OH)}_2/\text{NiOOH}$ transformation and improved charge transfer [174]. Jia et al. [193] demonstrated that electrodepositing Ni into a

MnO₂/MXene framework introduces defects and oxygen vacancies, increasing the Mn³⁺/Mn⁴⁺ ratio to enhance conductivity and reduce OER overpotential. To address the poor conductivity of pure MOFs, Sreekanth et al. [197] developed a 3D flower-like Ni-MOF@CNT catalyst; its high ECSA and carbon nanotubes prevent aggregation, ensuring accessible Ni sites for alcohol oxidation and OER. While Liu et al. [187] noted that Ni facilitates MOR via NiOOH species, the overlap with OER potentials remains a challenge [198]. Future research must prioritize synthetic strategies that lower the Ni(OH)₂/NiOOH redox potential to improve MOR efficiency and selectivity.

1.7 Research gaps and challenges

Despite the theoretical promise of transition metal oxides and carbon-based nanomaterials, several fundamental challenges continue to hinder the large-scale commercialization of high-performance electrochemical devices. A primary bottleneck remains the performance limitations of pristine manganese oxides; while they offer high abundance and versatile redox chemistry, their practical application in supercapacitors and fuel cells is restricted by poor intrinsic conductivity and structural instability during prolonged cycling. In the context of energy conversion, the prohibitive cost and scarcity of noble metals like Platinum and Palladium necessitate a shift towards earth-abundant transition metals. However, non-precious alternatives often suffer from lower current densities and poor durability, especially during the demanding kinetics of the methanol oxidation and oxygen evolution reaction. Furthermore, while alkaline media offer superior charge storage and oxidation kinetics for the methanol and water oxidation, there is a distinct lack of research focused on the synergistic integration of dual-doped graphene with functionalized molecular sieves. Crucially, the potential of transforming the Cryptomelane (OMS-2) framework through the dual strategy of nickel substitution and cerium doping remains under-explored. While cerium is known to enhance redox activity and induce beneficial structural modifications, and nickel provides excellent active sites for OER and MOR, their combined effect within a stable, reflux-synthesized ternary nanocomposite is not well-documented. This research addresses these gaps by engineering nickel and cerium modified OMS-2 nanostructures supported on heteroatom-doped reduced graphene oxide, aiming to overcome the conductivity and stability barriers of manganese catalysts to provide a robust, platinum group metal (PGM) free solution for both efficient energy storage and energy conversion reactions.

1.8 References

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CHAPTER II

**SYNTHESIS, CHARACTERISATION AND
ELECTROCHEMICAL APPLICATIONS
OF HETEROATOM DOPED REDUCED
GRAPHENE OXIDE**

- I. Effect of thiourea concentration on supercapacitive performance of 1:KrGO
- II. Critical role of sulfur co-dopant in enhanced supercapacitance of RGO
- III. Catalytic application of doped RGO as a support for Pt nanoparticles in methanol oxidation reaction

Chapter 2

Synthesis, Characterisation and Electrochemical Applications of Heteroatom Doped Reduced Graphene Oxide

2.1 Introduction

The diverse allotropes of carbon have found extensive use across various fields, particularly in electrochemical applications. Among these, graphene stands out as a two-dimensional, single atom thick network of sp^2 -bonded carbon atoms. Its exceptional properties, including a large surface area, high electrical conductivity and robust mechanical strength, make it a premier candidate for next-generation materials in areas like energy storage, catalysis, and sensing. However, synthesizing graphene in large quantities is a key challenge. While various methods exist, chemical synthesis, particularly the improved Hummer's method, offers a cost-effective and less toxic way to produce graphene oxide (GO) from graphite [1,2]. However, poor electrical conductivity of GO arising from disrupted π - π interactions resulting from oxygen functionalities necessitates its reduction. Reduced graphene oxide (RGO), created by chemically removing oxygen functionalities, partially restores the graphene structure and its properties, however, it also leads to irreversible restacking or aggregation of graphene sheets [3].

Despite several improvements, RGO still has limitations like electro-neutrality, lower effective surface area, low energy density, feeble active sites etc. With a theoretical capacitance of 520 F.g^{-1} , graphene has immense potential for supercapacitor applications, however, above limitations lead to poor performance delivering only $100\text{--}200 \text{ F.g}^{-1}$, highlighting a significant performance gap. [4]. To overcome this, reduction of GO with simultaneous substitutional heteroatom doping (N, S, P, B, F, Cl) has emerged as a powerful strategy by utilising heteroatom containing reducing agents like hydrazine, urea, sodium sulphide, boric acid, ammonium thiocyanate, ammonium dihydrogen phosphate, L-cysteine etc., in modifying its surface characteristics by tuning electronic properties and surface activity of the material, significantly improving its performance and mechanical

strength for energy storage and electrocatalysis [5–10]. Among various dopants, nitrogen atoms have been found to have profound impact on specific capacitance especially in acidic electrolytes, due to increased electron charge density by N incorporation in graphene lattice in the form of basic functional groups like pyridinic-N and pyrrolic-N/pyridone-N which undergo redox reactions through protons, subsequently contributing pseudocapacitive properties to RGO [11]. Similarly, introducing S dopant in graphene lattice led a more polarised structure due to its wide band gap, creating more active and hydrophilic sites [7]. Over single heteroatom doping, excellent electrochemical properties are observed with co-doping heteroatoms, especially N and S. Various compounds with sulfur or diamine structure have served as efficient reducing agents to convert graphene oxide to reduced graphene oxide with simultaneous N and S doping. A study by Liu et al. demonstrated thiourea, as a safe and less toxic alternative to traditional agents, and can be used to produce few-layered, highly conductive RGO (635 S.m^{-1}) with enhanced dispersibility in organic solvents, attributed to thiourea molecules grafting onto the carboxyl groups on RGO [12]. Upon co-doping N and S in porous carbon, the electronegativity differences between co-doped heteroatoms and carbon synergistically modulates surface charge density, leading to more pronounced changes in conductivity and surface hydrophilicity of carbon, making it exceptionally effective for SC applications [13]. Similar improvement is also observed on charge storage properties of graphene through faradaic redox reactions of N and S functionalities on the periphery as well as on the aromatics of graphene [14]. The effectiveness of thiourea reduced RGO via thermal annealing method exhibited metal free ORR electrocatalysis with high current density and stability [15]. Moreover, such material when utilised as a support, the heteroatoms reportedly served as anchoring sites for various catalysts, by preventing agglomeration and improving dispersion of catalyst particles [16]. Sun et al. [17] have well demonstrated the effect of N and S configurations in graphene lattice support obtained by reducing GO with thiourea via hydrothermal approach, for depositing Pt nanoparticles to catalyse methanol oxidation, wherein they reported the superiority of pyrrolic form of N and oxidised forms of S in improving catalytic performance over other configurations.

However, optimizing co-doped RGO for energy storage applications requires a precise understanding of how the concentration of N and S atoms impact its electrochemical behaviour. While thiourea provides a safer pathway for this co-doping, a clear relationship between the concentration of precursor and the final N and S content remains largely

unestablished. This research fills this void by investigating how controlled variations in the N and S heteroatom percentages on the RGO surface influence its charge storage capacity and stability, thereby providing a basis for rational design of energy storage.

The first section of this chapter details the synthesis of N,S co-doped RGO using a simple and less toxic reflux method. We employed thiourea as both, a reducing agent for graphene oxide and a dual precursor for introducing nitrogen and sulfur heteroatoms. This study investigates the correlation between the amount of thiourea used, the resulting N and S content in the RGO along with structural impact and its electrochemical performance. By assessing the N, S concentration dependant supercapacitive performance and stability, this research aims to provide insights for developing advanced energy storage devices. The second section of this chapter examines the influence of sulfur on RGO's supercapacitance. Using urea as a sulfur-free precursor and a reducing agent, N-doped RGO is prepared and compared with the N,S co-doped RGO from the first section. This comparative study isolates the effect of the additional sulfur atom on the material's charge storage capacity and stability, providing specific insights into the benefits of N,S co-doping for supercapacitor applications. Finally, building on the foundational work of the previous sections, the third section explores the application of optimized N,S co-doped RGO and N-doped RGO as a catalyst support for platinum nanoparticles in the methanol oxidation reaction (MOR), a key process in direct methanol fuel cells (DMFC). The comparative study revealed a co-relation between different doping strategies and catalytic performance. This chapter aims to identify the key trade-offs in catalyst design, examining how support properties affect crucial parameters such as initial activity, long-term stability and reaction kinetics. This work highlights a multi-faceted approach to leveraging heteroatom doping to create advanced materials for both energy storage and catalysis.

2.2 Methodology

All chemicals and reagents used in this study were of analytical grade. Detailed information regarding the purity and suppliers of these materials is documented in the Appendix following the final chapter.

2.2.1 Synthesis of Graphene Oxide

This investigation presents the synthesis of graphite oxide using an improved method that builds upon the work of Marcano et al. [1,2], but with an intentional reduction in the volume of acids to enhance the economic viability of the process. The procedure commenced with the dispersion of 6 g of graphite powder into a 9:1 ratio of 270 mL of H_2SO_4 and 30 mL of H_3PO_4 . The mixture was stirred for one hour at 35–40°C. To safely oxidize the graphite, 30 g of KMnO_4 was slowly added in six portions, by carefully controlling temperature at 60–65°C. After the solution turned green, it was stirred for an additional 24 hours to form a brownish paste-like substance. The reaction was then quenched by the addition of 400 mL of ice and 10 mL of 30% H_2O_2 , which resulted in a bright yellow solution with effervescence. After the mixture was left undisturbed overnight, the supernatant pink solution containing unreacted KMnO_4 was discarded. The remaining thick yellow solution was purified by centrifugation and washed with 200 mL of 10% HCl and distilled water until the pH was neutral. A final centrifugation with 100 mL of ethanol was performed. To exfoliate and unstack the graphite oxide sheets, the solution was ultrasonicated for one hour, producing a few-layered Graphene Oxide (GO) solution which was then dried at 45°C to yield a brownish Graphene Oxide film.

2.2.2 Synthesis of Reduced Graphene Oxide (1:XrGO, X = 1, 3, 5, 8, 12 and 15)

RGO was synthesized using a simple reflux technique to assess the impact of thiourea concentration on the final product. Initially, 0.1g of GO was dispersed in 50 mL of distilled water via ultrasonication for 1 hour. To this suspension, 0.1g thiourea was added to produce 1:1rGO sample. While subsequent 1:3, 1:5, 1:8, 1:12, and 1:15rGO were synthesized by incrementally increasing the thiourea mass to 0.3g, 0.5g, 0.8g, 1.2g and 1.5g, respectively. Each mixture was refluxed at 100°C for 18 hours, and the resulting black RGO powder was isolated through repeated centrifugation and washing with

distilled water, followed by drying at 90°C. The obtained samples were labelled as 1:1rGO, 1:3rGO, 1:5rGO, 1:8rGO, 1:12rGO and 1:15rGO, accordingly.

2.2.3 Synthesis of N and S co-doped Reduced Graphene Oxide (TURGO)

The synthesis of N and S co-doped RGO was carried out using a similar method to that detailed in Section 2.2.2 for the 1:8rGO sample. A fixed mass ratio of 1:8 for GO:thiourea reductant was maintained, to yield the product TURGO.

2.2.4 Synthesis of N doped Reduced Graphene Oxide (URGO)

To isolate the impact of sulfur atoms, N doped RGO was synthesized using urea as a sulfur-free precursor. In this process, 0.1g of GO was first ultrasonically dispersed in 50 mL of distilled water for 1 hour at room temperature. Further, 0.8g of urea was added to the dispersion and the mixture was refluxed for 18 hours at 100°C. The resulting product was purified via centrifugation and washing with distilled water followed by drying at 90°C to yield a black N doped RGO powder referred as URGO. The mass ratio of 1:8 (GO : urea) was selected to provide a direct comparison with the optimized 1:8rGO sample from the preceding study, thereby enabling a clear assessment of contribution of sulphur to the materials electrochemical performance.

2.2.5 Synthesis of Pt loaded RGO catalysts

Platinum loaded N,S co-doped RGO was prepared via a wet chemical reduction method. Initially, 0.02g of TURGO was dispersed in 37 mL of double-distilled water using ultrasonication for one hour. Following this, 13.33 mL of a 3 mM hexachloroplatinic acid (40 μ moles) solution was added to the suspension while stirring for an additional hour. The pH of the mixture was then adjusted to 10 with 1 M NaOH solution (approx. 4 drops). Pt was reduced and deposited onto TURGO by adding 0.124g of sodium borohydride to the mixture, which was then continuously stirred for 24 hours at room temperature. The final solid product was isolated by centrifugation, and thoroughly washed with double-distilled water and ethanol, with further drying in a hot air oven at 60°C, to be referred as Pt/TURGO. An identical procedure was also used to synthesize Pt loaded N doped RGO, by replacing TURGO with URGO and the subsequent product was referred as Pt/URGO.

2.2.6 Materials Characterisation

A suite of analytical techniques was employed to fully characterize the synthesized samples. Fourier Transform Infrared (FTIR) spectra were obtained using an IRAffinity –

1S SHIMADZU 00822 spectrophotometer in the range of 400–4000 cm^{-1} . Raman spectroscopy was performed on an Agiltron PeakSeeker Pro instrument with a 532 nm laser at 100 mW to analyse molecular vibrations and structural information. X-ray Diffraction (XRD) patterns were recorded on a Bruker D8Advance diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) to study the crystal structure. For thermal analysis, simultaneous Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out using a SHIMADZU DTG-60 analyser. Samples were heated from 25°C to 800°C at a rate of 10°C/min under a nitrogen atmosphere to assess thermal stability. The surface morphology and elemental distribution were examined using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX), respectively, on a JEOL JSM-7610F FEG-SEM equipped with an Ametek EDX PV6500. Elemental composition was determined using a Vario Elementar MICRO CHNS analyser. The oxidation states and elemental composition were further investigated via X-ray Photoelectron Spectroscopy (XPS) using a Kratos Analytical Ltd. Axis Supra, FEI Inc. model, with an Al $K\alpha$ X-ray source (1486.6 eV). All spectra were first charge-corrected by referencing the adventitious carbon C1s peak to 284.8 eV to account for electronic shifts and surface charging. Finally, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was performed on the ICP-MS system, Agilant 7900 to determine the elemental concentration of each sample.

2.2.7 Electrochemical Measurements

The electrochemical properties of all samples were systematically investigated using a three-electrode CHI6081E electrochemical workstation. This setup consisted of a modified glassy carbon electrode (GCE, 3 mm diameter) as the working electrode, a Pt wire as the counter electrode and an aqueous silver/silver chloride (Ag/AgCl) electrode as the reference electrode. The GCE was meticulously prepared by sequentially polishing with 1, 0.3 and 0.05 μm alumina slurry, followed by sonication in ethanol for 2 minutes. The RGO working electrode was fabricated by drop-casting sample ink onto the dried GCE. The sample ink was prepared by dispersing 2 mg of the sample in a 40 μL solution of isopropyl alcohol for 10 minutes, following which 20 μL Nafion binder was added and dispersed for another 5 minutes. The modified electrode was then air-dried overnight. A 2.5 M H_2SO_4 solution served as the electrolyte for supercapacitance measurements. Cyclic voltammetry (CV) was performed at varying scan rates of 1, 2, 5, 10, 20, 30, 40, and 50 $\text{mV} \cdot \text{s}^{-1}$ within a potential range of -0.2 V to 1.2 V to assess the effect of scan rate on the charge storage

capacity. Galvanostatic charge-discharge (GCD) curves were recorded in an optimized potential window of 0 V to 0.8 V at various current densities to determine the specific capacitance and compare it with the CV results. Furthermore, the cyclic stability of the samples was evaluated, and electrochemical impedance spectroscopy (EIS) was conducted from 100 kHz to 1 Hz to further assess the electrode kinetics.

For methanol oxidation studies on Pt loaded samples, an equimolar mixture of 1M methanol and 1M H₂SO₄ solution was used. CVs were recorded by scanning working electrode within a potential span of 0 to 1 V at varying scan rates from 2 to 100 mV.s⁻¹. To understand the effect of methanol concentration, CVs were also recorded in 1.5 and 2.5M CH₃OH in 1M H₂SO₄. Similarly, the effect of temperature was studied by recording CVs at room, 40 and 60°C in 2.5M CH₃OH with 1M H₂SO₄. Chronoamperometric (CA) stability tests were performed at 0.85V for 400s. The Tafel plots and EIS data were obtained to gain insights of the electrode kinetics.

2.3 Results & discussion

1. Effect of thiourea concentration on supercapacitive performance of 1:1XrGO

2.3.1 Structural and morphological analysis of 1:1XrGO as a function of thiourea concentration

1. FTIR and Raman spectral analysis

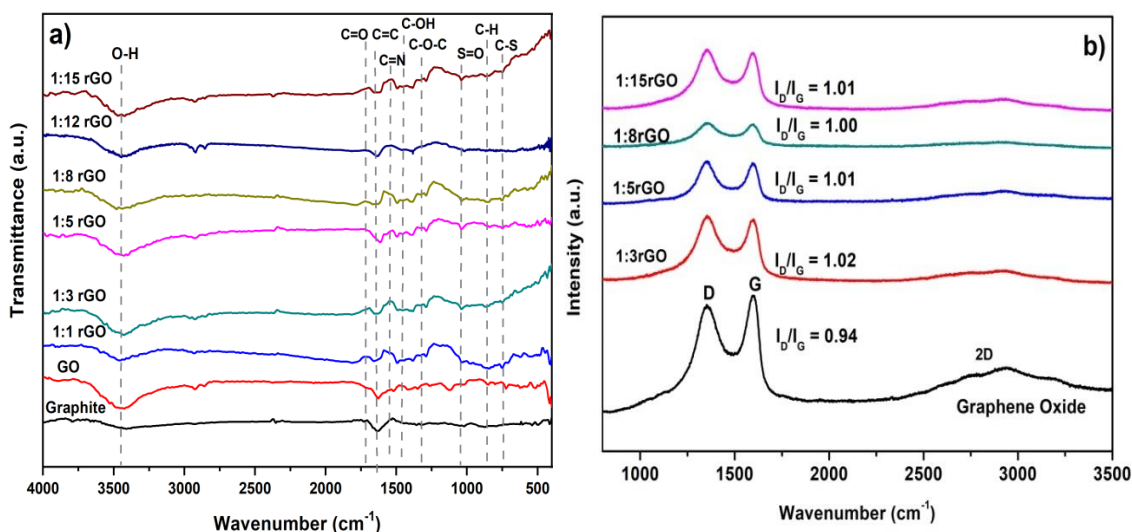


Figure 2.1: (a) FTIR spectra of Graphite, GO and 1:1XrGO samples (b) Raman spectra of GO and 1:1XrGO samples

Table 2.1: FTIR peak assignments and functional groups for Graphite, GO and 1:1XrGO

Frequency (cm ⁻¹)	Functionality	Graphite	GO	1:1XrGO
~ 3400	O-H stretching (Adsorbed water, free hydroxyl groups)	Absent	Broad, intense band	Reduced intensity
1720	C=O stretching (carbonyl, carboxylic acid)	Absent	Present	Absent
~1581	Skeletal C=C stretching	Present	Less intense (unoxidized)	Broad (partially restored graphene)

			graphitic domains)	domains)
1380	C-OH bending (hydroxyl groups, carboxylic acids)	Absent	Present	Weak
1327	C-O-C stretching (epoxy groups)	Absent	Present	Weak
1226	C-N stretching (aromatic amine)	Absent	Absent	Present
1041, 1180	S=O stretching (sulfoxide/ sulfone)	Absent	Absent	Present
825, 725	C-S stretching (thiophenic sulfur)	Absent	Absent	Present

The surface functionalities along with the degree of structural order/disorder were determined from FTIR and Raman spectroscopic method. The FTIR spectra in Fig. 2.1(a) indicates the formation of various functional groups on GO surface upon oxidation of graphite and the variation in the intensity of the bands upon its reduction, as observed for the RGO samples. The FTIR analysis, summarized in Table 2.1, confirms the successful oxidation of graphite to GO and subsequent reduction to RGO. The disappearance of oxygen-containing functional groups and the emergence of new peaks corresponding to C-N, C-S and S=O vibrations provide strong evidence for the simultaneous reduction and successful incorporation of N and S atoms into the graphene lattice.

The Raman spectra in Fig. 2.1(b) provides clear evidence of structural changes when GO is reduced to 1:3rGO. Both GO and 1:3rGO show a D band ($\sim 1357\text{ cm}^{-1}$), signifying structural defects, and a G band ($\sim 1598\text{ cm}^{-1}$) from sp^2 hybridized carbon networks. The I_D/I_G ratio, a key measure of graphitic disorder, increased from 0.94 in GO to 1.02 in the 1:3rGO sample. This confirms that the reduction process introduces defects, likely due to the incorporation of nitrogen and sulfur heteroatoms. The 1:8rGO sample showed the most favorable result with an I_D/I_G ratio of 1.00, demonstrating that this ratio of GO to thiourea is ideal for creating a balanced structure with optimal oxygen removal and minimal defects, however the intensity of D and G bands were lower than other rGO forms possibly due to highly fragmented structure resulting in graphitic domains of short range order with

exposed edge sites. Beyond this 1:8 ratio, the I_D/I_G value increased, indicating a highly defective structure caused by an excess of bulky sulfur atoms in the 1:12rGO and 1:15rGO samples. A 2D band ($\sim 2700\text{ cm}^{-1}$) which represents long-range ordered sp^2 graphitic structure, was also present in all samples, but reduced in intensity in 1:8rGO indicating highly disordered, amorphous-like carbon structure with increased surface area adding to electrical double layer capacitance with pseudocapacitance from defect sites. As the number of layers increases, the 2D band broadens. The reduced intensity of this band in rGO samples is attributed to the restacking of graphene sheets after oxygen groups are removed.

II. Structural Analysis by X-ray Diffraction

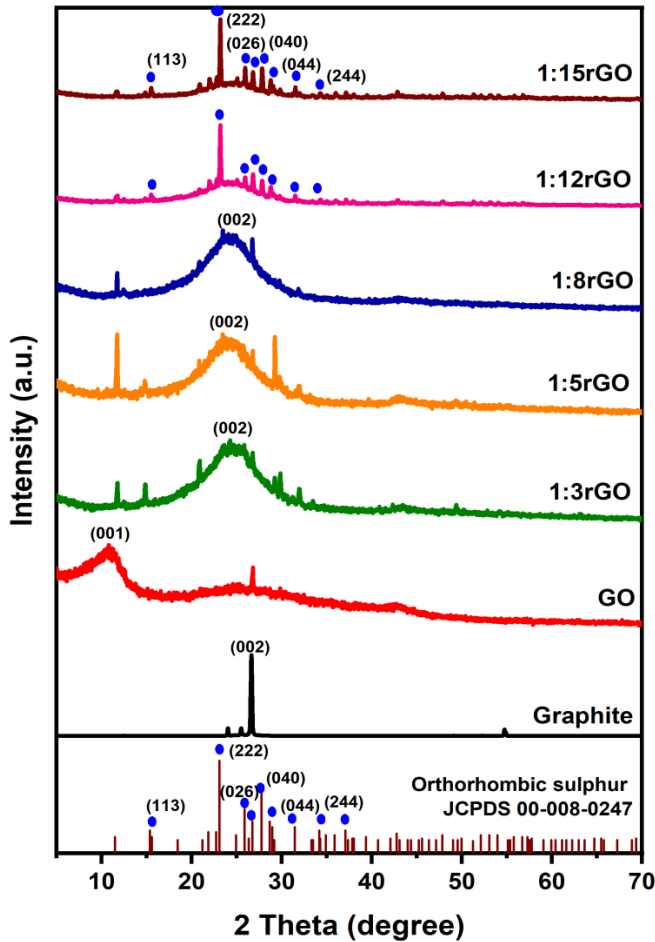


Table 2.2: Structural Parameters from XRD Spectra

Sample	2 Theta (degree)	Interplanar spacing, d (Å)
Graphite	26.65	3.340
GO	10.75	8.220
1:3rGO	24.66	3.606
1:5rGO	24.11	3.687
1:8rGO	24.09	3.690
1:12 rGO	23.19	3.831
1:15rGO	23.19	3.831

Figure 2.2: X-ray diffractograms of Graphite, GO and N,S-RGO samples

X-ray Diffraction (XRD) analysis, as illustrated in Figure 2.2, was utilized to characterize the structural evolution of the 1:XRGO samples. The intense (002) peak of graphite at 2θ

value of 26.65° underwent a dramatic shift to 10.75° in GO, corresponding to the (001) plane. This shift indicated a substantial increase in interplanar spacing from $3.34\text{\AA}$ to $8.22\text{\AA}$, (from the Bragg equation), which was directly attributed to the intercalation of oxygenated functionalities and the subsequent exfoliation of graphite layers. Concurrently, a decrease in crystallite size was observed as shown in Table 2.2. The reduction process led to the emergence of a broad (002) peak in the 2θ range of $22^\circ - 25^\circ$. This broadening and a reduced interplanar spacing were indicative of the effective removal of oxygen moieties and the restacking of graphene sheets. It also signified a lower degree of graphitization in the structure [18,19]. As the concentration of N and S heteroatoms increased, the interplanar spacing and crystallite size showed a progressive increase, while the intensity of the (002) peak diminished. The XRD patterns of 1:12rGO and 1:15rGO were distinguished by the presence of sharp, distinct peaks that were identified as orthorhombic sulfur crystallites, matching JCPDS card no. 00-008-0247. This evidence confirmed the formation of sulfur crystals on the RGO surface, a factor that likely introduced more defects and could have compromised electrical conductivity [7]. The sharp nature of these peaks also pointed to an increase in the overall crystallinity. Notably, the 1:8rGO sample exhibited lower degree of crystallinity and highly disordered nature.

III. Thermal analysis

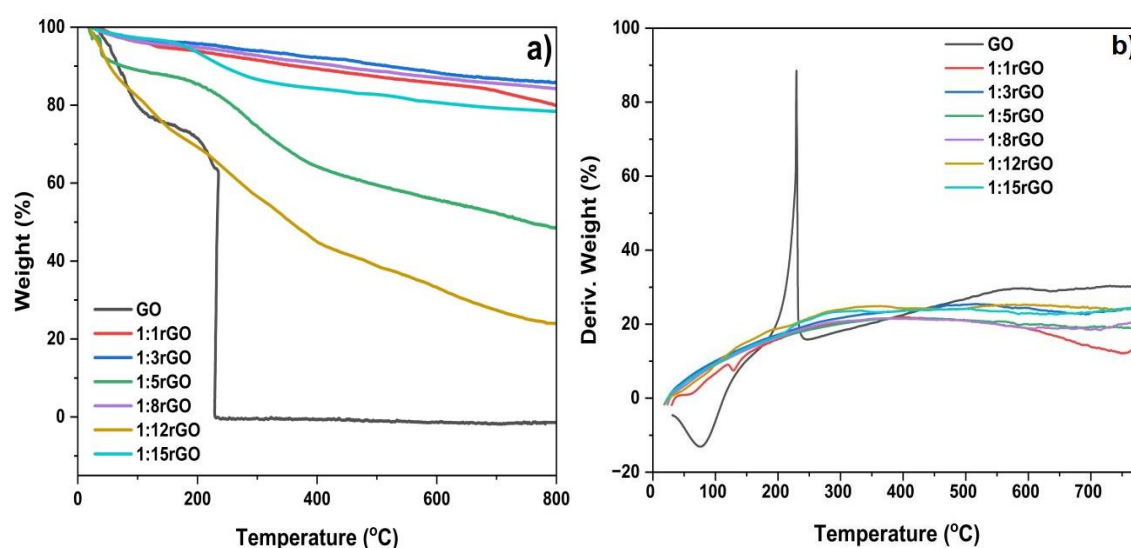


Figure 2.3: (a) Thermogram (b) Differential thermogram of GO and 1:XrGO samples

The thermal stability of the samples, as correlated by the TGA and DTA curves in Fig. 2.3 (a) and (b), respectively, reveals a clear distinction between GO and its reduced forms. The GO sample initially shows an endothermic peak on the DTA curve below 145°C, corresponding to a ~25% weight loss from the elimination of adsorbed water. This is followed by a dramatic ~75% weight loss at 235°C, marked by a sharp exothermic peak. This exothermic event signifies the decomposition of stable oxygen functional groups and the basal carbon structure itself, which leads to a complete weight loss [30]. The 1:XrGO samples, conversely, demonstrate significantly enhanced thermal stability. The absence of any major exothermic peaks confirms the improved stability of the carbon framework after reduction. While an initial weight loss of only 4% at 228°C is observed for the 1:XrGO samples at low thiourea concentration. As the concentration of thiourea increases, a subtle decrease in overall thermal stability is observed. This suggests that while reduction removes oxygen groups, the higher incorporation of N and S heteroatoms, particularly sulfur, introduces new defects and less stable sites into the graphene lattice, as evidenced by a higher total weight loss at higher temperatures. The samples with the highest thermal stability were 1:3rGO and 1:8rGO, which maintained a total weight loss of only 16% at 800°C.

IV. Surface morphology analysis

The SEM images illustrating the distinct surface morphologies of GO and the electronically superior 1:8rGO are represented in Fig. 2.4 (a) and (b), respectively. The GO displays a highly exfoliated and thin sheet-like structure with a pronounced wrinkled texture, a direct outcome of the oxidative process. In contrast, the morphology of 1:8rGO is characterized by a significant decrease in sheet transparency and the presence of restacked layers. This morphological change highlights the effect of the reduction process, where the removal of oxygen functionalities allows the graphene sheets to restack, altering the overall surface texture from exfoliated to a more layered structure.

Elemental analysis of the samples was performed using EDAX to determine the percentage of incorporated heteroatoms in the 1:XrGO structure. The elemental mapping of GO and 1:8rGO, shown in Fig. 2.4(c) and 2.4(d) respectively, highlights the spectral intensities and elemental percentages (see inset table). The high proportion of oxygen in GO, with a C/O ratio of 56.28%, confirms the successful oxidation of graphite. Upon

reduction, the C/O ratio significantly increased to 74.4% in the 1:8rGO sample, which directly correlates with its improved charge conduction properties. The EDAX spectrum also confirmed the presence of sulfur and nitrogen atoms in the reduced graphene oxide, indicating that the heteroatom doping was successful and also contributed to enhancing the electrical conductivity of the 1:8rGO sample with increased electron density.

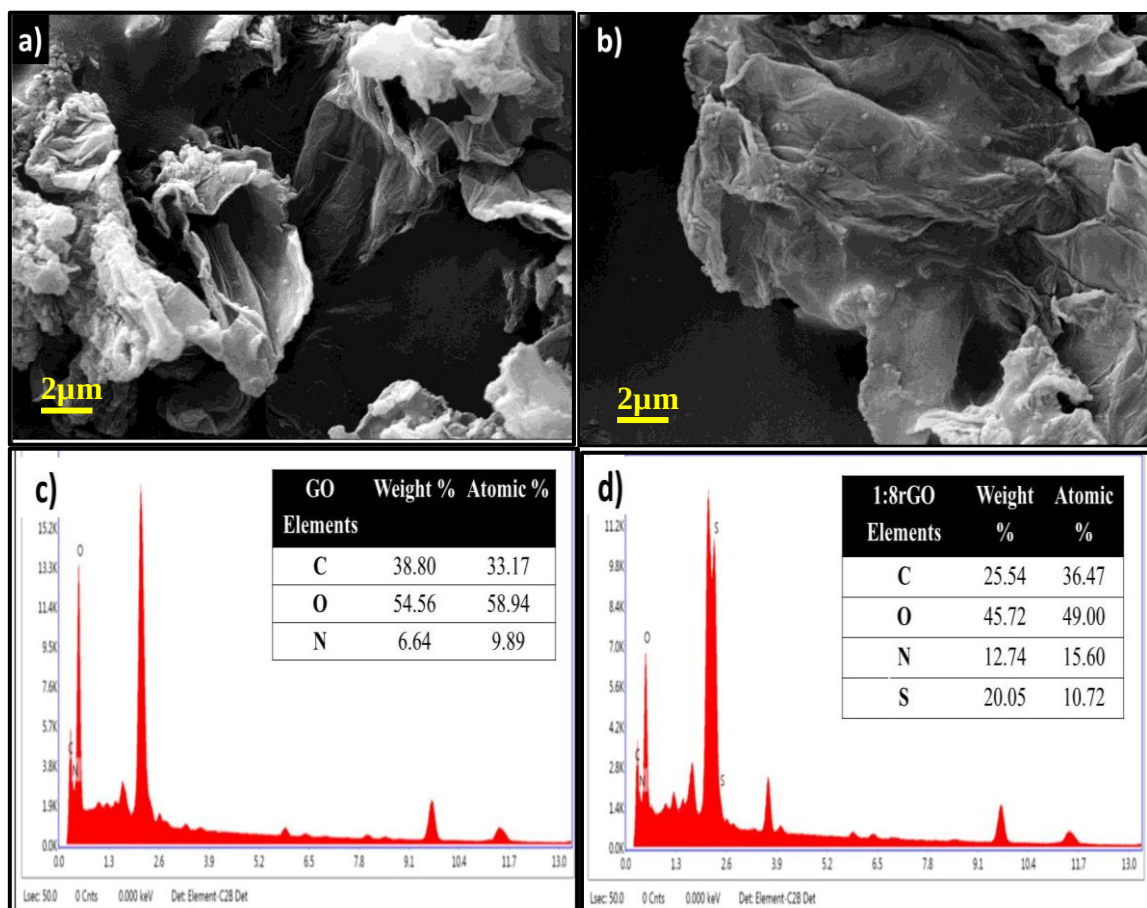


Figure 2.4: Scanning electron micrographs of (a) GO and (b) 1:8rGO, with corresponding EDAX spectra and inset elemental distribution tables for (c) GO and (d) 1:8rGO.

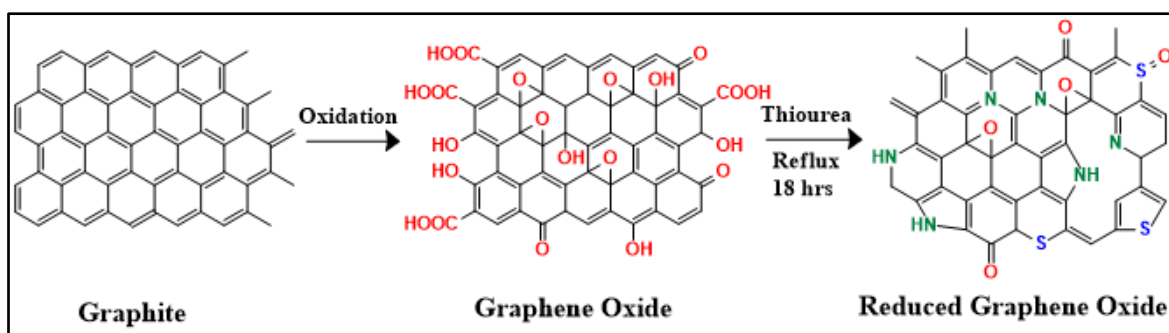
V. CHNS Analysis

Elemental analysis by CHNS analyser, was performed to investigate the chemical composition of GO and 1:8rGO samples. The analysis revealed that the weight percentage of carbon decreased upon oxidation of graphite and subsequently increased upon reduction, a finding consistent with EDAX results. The comparative distribution of weight percentages of C, H, N and S in the GO and 1:8rGO samples, prepared with varying proportions of thiourea, is presented in Table 2.3.

The elemental analysis further demonstrated that increasing the concentration of thiourea during the reduction process led to a progressive increase in the N/C and S/C ratios, supporting successful incorporation of N and S atoms in graphene framework. Nitrogen was substituted for carbon primarily in the form of pyridinic-N with some proportions of pyrrolic-N, quaternary-N, and oxidised N while sulfur occupied positions such as thiophenic-S, sulphides and majorly as oxidised sulfur upon reaction with oxygenated functionalities on edges of GO, as confirmed from XPS data presented in later sections. The schematic illustration in Scheme 2.1 provides a visual representation of this process.

Table 2.3: Elemental distribution in Graphite, GO and 1:XrGO from CHNS analysis

Sample	C (wt %)	H (wt%)	N (wt%)	S (wt %)	C/H ratio	N/C ratio	S/C ratio	S/N ratio
Graphite	90.38	0.671	1.209	0.449	134.694	0.134	0.005	0.037
GO	40.78	4.050	1.637	0.709	10.069	0.401	0.017	0.043
1:1rGO	51.22	3.021	14.88	2.582	16.955	0.291	0.050	0.174
1:3rGO	60.50	2.006	15.10	4.875	30.160	0.250	0.081	0.323
1:5rGO	50.88	1.487	15.14	16.309	34.217	0.298	0.321	1.077
1:8rGO	47.87	1.393	15.19	26.849	34.365	0.317	0.561	1.768
1:12rGO	43.81	1.129	15.27	31.563	38.804	0.349	0.720	2.067
1:15rGO	38.57	0.948	15.49	35.876	40.686	0.402	0.930	2.316



Scheme 2.1: Structural evolution from graphite to N,S-RGO

Doping RGO with nitrogen and sulfur introduces defects that enhance its electrochemical performance by modulating surface charge, enabling pseudocapacitive behavior, and improving wettability. An optimal 1:8 ratio of GO/thiourea yielded the best results, with N

and S concentrations of 15.190 wt% and 26.849 wt%, respectively, with N/C and S/C ratios of 0.317 and 0.561. Higher thiourea concentrations (e.g., 1:12) led to excess sulfur with the formation of their clusters and additional defects that ultimately harm the performance of N,S-RGO, underscoring the need for careful control over doping concentration.

2.3.2 Supercapacitive performance of 1:XrGO as a function of thiourea concentration

I. Cyclic voltammetric studies

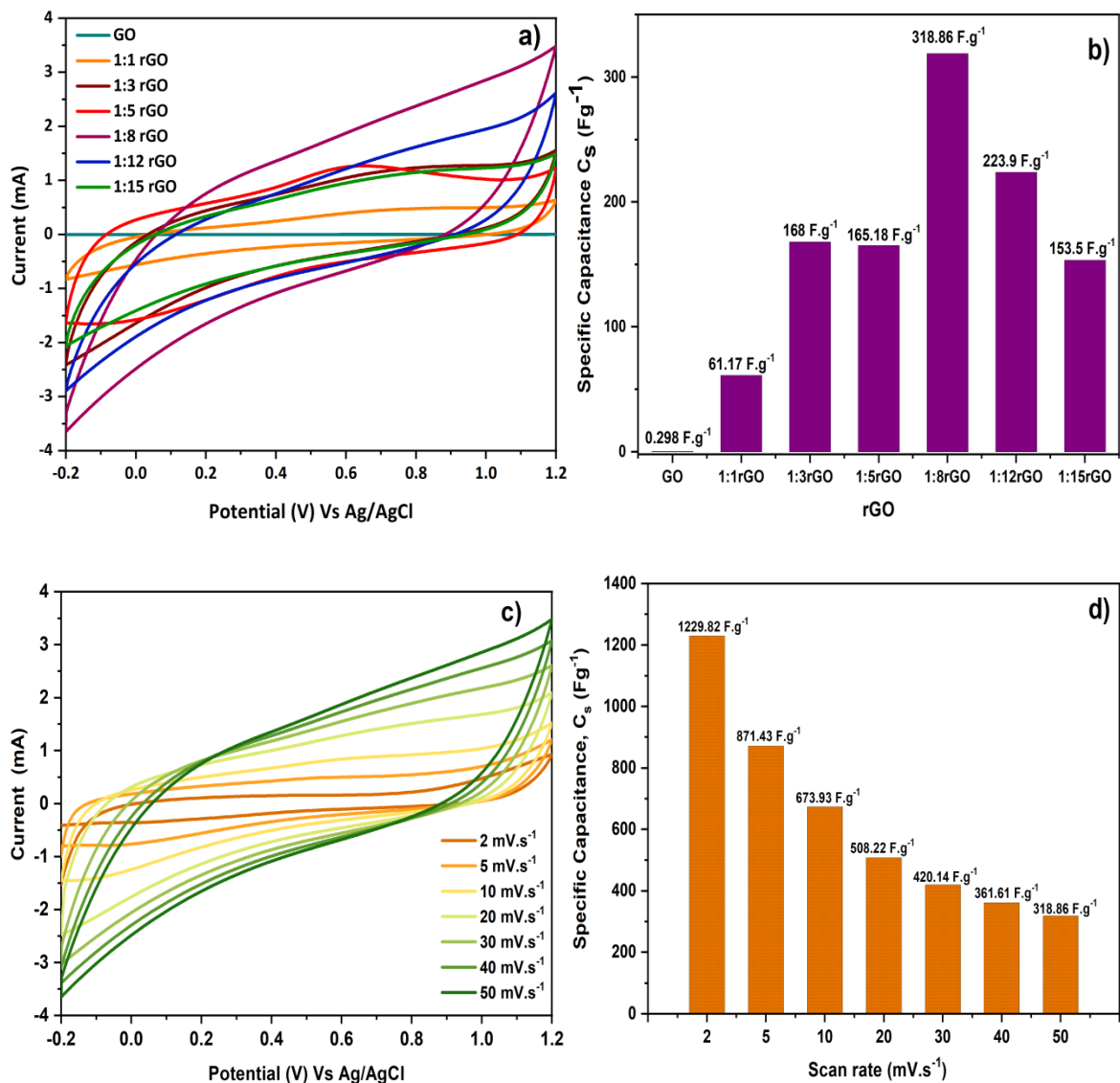


Figure 2.5: (a) CV plots of GO and 1:XrGOs in 2.5M H₂SO₄ recorded at 50 mV.s⁻¹ scan rate within a potential window of -0.2 to 1.2 V (b) Bar graph representing specific capacitance of GO and 1:XrGOs derived from CV (c) CV of 1:8rGO at varying scan rates (d) Bar graph representing specific capacitance of 1:8rGO at varying scan rates

(d) Bar graph representing specific capacitance of 1:8rGO derived from CV at various scan rates.

The supercapacitive performance of GO and various 1:XrGO forms were studied from the integral area of their cyclic voltammograms recorded in 2.5M H₂SO₄ electrolyte by scanning within a potential span of -0.2 to 1.2 V at 50 mV.s⁻¹ scan rates.

The specific capacitance (C_s) of the samples in F.g⁻¹ were calculated from the formula:

$$C_s = \frac{\int Idv}{\Delta V * m * v} \text{----- (1)}$$

Here, the integral ($\int Idv$) represents the area of the CV curve, which corresponds to the total charge stored. This value is then normalized by dividing it by the product of mass of active material on working electrode (m) in grams, potential scan rate (v) in V.s⁻¹, and working potential window (ΔV) in volts.

The cyclic voltammograms of GO and 1:XrGO and their respective specific capacitance represented in the form of bar graphs is shown in Fig. 2.5(a) and (b), respectively. The CV of all 1:XrGO samples in Fig. 2.5(a) show a roughly rectangular shape, which is a key characteristic of an Electric Double Layer Capacitor (EDLC). This indicates that charge is stored electrostatically at the interface between the electrode and electrolyte. Additionally, the presence of small redox peaks suggests a component of pseudocapacitance occurring due to fast, reversible Faradaic reactions involving the N and S heteroatoms incorporated into the RGO structure, which provides an extra mechanism for charge storage. The area enclosed by the CV curve, which is proportional to the specific capacitance, initially increases with the concentration of thiourea. This happens because thiourea helps remove oxygen-containing groups successfully from the graphene oxide and introduces N and S atoms. This process improves the electrical conductivity of RGO and increases its accessible surface area, leading to a better charge transfer and more active sites for charge storage. However, increasing the thiourea concentration beyond 8 times as observed in 1:12 and 1:15 rGO, the CV area tends to decrease. This is because too much thiourea leads to the formation and aggregation of sulfur clusters on the RGO surface, confirmed from XRD data, creating defects that hinder ion diffusion and charge transfer at the electrode-electrolyte interface. The bar graph in Fig. 2.5(b) confirms that the 1:8rGO sample has the highest specific capacitance reaching 318.86 F.g⁻¹, achieving a specific capacitance remarkably 1070 times greater than the specific capacitance of the original GO. This

finding demonstrates that a 1:8 ratio is the optimum ratio for reducing GO with thiourea to produce an RGO material with superior charge storage and conduction capabilities, owing to a synergistic balance of N and S heteroatoms.

Further analysis of the most active 1:8rGO electrode at different scan rates (from $2 \text{ mV}\cdot\text{s}^{-1}$ to $50 \text{ mV}\cdot\text{s}^{-1}$) in Fig. 2.5(c) reveals a proportionate decrease in both the area of its CV curves and its specific capacitance at higher scan rates. This behavior is primarily attributed to ohmic drop. Nevertheless, the consistent characteristics of the CV curves across all scan rates demonstrate a superior rate capability. The highest specific capacitance of $1229.82 \text{ F}\cdot\text{g}^{-1}$ was achieved at the lowest scan rate of $2 \text{ mV}\cdot\text{s}^{-1}$ (Fig. 2.5(d)) as ions have ample time to access the entire electrode surface, including its deeper pores, allowing for better charge penetration and more complete charge transfer at the heteroatom sites, maximizing the charge storage potential of the material at lower scan rates.

II. Galvanostatic Charge Discharge studies

The electrochemical performance of all GO and 1:XrGO samples was also evaluated using Galvanostatic Charge-Discharge profiles in a three-electrode system with a 2.5M H_2SO_4 electrolyte at $0.5 \text{ A}\cdot\text{g}^{-1}$ current density within 0 to 0.8V potential range. The specific capacitance of each electrode was calculated from the GCD curves using the relation:

$$C_s = \frac{I \times \Delta t}{\Delta V \cdot m} \text{ ----- (2)}$$

Here, I is the current (A), Δt is the discharge time (s), ΔV is the potential window (V) and m is the mass of the electroactive material (g). This formula enabled the quantitative analysis of charge storage capacity of the material.

The Fig. 2.6(a) displays GCD profiles, recorded at a current density of $0.5 \text{ A}\cdot\text{g}^{-1}$, confirming the supercapacitive performance of the GO and 1:XrGO samples. The symmetrical triangular shape of the curves is a clear indicator of EDLC behavior. The discharge time, which directly correlates with specific capacitance, increased with the thiourea concentration up to 1:8 ratio in the optimal 1:8rGO, which yielded the highest specific capacitance of $488.20 \text{ F}\cdot\text{g}^{-1}$, impressively 1205 times greater than that of GO similar to CV results as obvious from the bar graph in Fig. 2.6(b). This superior performance stems from the highly fragmented, amorphous carbon-like structure of the material in correlation with the Raman spectra. This disorder created a large number of

nanopores and accessible edge defects, which are ideal for both electrostatic charge storage as EDLC and fast, reversible faradaic reactions from the N and S heteroatoms, contributing to pseudocapacitance especially in acidic medium. In contrast, samples with an excessive thiourea proportion, in 1:12 and 1:15rGO, showed lower capacitance due to the formation of sulfur clusters on their surface, which physically blocked pores and hindered ion diffusion, thus impeding charge storage.

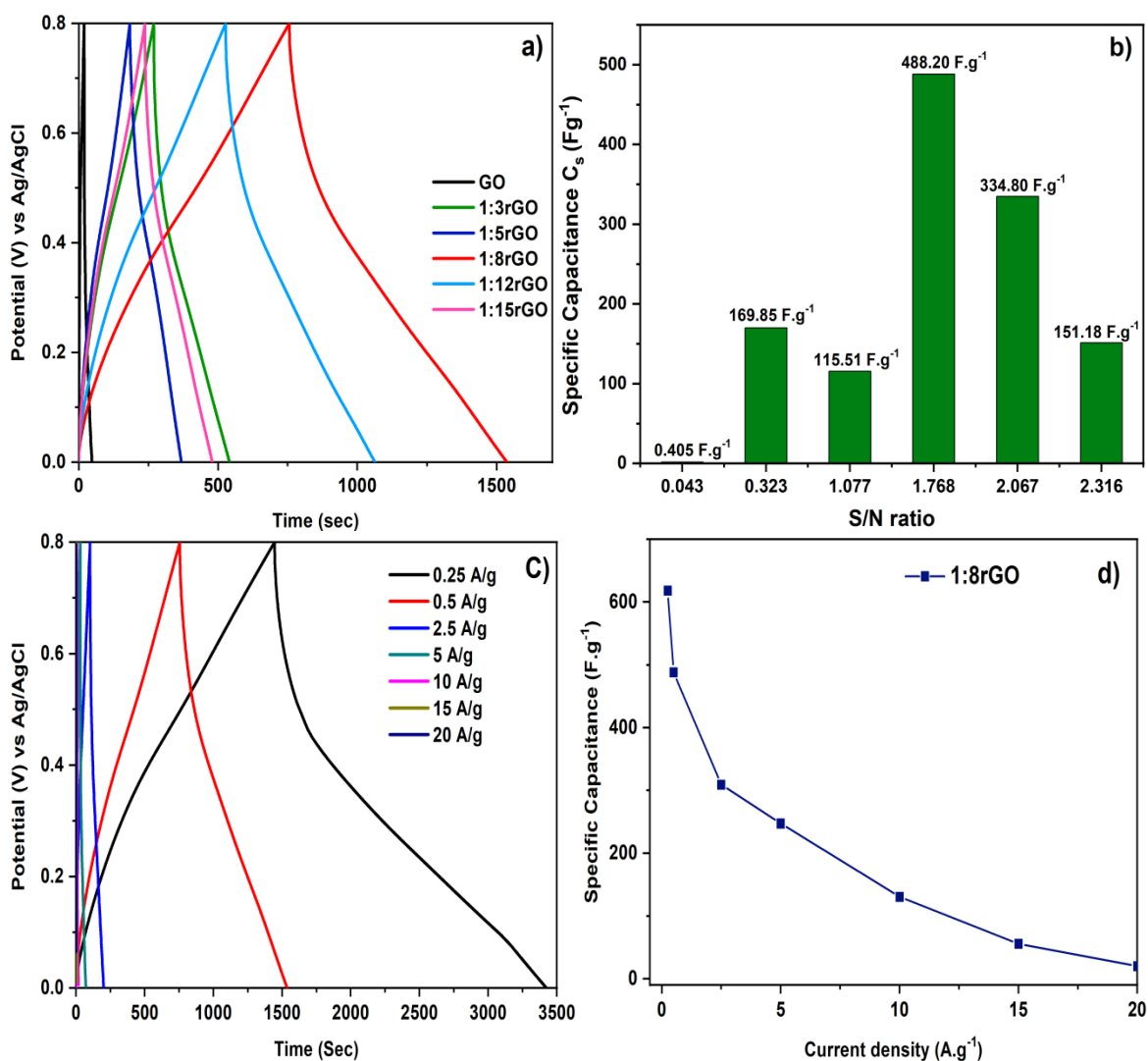


Figure 2.6: (a) GCD profile GO and 1:XrGOs in 2.5M H_2SO_4 at 0.5 $A \cdot g^{-1}$ within a potential window of 0 to 0.8 V (b) Bar graph representing specific capacitance of GO and 1:XrGOs derived from GCD (c) GCD profile of 1:8rGO at varying current densities (d) Specific Capacitance vs. current density plot of 1:8rGO.

Further analysis of the GCD profiles of 1:8rGO electrode at varying current densities in Fig. 2.6(c) revealed that its performance is highly rate-dependent. A higher specific

capacitance of $618.35 \text{ F}\cdot\text{g}^{-1}$ was achieved at the lowest current density of $0.25 \text{ A}\cdot\text{g}^{-1}$ as shown in Fig. 2.6(d), which subsequently reduced at higher current densities. This behavior is a result of the slower scan rate providing more time for ions to fully penetrate the bulk structure of electrode and access all available active sites, maximizing the charge transfer process and the utilization of the entire surface area. The synergistic effect of N and S co-doping further enhances performance by creating a favorable electronic structure. Nitrogen, being more electronegative than carbon, creates electron-deficient sites, while sulfur compensates, facilitating efficient charge transfer. This co-doping redistributes asymmetric spin and charge density and generates defects that function as active sites, improving both electrical conductivity and the overall interaction with the electrolyte due to modified surface chemistry, which is crucial for maximizing supercapacitive performance at low current densities.

III. Cyclic stability analysis

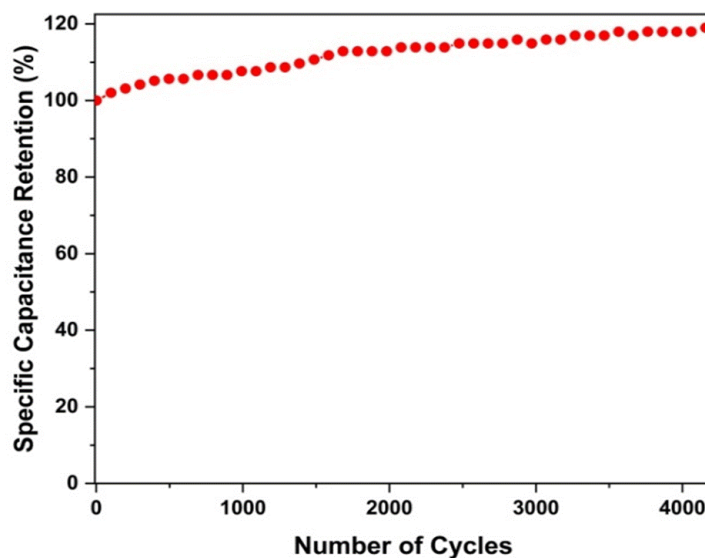


Figure 2.7: Cyclic stability performance of 1:8rGO in 2.5M H₂SO₄ electrolyte

The long-term stability of the 1:8rGO electrode was assessed through a cycle life test, where it was subjected to 4300 cycles at a current density of $1\text{A}\cdot\text{g}^{-1}$ represented in Fig. 2.7. The specific capacitance was measured after every 100th cycle. The results demonstrated a remarkable increase in specific capacitance retention, reaching 119% after the full cycling duration. This outcome surpasses the performance of most similar 1:XrGO materials reported in the literature, signifying that the 1:8rGO electrode possesses exceptional cyclic stability and long-lasting reliability, making it a highly promising candidate for energy storage applications.

IV. Electrochemical Impedance Spectra

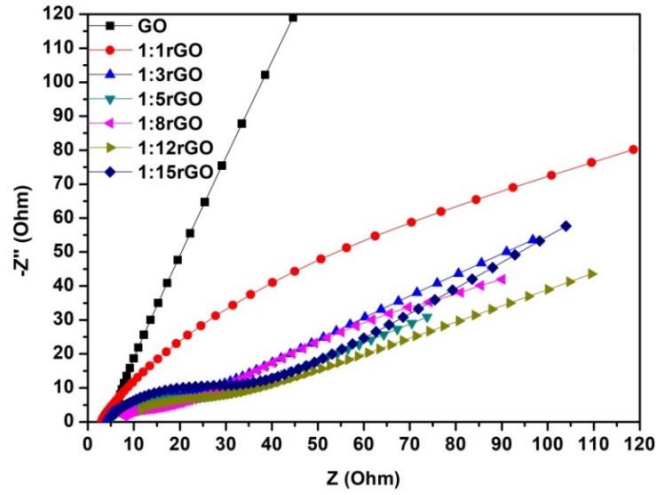


Figure 2.8: Nyquist plots of GO and 1:XrGOs

Electrochemical Impedance Spectroscopy (EIS) was performed to analyze electron transport and ion diffusion at the electrode-electrolyte interface. The resulting Nyquist plots, shown in Fig. 2.8, provide key insights into the materials internal resistance and charge transfer kinetics. In the high-frequency region, the Equivalent Series Resistance (ESR) is represented by the x-intercept of the semicircle. For the RGO samples, the ESR decreased as the thiourea concentration increased, which is attributed to the enhanced conductivity from the incorporated heteroatoms. The diameter of the semicircle in the mid-frequency region corresponds to the charge transfer resistance (R_{ct}) at the electrode-electrolyte interface. The poorly reduced GO samples showed a large R_{ct} , which decreased significantly as the proportion of thiourea increased, reaching a minimum of 5.498Ω for the optimal 1:8rGO sample. However, excessive thiourea led to the accumulation of heteroatom clusters, which compromised the charge transfer process and resulted in a higher R_{ct} . Finally, the vertical line in the low-frequency region indicates a fast ion transport with an ideal capacitive behavior. The shortest diffusion length observed for the 1:8rGO sample confirms a low resistance to charge storage.

This section is based on the published work: Naik AK, Samant P V. Thiourea modulated supercapacitive behavior of reduced graphene Diam Relat Mater. 2024;145(February):111122. Reprinted with permission [20] Copyright 2024, Elsevier".

II. Critical role of sulfur co-dopant in enhanced supercapacitance of RGO

This section of this chapter investigates the specific influence of the sulfur atom on the electrochemical performance of RGO in supercapacitors. To achieve this, a nitrogen-doped RGO (URGO) was synthesized using urea as a reducing agent at the same optimized proportion as thiourea from the previous study. Urea was chosen for its structural similarity to thiourea but with the deliberate absence of sulphur. By comparing the structural and electrochemical properties of the URGO (N-RGO) with TURGO (N,S-RGO), this study isolates the effect of the additional sulfur atom on the charge storage capacity and stability of RGO, thereby providing valuable insights into the synergistic role of co-doping.

2.3.3 Comparative characterisation of N,S-RGO with N-RGO

I. FTIR and Raman Spectra

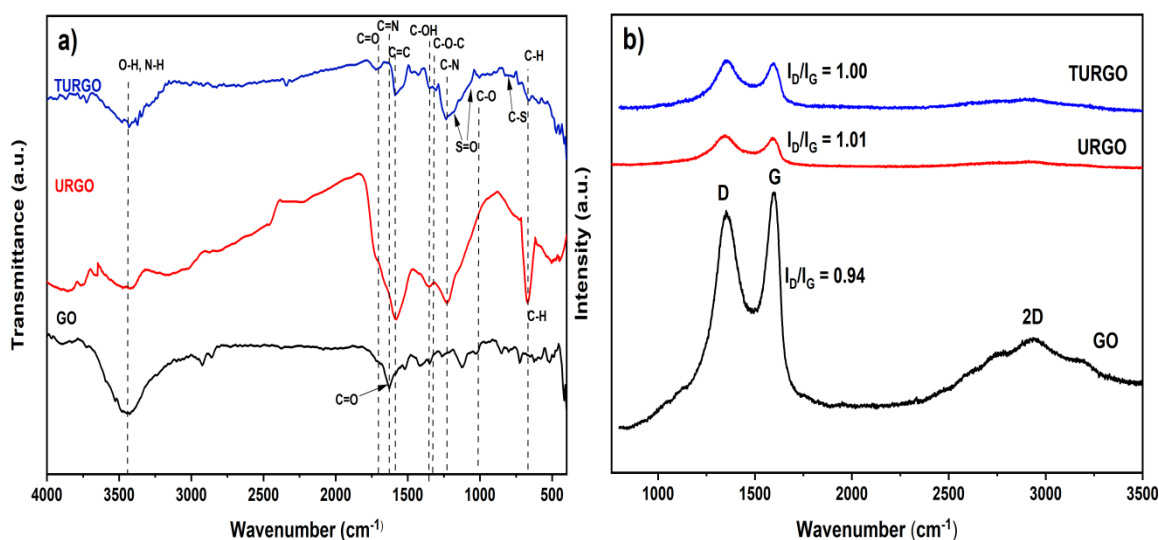


Figure 2.9: (a) FTIR spectra (b) Raman spectra of GO, URGO and TURGO

The comparative FTIR spectra of GO, URGO and TURGO is represented in Fig. 2.9(a). A comparison of these spectra with the pristine GO spectrum reveals reduction in the intensity of several bands, which confirms the reduction of GO. Specifically, the broad O–H stretching band at ~3400 cm⁻¹, the C=O stretching band at ~1720 cm⁻¹, and the C–O stretching bands of epoxy and alkoxy groups at 1300 cm⁻¹ and 1010 cm⁻¹, showed a notable decrease in intensity in both URGO and TURGO. The change in the shape of the broad O–H stretching band upon reduction, also suggests the presence of N–H stretching vibrations in URGO and TURGO, which is consistent with nitrogen doping. The URGO

spectrum displays a prominent band at 1581 cm^{-1} . This band is attributed to the restoration of the C=C stretching vibrations of the graphene lattice along with the newly formed C=N stretching bonds. Furthermore, a broad shoulder corresponding to C–N stretching vibrations with a peak at 1226 cm^{-1} further supports the incorporation of nitrogen. A sharp band at 675 cm^{-1} , is associated with C–H out-of-plane bending vibrations in reduced forms. In contrast, the TURGO spectrum represents the most highly reduced material. It exhibits minimal absorption, indicating a nearly complete removal of oxygen-containing groups. The presence of both N and S heteroatoms in TURGO has been previously confirmed in previous section, supporting successful reduction and doping process.

The Raman spectra of these materials in Fig. 2.9(b) show that the type of dopant significantly impact the structural integrity of the graphene lattice. The GO spectrum has an I_D/I_G ratio of 0.94, which is typical for a highly defective structure. The ratio increased to 1.01 upon N doping in URGO, which indicates formation of more disordered structure on sole N doping while partially restoring graphene structure. In contrast, doping S with N resulted in I_D/I_G ratio of 1.00 for TURGO as incorporation of S facilitated a more controlled doping process with balanced in plane defects and better restored sp^2 carbon network.

II. Structural Analysis by X-ray Diffraction

Building upon the XRD data of Graphite and GO discussed in the previous section, the comparative analysis of URGO and TURGO in Fig. 2.10, provides critical insights into the distinct effects of single versus co-doping on the RGO structure with simultaneous GO reduction. Both URGO and TURGO show a broad (002) peak, a clear sign that the graphitic structure has been largely restored from GO upon reduction. However, their patterns reveal key differences. The URGO peak is located at $2\theta = 24.86^\circ$, while the TURGO peak is slightly shifted to a lower angle, at $2\theta = 24.25^\circ$. This shift suggests that the co-doping with sulfur, being a larger atom than nitrogen, introduces more significant steric hindrance between the graphene sheets. This results in a greater interlayer spacing for TURGO ($3.67\text{ \AA}$) compared to URGO ($3.57\text{ \AA}$). Furthermore, the (002) peak of TURGO is notably less intense and broader, indicating a higher degree of out-of-plane stacking disorder and a smaller crystallite size of 10.17 nm , while URGO exhibited 16.86 nm crystallite size. This crucial finding, in conjunction with the Raman spectroscopy data showing a lower I_D/I_G ratio for TURGO, highlighted a fascinating trade-off. While N,S co-

doping is more effective at healing in-plane defects, it simultaneously creates a more disordered and less crystalline stacking arrangement. This comparative analysis demonstrates how tailored doping strategies can be used to precisely control different structural aspects of reduced graphene oxide.

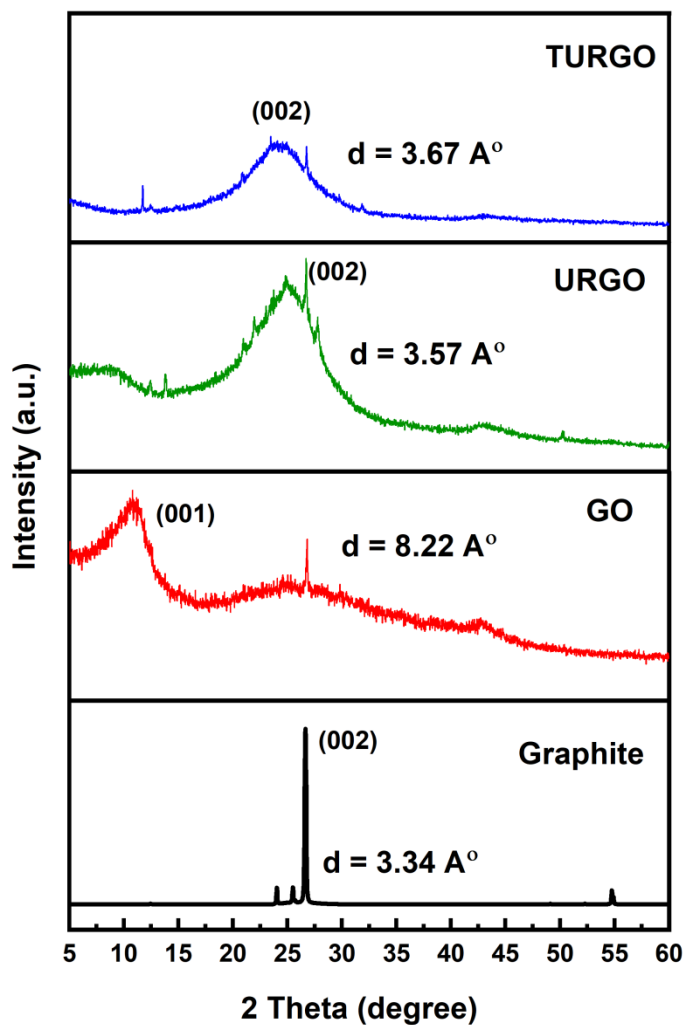


Figure 2.10: X-ray diffractograms of Graphite, GO, URGO and TURGO

III. Thermal Analysis

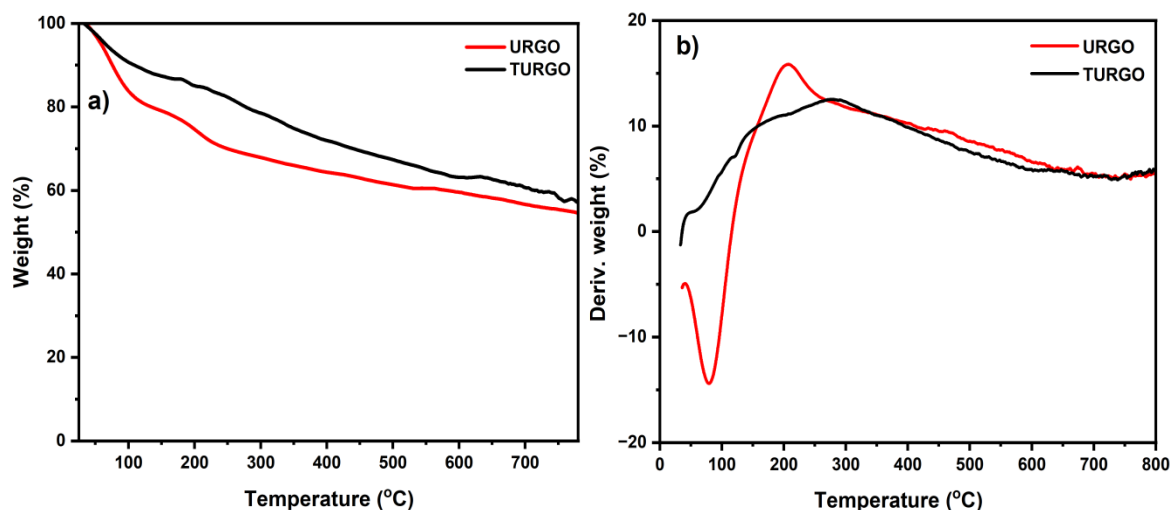


Figure 2.11: (a) Thermogram (b) Differential thermogram of URGO and TURGO

The thermal analysis results show a clear distinction in the stability of URGO and TURGO in Fig. 2.11(a) and (b). Initially, URGO and TURGO showed 18.81% and 10.76% loss of physisorbed water molecules represented by sharp endotherm in URGO at 120°C. A further weight loss of 10.29% is observed upto 230°C for URGO due to the rapid thermal decomposition and oxidation of a large number of residual oxygen-containing functional groups (such as hydroxyl, epoxy and carboxyl groups) with a small exothermic peak, in DTA plot. In the final higher temperature stage from 450 to 780°C, URGO loses an additional 17.38%. In contrast, TURGO shows a gradual weight loss of 32.13% upto 780°C. This weight loss is primarily due to the decomposition of more persistent and thermally stable functional groups and pyrolytic decomposition of framework carbon. The DTA results for both show minor endothermic changes, corresponding to the gradual degradation of these structures at higher temperatures.

Overall, the total weight loss of 46.23% for URGO versus 43.2% for TURGO demonstrates that URGO remains highly reactive and unstable apparent from more significant endo and exothermic events, whereas the N,S co-doping process for TURGO results in a more thoroughly reduced and thermally robust material.

IV. X-ray Photoelectron Spectral Analysis

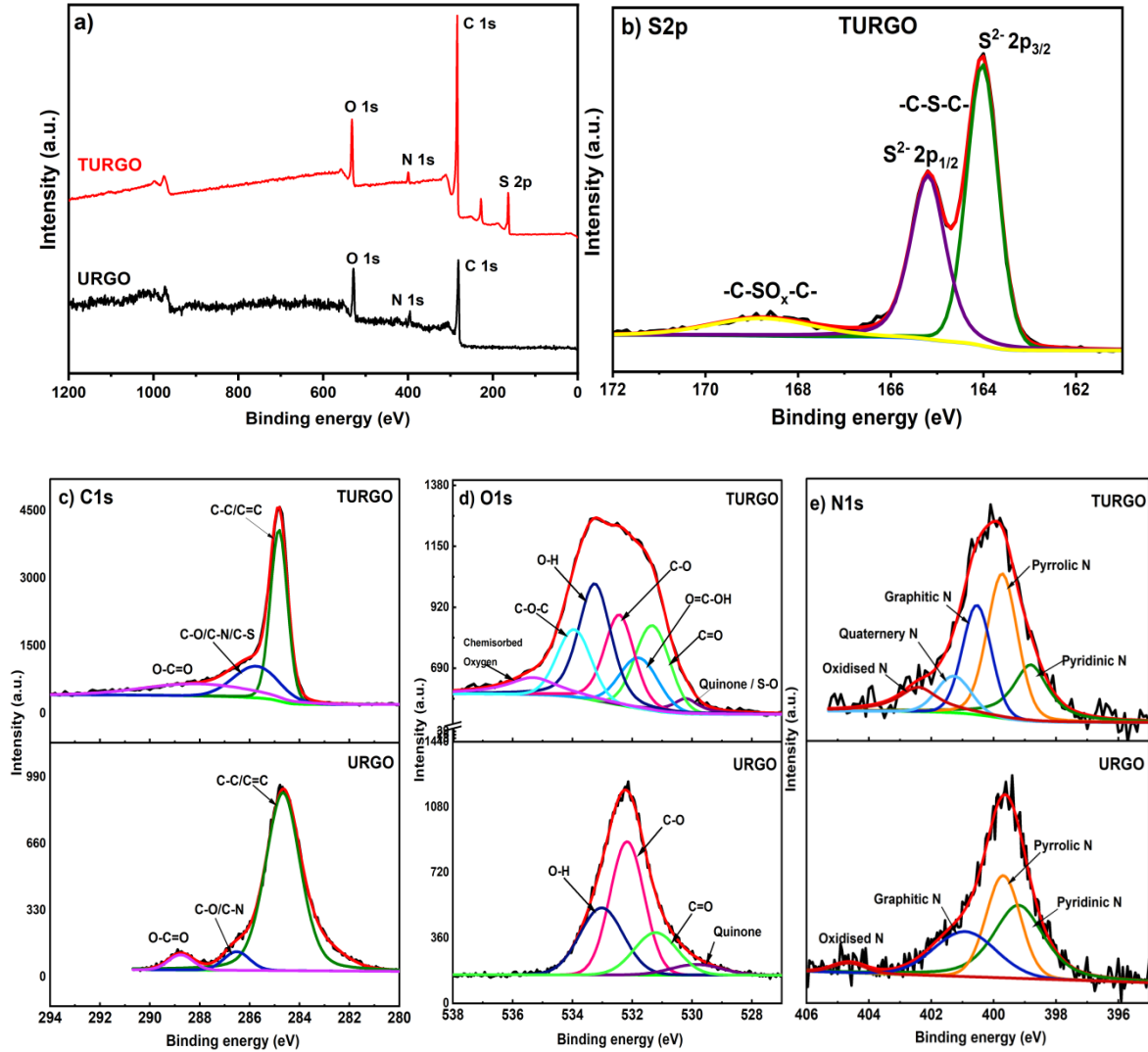


Figure 2.12: (a) XPS survey scan of URGO and TURGO (b) S2p core scan in TURGO (c) C1s (d) O1s (e) N1s core scan in URGO and TURGO

The XPS survey spectra in Fig. 2.12(a) and the relative elemental distribution in Table 2.4 compares the surface elemental composition of URGO and TURGO. The TURGO sample exhibits a high C/O atomic ratio, as evidenced by a dominant C1s peak and a weak O1s peak, which is characteristic of a highly reduced material. The URGO sample, however, shows a significantly lower C/O ratio indicating poor reduction. The presence of a distinct sulfur (S2p) photoemission peak in the TURGO spectrum, and minor nitrogen (N1s) in both samples confirms successful incorporation and modification of structure with heteroatoms along with a significant difference in their degree of oxidation and elemental

functionalization. The respective chemical states of each elements could be well established from core scans of each element.

The core level S2p spectra in Fig. 2.12(b) could be fitted into 3 peaks, among which the doublet corresponding to $2p_{3/2}$ and $2p_{1/2}$, originated from thiophenic-S in the framework at 164 and 165.2 eV, respectively and another small peak of oxidised-S species arising at 168.7 eV.

The Fig. 2.12(c) represents a high resolution XPS core level spectra of C1s in TURGO and URGO. De-convolution of the C1s spectra for both samples revealed three distinct bonding environments. For TURGO, the main peak at 284.8 eV corresponds to sp^2 hybridized graphitic carbon (C=C) and sp^3 hybridized carbon (C-C). The peaks at 285.8 eV and 288.2 eV are attributed to carbon bonded to oxygen or other heteroatoms (C-O, C-N, C-S) and carbonyl carbon (O-C=O), respectively. While URGO exhibited similar peaks, their lower intensities indicated a more reduced state in TURGO. Quantitative analysis from peak area showed that TURGO possessed 37.02% graphitic carbon and 31.71% of carbon bonded to heteroatoms, confirming successful incorporation of heteroatoms into the carbon framework in Table 2.5. Conversely, URGO's C1s spectrum was dominated by the C=C and C-C bonding (68.81%), suggesting a more intact carbon structure with only 16.10% heteroatom bonding.

The de-convolution of core scan spectra of O1s in Fig. 2.12(d) compares the surface chemistry of TURGO and URGO revealing multiple oxygen functionalities, including quinone, C=O, O=C-OH, C-O, O-H, C-O-C and adsorbed oxygen at 530.2, 531.3, 531.8, 532.4, 533.3, 534, and 535.3 eV in TURGO, while with higher intensities at 529.6, 531.2, 532.2, 533.1 eV in URGO representing quinone, C=O, C-O and O-H functionalities. This showed a significant reduction in oxygen content with residual oxygenated functionalities primarily in the form of O-H groups in TURGO, while C-O in URGO. Their relative distribution is presented in Table 2.5.

The N1s XPS spectra in Fig. 2.12(e) elucidates the distinct nitrogen doping profiles of TURGO and URGO. The complex de-convolution for TURGO, synthesized using thiourea, reveals multiple nitrogen configurations including Graphitic-N (400.5 eV), quaternary N (401.3 eV) into the basal framework, while pyrrolic-N (399.7 eV), pyridinic N (398.8 eV), at the edges and defect sites alongwith N-oxides of pyridinic-N (402.4 eV). Notably, thiourea yielded a predominant 38.31% Graphitic-N, which is known to enhance

n-type conductivity through π electron transfer to graphene structure. While in pyridinic N and pyrrolic-N, electron withdrawal effect created by electronegative nitrogen created localized areas of positive charge density on the carbon atoms neighbouring the nitrogen, inducing p-type conductivity. In contrast, the N1s spectrum for URGO, synthesised from urea, showed a reduced percentage of conductive Graphitic-N (400.95 eV) and is dominated by pyridinic-N (399.2 eV) at 37.85%, with lower contributions from pyrrolic-N (399.7 eV), and feeble oxidized nitrogen species (404.65 eV). This difference demonstrates that the choice of reducing agent critically influences the resulting nitrogen configurations, thereby affecting the overall conductivity and electronic properties of the material.

The CHNS elemental analysis in Table 2.4 offered direct quantitative evidence of the chemical transformations from GO to its successive reduced forms. The GO sample served as the baseline, with its moderate carbon and significant hydrogen content indicating the presence of oxygen- and hydrogen-rich functional groups upon oxidation. The reduction process is evidenced by the notable increase in carbon content from GO (40.78%) to URGO (57.91%) and TURGO (47.87%) with a corresponding decrease in hydrogen content, confirming the removal of these groups. The dramatic rise in the C/H ratio from GO (10.069) to URGO (22.137) and TURGO (34.365) signifies the successful de-oxygenation and restoration of a more graphitic, aromatic carbon framework in TURGO. Furthermore, the Table 2.4 confirms successful heteroatom doping from a significant increase in nitrogen (15.35 wt%) in URGO, validating its synthesis using urea as a nitrogen source. In contrast, TURGO exhibited very high Sulfur (26.849 wt%) and similar nitrogen content as URGO, along with a high S/N ratio (1.768), confirming that thiourea successfully incorporated both elements into the graphene structure, with sulfur being the predominant dopant resulting in reduced C content due to framework substitutional doping, validating the successful functionalization and reduction of graphene oxide.

Table 2.4: Elemental distribution in TURGO and URGO from CHNS and XPS analysis

Sample	C(wt %)		H(wt %)	N(wt %)		S(wt %)		O(wt %)	C/O	C/H	N/C	S/C	S/N
	CHNS	XPS	CHNS	CHNS	XPS	CHNS	XPS	XPS	ratio	ratio	ratio	ratio	ratio
GO	40.78		4.050	1.637		0.709				10.069	0.040	0.017	0.433
URGO	57.91	68.19	2.616	15.35	3.9			27.91	2.44	22.137	0.265		
TURGO	47.87	73.5	1.393	15.19	2.8	26.849	11.6	12.2	6.02	34.365	0.317	0.561	1.768

Table 2.5: Relative percentages of elements and their chemical states derived from XPS plots

Sample	C=C/C-C	C-O/C-N/C-S	O-C=O	Carboxyl O	Carbonyl O	Ether/Epoxy O	Hydroxyl O
TURGO	37.02%	31.71%	31.27%	12.24%	21.63%	33.06%	21.90%
URGO	68.81%	16.10%	15.09%	--	23.91%	46.28%	29.81%

	-C-S-C-	-C-(SO _x)-C-	Pyridinic N	Pyrolic N	Graphitic / Quaternary N	Oxidised N
TURGO	82.92%	17.08%	16.74%	34.05%	38.31%	10.91%
URGO	--	--	37.85%	33.30%	25.92%	2.92%

2.3.4 Comparative charge storage performance of N,S-RGO and N-RGO

The critical role of sulfur dopant on charge storage property of RGO was evaluated from comparative analysis of electrochemical performance of URGO and TURGO. The cyclic voltammograms were recorded in 2.5M H_2SO_4 electrolyte scanned within a potential span of -0.2 to 1.2 V at 50 $\text{mV}\cdot\text{s}^{-1}$ scan rates. Galvanostatic Charge-Discharge profiles were obtained at 0.5 $\text{A}\cdot\text{g}^{-1}$ current density within 0 to 0.8V potential range in 2.5M H_2SO_4 electrolyte.

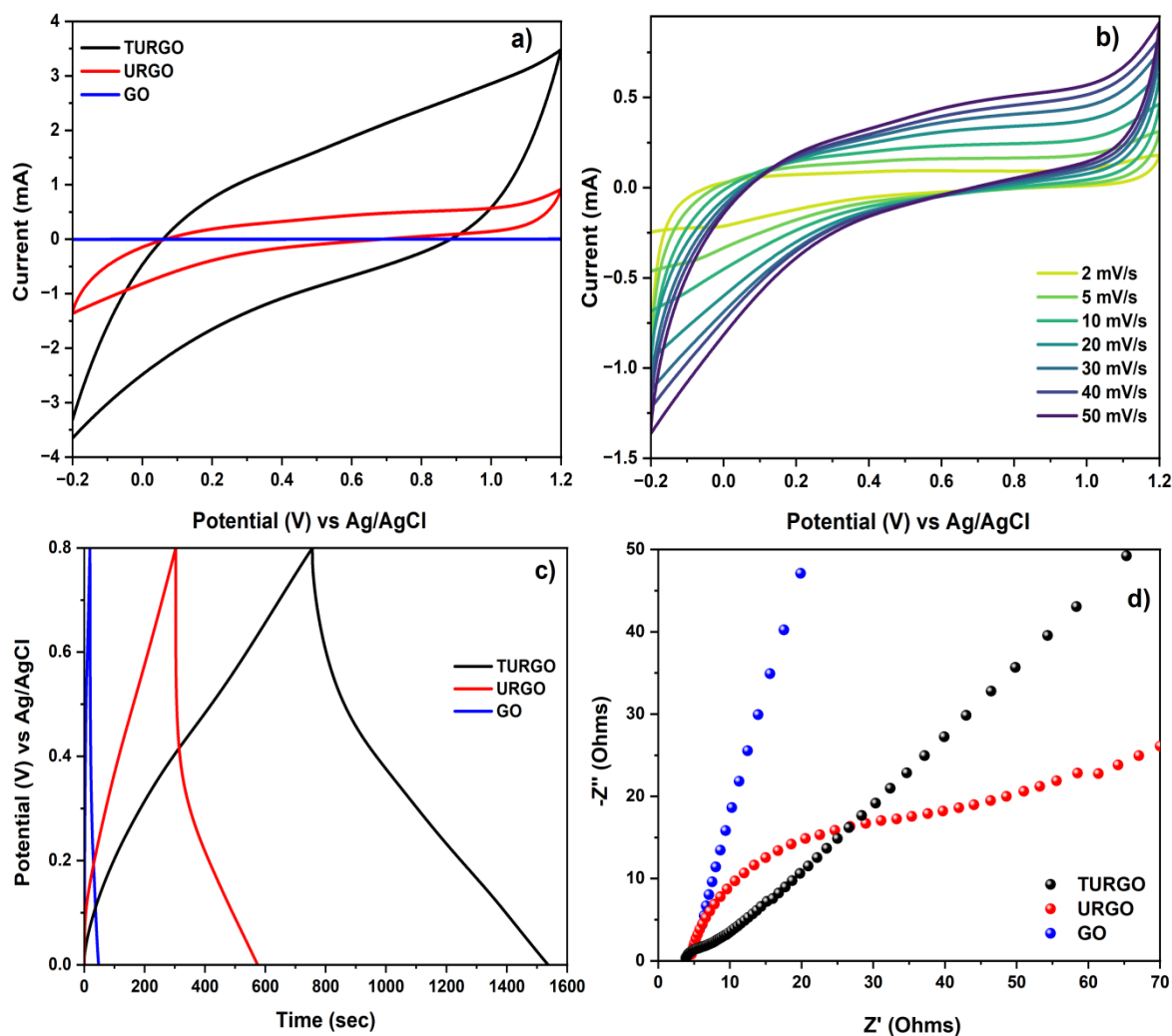
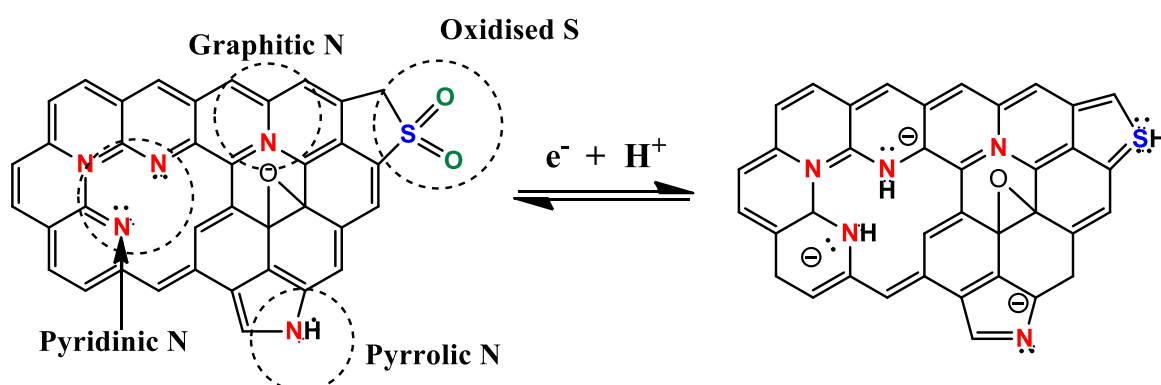


Figure 2.13: (a) CV of GO, URGO and TURGO in 2.5M H_2SO_4 at 50 $\text{mV}\cdot\text{s}^{-1}$ scan rate spanning a potential window of -0.2 to 1.2 V (b) CV of URGO at varying scan rates (c) GCD profile GO, URGO and TURGO in 2.5M H_2SO_4 at 0.5 $\text{A}\cdot\text{g}^{-1}$ between a potential window of 0 to 0.8 V (d) Nyquist plots of GO, URGO and TURGO

The CV curves for all three samples in Fig. 2.13(a) exhibited a quasi-rectangular shape, which is a characteristic of electrical double-layer capacitance and partial Faradaic pseudocapacitance. The area enclosed by each curve is directly proportional to the charge storage capacity of the material. The CV of TURGO showed the largest enclosed area and highest current response, indicating 6.24 times superior charge storage capacity than URGO due to a combination of EDLC and pseudocapacitance from Faradaic reactions at N and S sites, making it the most promising candidate for supercapacitor applications. In contrast, the URGO CV had a much smaller area, reflecting a lower capacitance of 78.23 F.g⁻¹ due to lesser percentage of heteroatoms and unfavourable configurations of N in graphene lattice. Moreover, the quasi-rectangular shape indicated pseudocapacitance arising from lower degree of reduction in URGO. The GO being an electrical insulator, shows a negligible enclosed CV area and a specific capacitance as low as 2.63 F.g⁻¹, with poor electrochemical activity due to high concentration of oxygen-containing functional groups and a disrupted π -electron system severely limiting its conductivity. For the cyclic voltammograms, TURGO and URGO showed different responses to increasing scan rates. As discussed in previous section, the CV profiles of TURGO maintained a robust, quasi-rectangular shape and showed a proportionally high current increase, indicating superior kinetic stability and excellent rate capability for high-power applications. In contrast, URGO exhibited a much lower current response, and its curves become more distorted at high scan rates as shown in Fig. 2.13(b) suggesting slower ion diffusion and less efficient kinetics.

The said data is further confirmed from GCD profiles in Fig. 2.13(c), wherein, highly symmetrical charge-discharge curves, and longer discharge times are obtained with TURGO indicating excellent capacitance of 488.20 F.g⁻¹ at 0.5 A.g⁻¹, with electrochemical reversibility and low internal resistance. In contrast, URGO had a significantly shorter discharge, reflecting its lower capacitance of 169.81 F.g⁻¹ while GO showed a negligible discharge time, confirming its poor conductivity and inability to store charge. The electrochemical performance difference between TURGO and URGO is due to their distinct heteroatom doping. TURGO is co-doped with both nitrogen (N) and sulfur (S), with varying configurations such as graphitic, pyrrolic and pyridinic form while sulfur as thiophenic and oxidized species. This combination provides a synergistic effect, wherein Graphitic-N preserves the conductive carbon framework and improves conductivity through sp² hybridisation, favouring efficient electron flow and enhances rate capability

while pyridinic N and pyrrolic-N enhances pseudocapacitance through reversible redox reactions with protons and increased wettability. However, excess pyridinic-N form has been reported to create more defects in the structure, hampering its conductivity over pyrrolic form [5]. The balanced contribution of all N configurations has been reported to be very beneficial in enhancing overall capacitance of the material [21]. The bulky sulfur doping has also been reported to enhance RGO conductivity effectively than N doping due to its higher electron donating ability [22]. Doping sulfur in the form of thiophenic-S increased electron concentration subsequently boosting conductivity and number of active sites in RGO by polarising its surface. Besides the oxidised form of S induced reversible redox reactions with electrolyte ions as represented in Scheme 2.2, thus contributing towards pseudocapacitance, leading to a superior specific capacitance and rate capability in TURGO.



Scheme 2.2: Reversible redox reactions at N and S functionalities on RGO surface in acidic electrolyte

In contrast, URGO is only nitrogen-doped, with the dominant form being pyridinic, followed by pyrrolic and graphitic. However, the lower proportion of highly conducting Graphitic-N and active pyrrolic sites in the absence of sulfur, limit its overall charge storage efficiency and kinetic performance, justifying its lower electrochemical metrics than TURGO. Thus, the CV and GCD plots effectively rank the materials performance, demonstrating that the synthesis of TURGO yields a material with an ideal balance of heteroatoms and their favourable configurations offering high conductivity and active sites for high-performance supercapacitors.

The electrochemical impedance spectroscopy (EIS) data, particularly the Nyquist plot in Fig. 2.13 (d), provides a detailed comparison of the resistive and kinetic properties of the

three samples, highlighting the superior performance of the TURGO material. As illustrated by the plot, TURGO exhibits the lowest equivalent series resistance, ESR (R_s) at 3.85Ω , indicating excellent overall electrical conductivity, a significant improvement over URGO (4.656Ω) and GO (6.136Ω). Furthermore, the charge transfer resistance (R_{ct}), represented by the semicircle diameter in low frequency region, is exceptionally low for TURGO at 5.498Ω in comparison to URGO with 30.724Ω and GO with 2391Ω , signifying much faster charge transfer kinetics at the electrode-electrolyte interface due to improved wettability harnessed from defects created by multiple heteroatoms doping approach in favoured configurations. While URGO benefits from nitrogen doping, the simultaneous incorporation of both N and S, with appropriate balance of their respective configurations, creates a more effective doping strategy, optimizing the electronic properties and introducing a higher density of active sites. The performance of a supercapacitor is characterized by its energy density (E) and power density (P), which are calculated from the galvanostatic discharge curve. These parameters quantify the materials ability to store energy and the rate at which it can deliver that energy, respectively. Energy density in $W \cdot h \cdot kg^{-1}$ is calculated using the relation:

$$E = \frac{1}{2 \times 3.6} \times C_s \times \Delta V^2 \quad \text{----- (3)}$$

Where, C_{sp} is the specific capacitance ($F \cdot g^{-1}$) and ΔV is the potential window during discharge (V). While power density is calculated using the relation:

$$P = \frac{E \times 3600}{\Delta t} \quad \text{----- (4)}$$

Where, P is the power density ($W \cdot kg^{-1}$), E is energy density ($W \cdot h \cdot kg^{-1}$) and Δt is discharge time (s).

The enhancement in charge storage properties is reflected in the macroscopic performance metrics presented in the Table 2.6. The high specific capacitance of TURGO ($1229.8 F \cdot g^{-1}$) translates into an outstanding energy density of $54.96 W \cdot h \cdot kg^{-1}$ at a power density of $100 W \cdot kg^{-1}$ while it maintained an energy density of $21.98 W \cdot h \cdot kg^{-1}$ at a power density of $2000 W \cdot kg^{-1}$, enabled by a low charge transfer resistance. In contrast, the single N-doping in URGO and the pristine nature of GO resulted in lower energy densities of $15.09 W \cdot h \cdot kg^{-1}$ and $1.59 W \cdot h \cdot kg^{-1}$ at power densities of $200 W \cdot kg^{-1}$ and $199.25 W \cdot kg^{-1}$, respectively,

confirming the critical role of N and S co-doping in achieving high-performance supercapacitor electrodes.

Table 2.6: Electrochemical performance metrics of GO, URGO and TURGO

Sample	Specific capacitance $F.g^{-1}$ (CV at 2 mV/s)	Specific capacitance (GCD) at 0.5 $A.g^{-1}$	R_{ct} (Ω)	Energy density $W.h.kg^{-1}$ (E)	Power density $W.kg^{-1}$ (P)
TURGO	1229.8	488.20	5.498	54.96	100
URGO	455.4	169.81	30.724	15.09	200
GO	2.63	17.87	2391	1.59	199.25

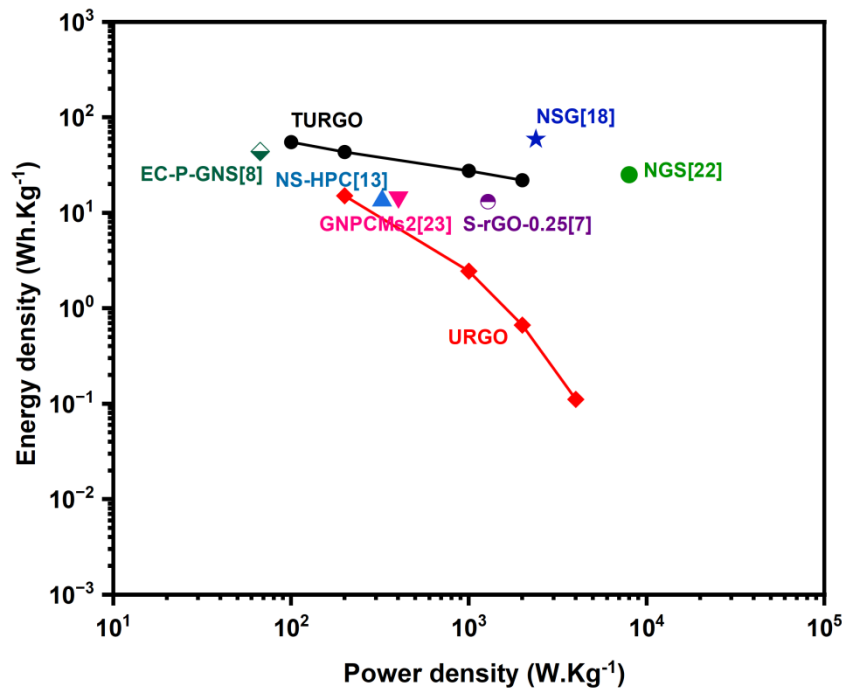


Figure 2.14: Ragone plot of energy density vs. power density of TURGO, URGO and reported RGO based materials

The Ragone plot in Fig. 2.16 visually represents the performance of the supercapacitors, highlighting the critical trade-off between specific energy and specific power. Crucially, TURGO occupies the superior performance domain on the plot, demonstrating significantly higher specific energy across all power densities compared to the solely nitrogen-doped URGO. This finding validates that the synergistic effect of optimised N,S

co-doping is highly effective in enhancing both the capacity and the rate capability, and successfully addressing the primary low energy density drawback of traditional supercapacitors while retaining the characteristic high power. This places TURGO in a superior domain on the Ragone plot, positioning it as a powerful bridge between batteries and conventional capacitors. Its high energy/high power combination makes it ideal for systems requiring rapid charge/discharge and competitive energy storage while surpassing the performance benchmarks of many established RGO based supercapacitors reported in the literature [7,8,13,18,23,24], positioning it as a next-generation, high-performance electrode material.

This suggests that enhancement in material structure upon N,S doping in graphene (TURGO) and its resultant properties such as higher conductivity, more accessible surface area, or more active sites are better optimized for rapid charge/discharge cycles than URGO, making it a more suitable material for high-power supercapacitor applications.

III. Catalytic Application of Doped RGO as a Support for Pt Nanoparticles in Methanol Oxidation Reaction

2.3.5 Structural and morphological analysis of Pt loaded N,S-RGO and N-RGO

I. Structural Analysis by X-ray Diffraction

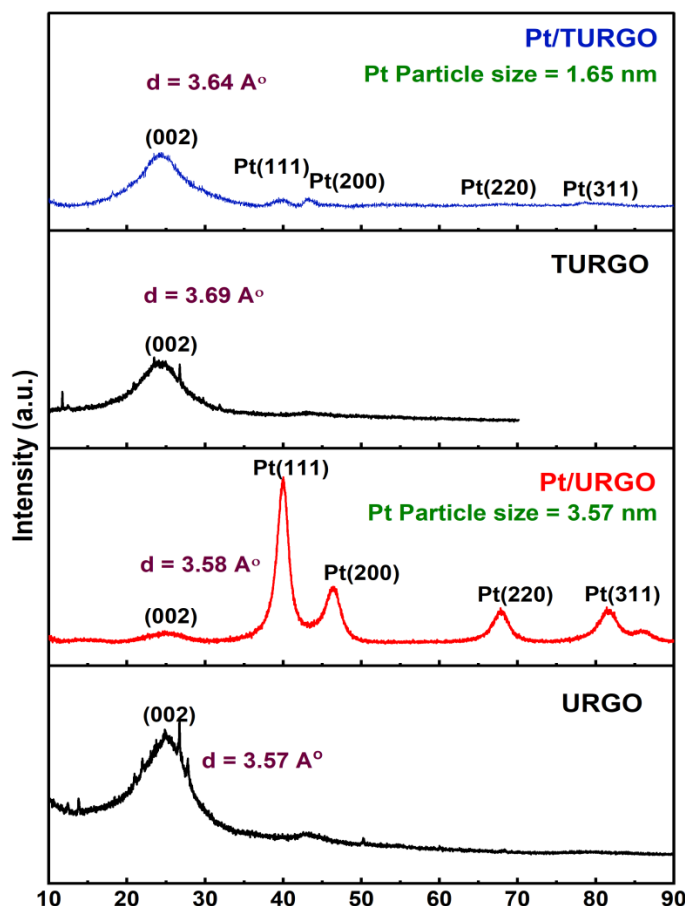


Figure 2.15: X-ray diffractograms of URGO, TURGO and their Pt composite forms

The XRD patterns reveal significant structural differences between the pure supports and their corresponding Pt composites. As seen in the Fig. 2.15, the pure RGO samples exhibit a broad diffraction peak at approximately 2θ value of 25° , which is a signature of the (002) plane of graphitic carbon. The broadness of this peak signifies the low degree of crystallinity and the few-layered nature of the RGO sheets. In contrast to URGO, TURGO is notably less intense and broader, indicating a higher degree of out-of-plane stacking disorder due to the incorporation of N and bulky S heteroatoms, which disrupt the long-range order of the carbon lattice, resulting in a higher interplanar spacing over URGO.

Upon the deposition of platinum, the (002) peak intensity decreases substantially in URGO, resulting in an almost flat peak, clearly indicating disrupted ordered stacking of the RGO layers, causing a loss of long-range crystallinity as the Pt nanoparticles physically intercalate between the layers, preventing the tight π - π stacking of the graphene sheets. While TURGO suggests a greater amount of the graphitic phase in the sample, with prominent but disordered stacking. The emergence of sharp peaks at 40, 46.56, 67.8, 81.63° correspond to (111), (200), (220), and (311) planes of crystalline Pt. This confirms the successful formation of Pt nanoparticles with a face-centered cubic (FCC) crystal structure. A comparison of these peaks between the two composites reveals crucial differences in the Pt catalyst. The Pt peaks in the Pt/URGO sample are notably sharper and more intense, which is indicative of the formation of larger and more highly crystalline nanoparticles with an average particle size of 3.57 nm. In contrast, the Pt peaks in the Pt/TURGO sample are broader and less intense. According to the Scherrer equation, peak broadening is inversely proportional to crystallite size, suggesting that the Pt nanoparticles on the TURGO support are smaller and less crystalline with an average particle size of 1.65 nm. This difference in crystallite size and crystallinity is a critical factor for understanding the varying catalytic performances of the two materials, as smaller particles offer a higher surface area to volume ratio, potentially enhancing catalytic activity.

II. Surface morphology analysis

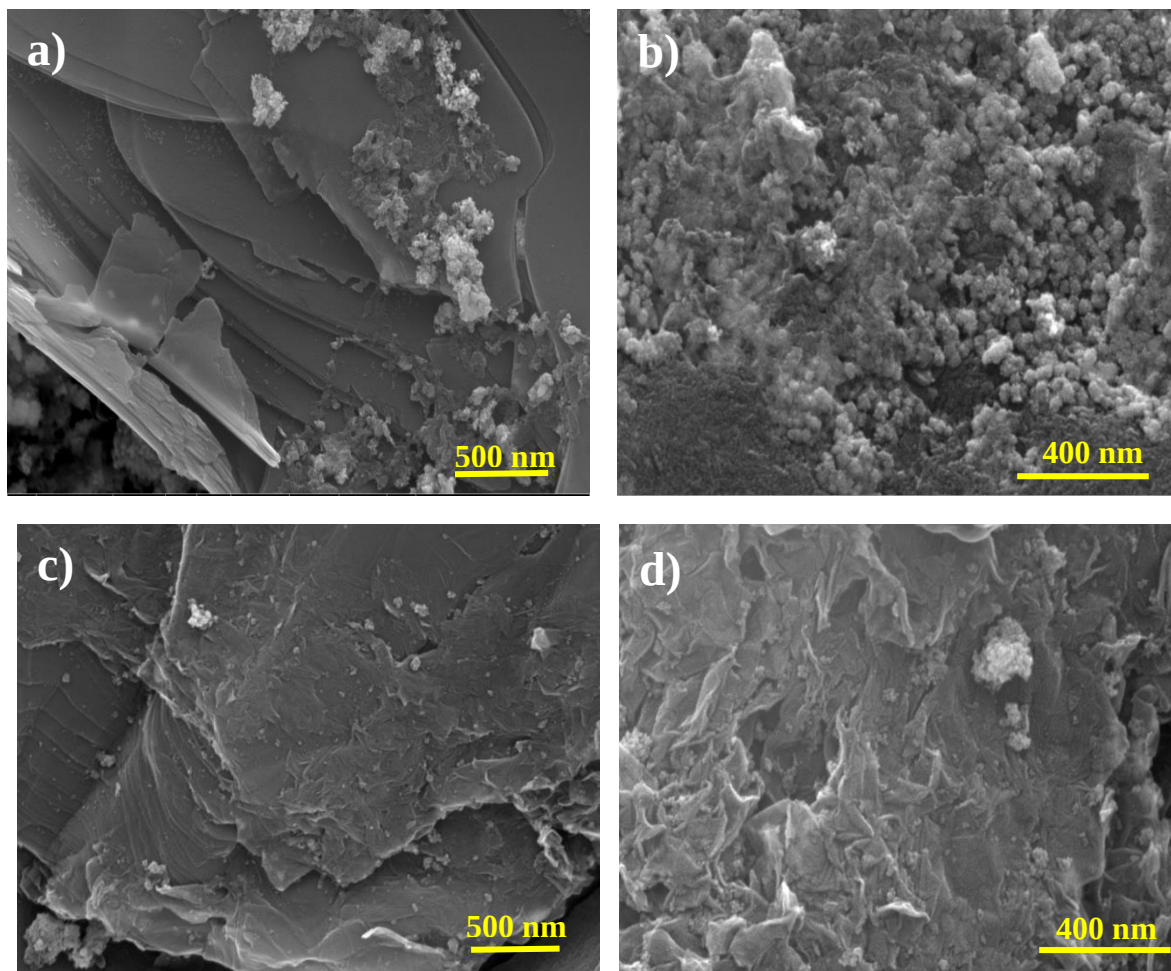


Figure 2.16: SEM images of (a) & (b) Pt/URGO (c) & (d) Pt/TURGO

The SEM images of Pt/TURGO and Pt/URGO reveal that the morphology and distribution of the Pt nanoparticles are directly influenced by the type of doping in the RGO support, revealing key insights into the catalyst properties. The morphology of Pt/URGO composite in Fig. 2.16(a) and (b) at varying magnification reveals deposition of relatively large sized Pt nanoparticles showing significant agglomeration. Although the N-dopants in the URGO support provide nucleation sites for Pt, they are not fully effective at preventing particle growth and coalescence. This leads to the formation of larger Pt particles and clusters as the nanoparticles migrate on the surface of support to reduce their high surface energy. This visual observation is consistent with the sharp and high-intensity Pt peaks seen in the XRD pattern, which are characteristic of larger crystalline domains.

In stark contrast, the Pt/TURGO composite images in Fig. 2.16(c) and (d) show a remarkably different morphology. The Pt nanoparticles are significantly smaller, highly

uniform in size and exceptionally well-dispersed across the RGO sheets with minimal agglomeration. This superior dispersion is a direct consequence of the synergistic effect of the N and S co-dopants in the TURGO support. These heteroatoms especially S, provide more effective nucleation and anchoring sites than N-doping alone. The presence of highly polarising sulfur is critical for the superior dispersion and stability of the platinum nanoparticles. This is because sulfur acts as a better ligand for platinum than nitrogen. As a soft Lewis base, sulfur forms a stronger, more stable covalent bond with the soft Lewis acid platinum. This strong anchoring effect, enhanced by the availability of d-orbitals of sulphur for back-bonding with platinum, effectively locks the nanoparticles in place and prevents them from migrating and coalescing. The fine, uniform dispersion of small nanoparticles directly corresponds to the broad, less-intense Pt peaks observed in the XRD, which is an outcome of the synthesis method and presence of sulfur heteroatoms.

III. X-ray Photoelectron Spectral analysis

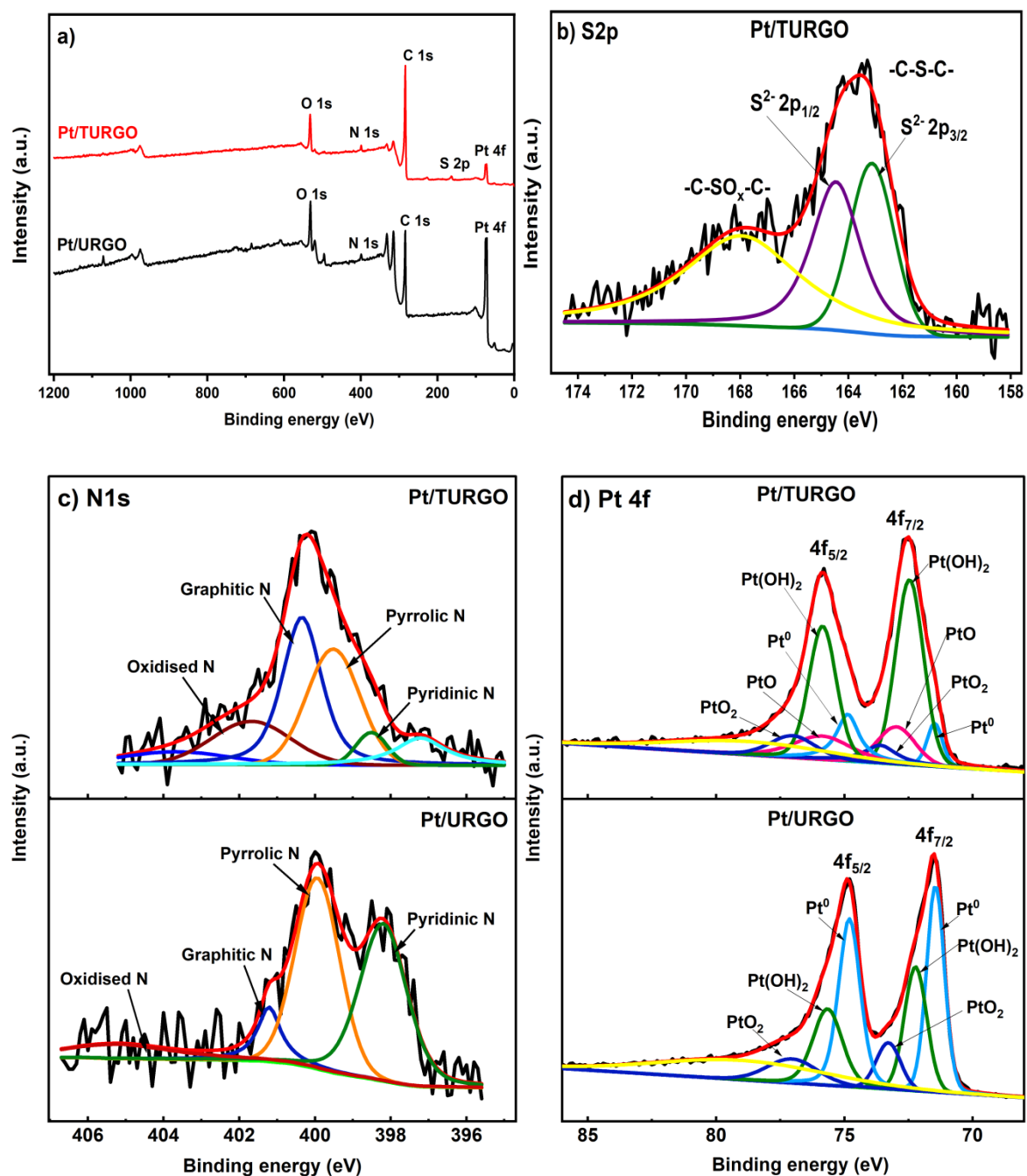


Figure 2.17: (a) XPS survey scan of Pt/URGO and Pt/TURGO (b) XPS core level spectra of N1s (c) S2p (d) Pt4f of Pt/URGO and Pt/TURGO

Table 2.7: Elemental Composition of TURGO, URGO and its Pt composite forms from XPS and ICP-MS analysis

	C (Wt.%)	O (Wt.%)	N (Wt.%)	S (Wt.%)	Pt (Wt.%)		C/O ratio
	XPS	XPS	XPS	XPS	ICP-MS	XPS	
TURGO	73.5	12.2	2.8	11.6			6.02
URGO	68.19	27.91	3.9				2.44
Pt/TURGO	69.4	10.3	2.1	4.1	3.072	14.1	6.73
Pt/URGO	43.3	12.5	2.3		35.211	42	3.46

Table 2.8: Chemical state distribution of elements derived from XPS plots

	Sulfur Chemical State Distribution		Nitrogen Chemical State Distribution				Platinum Chemical State Distribution		
	-C-S-C-	-C-(SO _x)-C-	Pyridinic N	Pyrolic N	Graphitic / Quaternary N	Oxidised N	Metallic Pt	Pt(OH) ₂	PtO/PtO ₂
TURGO	82.92%	17.08%	16.74%	34.05%	38.31%	10.91%			
URGO			37.85%	33.30%	25.92%	2.92%			
Pt/TURGO	62.56%	37.44%	5.94%	35.87%	38.31%	19.87%	13.64%	57.08%	29.28%
Pt/URGO			36.35%	41.88%	13.87%	7.89%	51.05%	33.56%	15.39%

The XPS survey plot in Fig. 2.17(a) and corresponding data Table 2.7 confirms the successful loading of Pt on both TURGO and URGO and their elemental distribution. TURGO is a more reduced material due to more deoxygenation with a high C/O ratio of 6.02, containing both nitrogen and sulfur. URGO, in contrast, is more oxidized, with a lower C/O ratio of 2.44. Upon loading platinum, both materials show a new Pt peak in their spectra. The Pt/URGO sample shows a highly intense Pt peak indicating a much higher Pt content compared to the Pt/TURGO which could also be confirmed from a significant decrease in carbon percentage of Pt/URGO than Pt/TURGO. The C/O ratio of Pt/URGO increases to 3.46 from 2.44 and that of Pt/TURGO increases to 6.73 from 6.02 suggesting further reduction of their surfaces with platinum deposition. The XPS core scan spectra of Pt loaded TURGO and URGO composites reveal significant changes in the distribution of chemical states of the elements upon Pt deposition, without significantly altering peak positions of pure TURGO and URGO as discussed previously in Fig. 2.12.

The core scan of S2p spectra in Fig. 2.17(b) could be fitted into 3 peaks similar to TURGO in Fig. 2.12(b), corresponding to thiophenic S and oxidised S species. However, introduction of Pt on TURGO altered bonding environment of sulfur, promoting its oxidation, as observed from decrease in proportion of -C-S-C- state to 62.56% from 82.92% and an increase in oxidised sulfur to 37.44%, as represented in Table 2.8. Similarly, a critical role of reducing agent could also be observed in the distribution of nitrogen configurations upon Pt loading in Fig. 2.17(c), with an enhancement in the amount of oxidised form and catalytically active pyrrolic form of nitrogen in Pt/TURGO as shown in Table 2.8. While Pt/URGO improved composition of pyrrolic-N and oxidised N by compromising conducting graphitic-N concentration. A remarkable change was observed with chemical states of Pt on TURGO and URGO supports in Fig. 2.17(d). In both cases, the spectra split into two prominent peaks due to spin-orbit coupling, corresponding to $4f_{7/2}$ and $4f_{5/2}$ energy levels, further deconvoluting into 4 doublet peaks in TURGO with intense doublet peak representing 57.08% Pt in +2 state as hydroxides (72.5 & 75.9 eV), while only 13.64% of the catalytically active metallic Pt was observed from peaks at 71.5 & 74.9 eV. Additionally the appearance of doublets at higher binding energy (73, 75.9, 73.6, 77.1 eV) confirmed the presence of Pt oxides. The dominant configuration of Pt in higher oxidation states could be attributed to its stronger interaction with N and especially S, which can be confirmed from conversion of significant amount of stable thiophenic-S into oxidised forms due to charge distribution upon binding with Pt

precursor. In contrast, Pt/URGO exhibited higher percentage of metallic Pt (51.05%) than its hydroxide and oxide forms due to the absence of sulfur. The presence of these different platinum oxidation states indicates that the nature of the graphene support material and type of heteroatoms directly affects the chemical state of the deposited platinum.

The accurate measurement of Pt content from ICP-MS analysis is shown in Table 2.7. The 35.211% Pt loading on the URGO suggested a highly efficient platinum deposition process, with N atoms existing in a favourable pyridinic configuration within graphene lattice acting as excellent nucleation sites for platinum nanoparticles alongwith their successive agglomeration, allowing a large amount of platinum to be successfully loaded onto the support material. In contrast, the 3.072% Pt loading on the TURGO indicated a much lower loading efficiency. The presence of sulfur with nitrogen in the graphene lattice altered the graphene surface, creating a less effective binding environment and inhibiting platinum deposition. This is evident from conversion of S and N heteroatoms to their oxidised forms upon Pt loading, as these groups form strong interactions with Pt precursors, preventing complete reduction of Pt to metallic state. The resultant changes in the reduction potential of graphene upon doping highly electronegative and polarising sulfur atoms alongwith the existence of less amount of highly nucleophilic pyridinic N in TURGO, which serve as anchoring sites for Pt, potentially led to a lesser and weaker interaction with the platinum precursors, ultimately causing poor Pt loading. This finding suggests that the co-doping of sulfur with nitrogen can be detrimental to the platinum loading process on RGO.

IV. Thermal Analysis

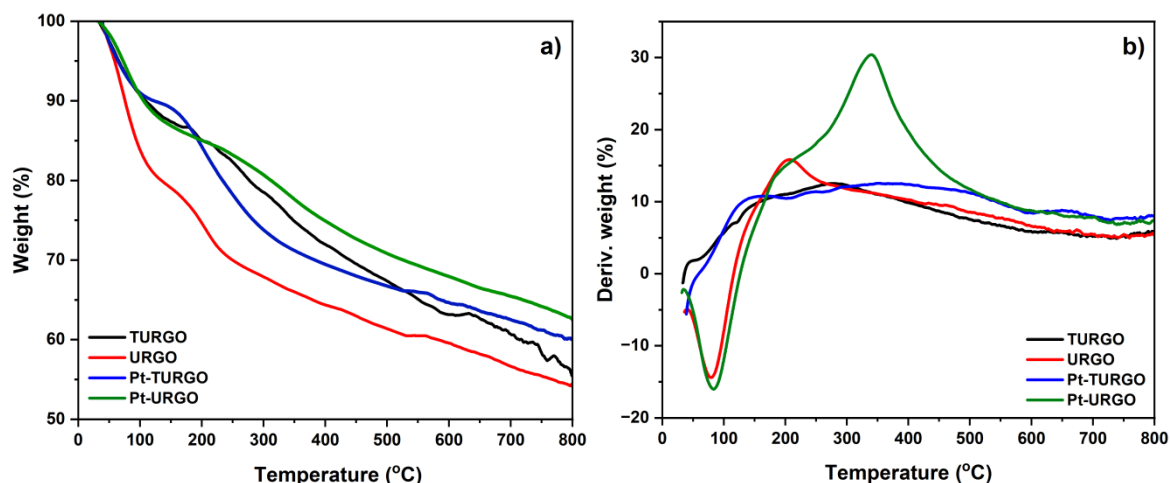


Figure 2.18: (a) Thermogram (b) Differential thermogram of URGO, TURGO and their Pt composites

The thermal stability analysis of Pt loaded TURGO and URGO can be visualised from their thermograms and differential thermograms in Fig. 2.18(a) and (b), respectively. The URGO undergoes a high total weight loss as its structure decomposes, leaving a comparatively lower final residue of 53.77%. However, the Pt/URGO composite contains a high mass percentage of platinum (35.21% from ICP-MS analysis) contributing a large, fixed mass to the final residue. The catalysing effect of Pt on the decomposition of the carbon support causes a rapid weight loss. However, the total percentage of material that can be lost is limited by the high mass of the stable platinum, which remains as a non-volatile residue. Therefore, the total weight loss of the Pt/URGO composite is significantly less than that of the pure URGO. The DTA plot for the Pt/URGO composite shows an initial endotherm similar to URGO due to the loss of physically adsorbed water. While, a large, sharp exothermic peak compared to the pure URGO support in the range of 250 to 500 °C corresponds to the catalytic decomposition of the RGO carbon framework by the highly concentrated Pt nanoparticles and the exothermic reduction of platinum oxides to metallic Pt. The TGA curve shows a dramatic weight loss corresponding to this event, leaving a high final residue that is consistent with the large amount of Pt.

The Pt/TURGO composite shows a similar thermal degradation pattern to TURGO, but with a slightly higher residual weight percentage. This is a direct consequence of the incorporation of the heavy Pt nanoparticles in TURGO. A higher initial weight loss of 10.4% could be attributed to loss of physisorbed oxygen functionalities followed by an

abrupt decrease in mass by 18.47% due to the loss of stable oxygen functionalities from RGO surface and pyrolytic decomposition of carbon framework into a stable form, along with the reduction of Pt oxides into metallic Pt under nitrogen atmosphere. This led to a slightly higher final residual weight of 60.18% than TURGO due to residual Pt with stable carbon framework. In contrast, the pure TURGO support in the absence of Pt showed a gradual weight loss owing to a lesser decomposition upto 530°C, retaining a final mass of 56.80% of stable graphitic carbon with heteroatoms embedded within the framework. The DTA curve of Pt/TURGO is nearly flat, with feeble exothermic peaks occurring at lower temperatures than Pt/URGO. This indicates that the catalytic effect on the carbon support and the heat released from the reduction of platinum oxides are both negligible due to the very low Pt content and presence of N and S heteroatoms preventing Pt nanoparticles from migrating and agglomerating into larger clusters even at high temperatures.

2.3.6 Methanol oxidation on Pt nanoparticles supported on URGO and TURGO

I. Cyclic voltammetry

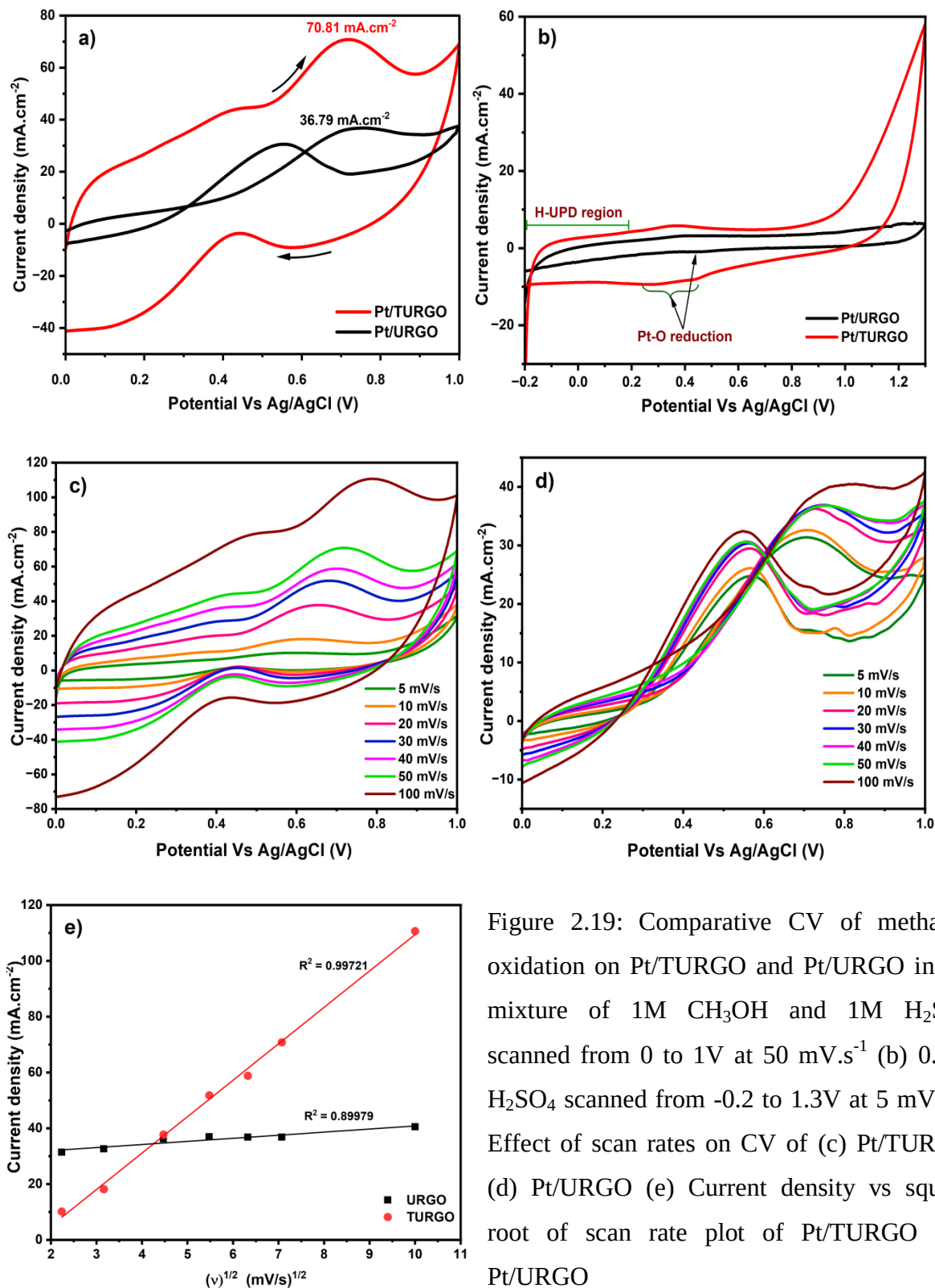


Figure 2.19: Comparative CV of methanol oxidation on Pt/TURGO and Pt/URGO in (a) mixture of 1M CH_3OH and 1M H_2SO_4 scanned from 0 to 1V at 50 mV.s^{-1} (b) 0.5M H_2SO_4 scanned from -0.2 to 1.3V at 5 mV.s^{-1} . Effect of scan rates on CV of (c) Pt/TURGO (d) Pt/URGO (e) Current density vs square root of scan rate plot of Pt/TURGO and Pt/URGO

The catalytic activity of Pt nanoparticles supported on URGO and TURGO was evaluated electrochemically by recording cyclic voltammograms within a potential span of 0 to 1 V at 50 mV.s⁻¹ scan rate in a mixture of 1M CH₃OH and 1M H₂SO₄ and at varying scan rates to understand the effect of scan rates on catalytic activity.

The catalytic activity difference between the TURGO and URGO supported Pt is studied from the cyclic voltammograms illustrated in Fig. 2.19(a) and their resulting electrochemical parameters in Table 2.9. The CV showed two distinct methanol oxidation peaks, a primary peak in the forward scan corresponding to electro-sorption of methanol, following dehydrogenation forming firmly adsorbing intermediates, and a smaller peak in the backward scan, attributed to the subsequent oxidation of these intermediate species like CO, adsorbed on the platinum surface. The most striking observation is that the Pt/TURGO catalyst with only 3.07% Pt loading exhibited a significantly 1.92 and 54.47 times higher anodic current density of 70.81 mA.cm⁻² (325.91 mA.mg_{Pt}⁻¹) for forward methanol oxidation peaks than Pt/URGO with 35.21% Pt exhibiting 36.79 mA.cm⁻² (14.57 mA.mg_{Pt}⁻¹) and commercial 20% Pt/C with reported current density of 4.2 mA.cm⁻² [25]. However, a negative shift in MOR onset potential was observed with Pt/URGO by 108 mV over the onset potential of Pt/TURGO, which demonstrated faster reaction kinetics on Pt/URGO caused by higher Pt loading. While, the synergistic effect of N and S co-doping and enhanced conductivity of TURGO led to a superior intrinsic activity of Pt/TURGO, despite lower Pt loading. Moreover, the i_f/i_b ratio, which is a measure of the tolerance of catalyst to poisoning by intermediate species like CO is found to be 19.4 and 1.20 for Pt/TURGO and Pt/URGO while reportedly 0.75 for commercial 20% Pt/C, respectively, indicating higher efficiency of Pt/TURGO at oxidizing methanol directly to CO₂, with minimal accumulation of poisoning species.

The electrochemically active surface area of both catalysts could be determined by recording their CV in 0.5M H₂SO₄ by sweeping within a potential window of -0.2 to 1.3V at 5 mV.s⁻¹ scan rate as shown in Fig. 2.19(b). The CVs revealed a significant deviation from bulk platinum behavior, specifically the absence of hydrogen adsorption/desorption peaks in the hydrogen underpotential deposition (H-UPD)) region. This phenomenon is a result of the extremely small size of the platinum nanoparticles and strong electronic interactions with the N,S-RGO support. These factors cause the H-UPD signal to be broadened and obscured by the high capacitive current of the RGO. Furthermore, the

strong electronic interaction between Pt and heteroatoms modified the electronic properties of the Pt surface, altering the binding energy of adsorbed hydrogen. Importantly, the catalysts still demonstrate electrochemical activity, as evidenced by the clear presence of platinum oxide formation and reduction peaks at higher potentials (in the range of 0.3-0.5 V). The integrated area under Pt oxide reduction peak represents the charge (Q_{Pt-O}) concerning to its reduction which determines the ECSA of the catalyst (in $\text{cm}^2.\text{mg}^{-1}$) calculated using equation

$$\text{ECSA} = \frac{Q_{Pt-O}}{Q_{Ref} \times [Pt]} \quad \text{-----} \quad (5)$$

Where, Q_{Ref} corresponds to the standard charge for Pt oxide reduction (420 mC.cm^{-2}), $[Pt]$ refers to the Pt loading on the electrode in mg.cm^{-2} . The ECSA was calculated to be $114.54 \text{ cm}^2.\text{mg}^{-1}$ and $0.306 \text{ cm}^2.\text{mg}^{-1}$ for Pt/TURGO and Pt/URGO, respectively. The difference in ECSA is a consequence of distinct morphology and platinum dispersion with large number of well-exfoliated graphene sheets and abundant nucleation sites forming highly dispersed, small Pt nanoparticles in Pt/TURGO. While low ECSA of Pt/URGO suggests agglomeration and poor dispersion of Pt nanoparticles forming large, inactive clusters, thereby drastically reducing the effective surface area available for the electrochemical reaction.

The Fig. 2.19(c) and (d) represents the effect of scan rates ranging from 5 to 100 mV.s^{-1} on CV of Pt/TURGO and Pt/URGO, respectively. From the figures, an increase in anodic peak current density was observed in both catalysts with increasing scan rates, alongwith a progressive positive shift in anodic peak potential, which is mainly attributed to the interplay of kinetic limitations and poor diffusion of reactant molecules to the electrode surface and higher Ohmic drop at increased scan rates. The plot of anodic peak current densities as a function of square root of scan rates in Fig. 2.19(e) showed a linear relation, revealing a diffusion controlled methanol electro-oxidation process on both catalysts.

II. Effect of methanol concentration and temperature on MOR activity

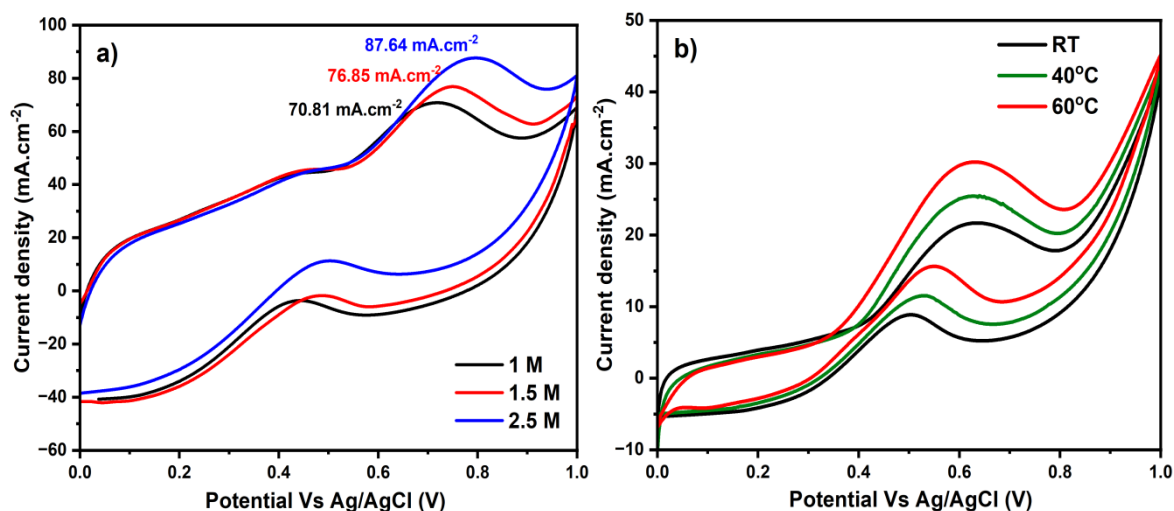


Figure 2.20: Effect of (a) methanol concentration (b) temperature on cyclic voltammogram of Pt/TURGO

Fig. 2.20(a) investigates the effect of methanol concentration (1, 1.5 and 2.5M) on the electrocatalytic performance of the Pt/TURGO catalyst from CVs recorded within a potential window of 0 to 1V at 50 mV.s⁻¹ in 1M H₂SO₄. The results displayed increase in peak current density with rising methanol concentration indicating a concentration-dependent methanol oxidation reaction. The increase in peak current density is because of a higher concentration of reactant molecules available to react at the electrode surface, leading to a faster overall reaction rate leading to a larger current. From the results, a highest current density of 87.64 mA.cm⁻² is observed at the highest concentration of 2.5 M. While a slight positive shift in the peak potential with increasing concentration is likely due to mass transport limitations and enhanced catalyst poisoning. At higher methanol concentrations, the rate of formation of carbonaceous intermediates, particularly carbon monoxide (CO), increases. This CO species adsorbs strongly to the active sites of the catalysts, thus effectively blocking them. A higher applied potential is therefore required to facilitate the oxidative removal of this poisoning species to sustain the methanol oxidation reaction, which causes a positive anodic shift of the main oxidation peak.

The influence of temperature on the electrocatalytic activity of the Pt/TURGO catalyst is measured by recording CV within a potential span of 0 to 1 V at 5 mV.s⁻¹ scan rate in a mixture of 1M CH₃OH and 1M H₂SO₄ at room, 40°C and 60°C temperature as represented

in Fig. 2.20(b). As the temperature increased from room temperature to 40°C and 60°C, a noticeable progressive increase in the current density was observed. At 60°C, the current density increased 1.4 times that at room temperature. This behaviour described the temperature dependence of reaction rates on the catalyst aligning with the Arrhenius equation. The frequent and energetic collisions of reactant molecules with the catalyst surface increases the rate of mass transport with easy desorption of reaction by-products. This improved the intrinsic activity of the catalyst by overcoming the activation energy barrier of the reaction.

From a practical standpoint, this data is crucial for the design and operation of DMFCs. A DMFC using Pt/TURGO catalyst would be most efficient when operated at temperatures above room temperature, for instance, in the 40-60°C range. The improved performance at higher temperatures is a strong indicator of the suitability of catalyst for commercial DMFC applications which is a common requirement for many fuel cells, as the reaction kinetics are often sluggish at ambient temperatures. The improved performance at higher methanol concentration and temperatures underscores the potential of the catalyst for practical applications where operating conditions can be controlled to maximize power output.

III. Tafel polarisation studies

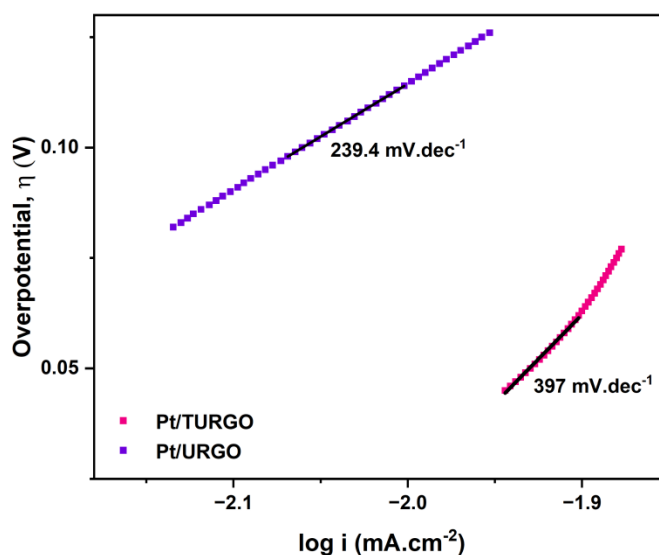


Figure 2.21: Tafel plots of Pt/TURGO and Pt/URGO

Tafel polarisation analysis is crucial electrochemical method to understand the reaction kinetics and reaction mechanism of catalytic reactions, with key resultant parameters like Tafel slope and exchange current density, wherein Tafel slope (in mV.dec^{-1}) quantifies the sensitivity of current density of an electrochemical reaction to changes in applied overpotential, with lower Tafel slope signifying highly efficient kinetics and a very active catalyst and vice versa. The exchange current density, j_0 (mA.cm^{-2}) represents the rate of a forward and backward electrochemical reaction at equilibrium, where the net current is zero. A higher exchange current density reveals intrinsically active catalyst. The Tafel equation provides a linear relationship between the overpotential, η (V) and logarithm of current density, j (mA.cm^{-2}) and is represented as:

$$\eta = a + b \log(j) \quad \text{----- (6)}$$

Where, a is exchange current density (mA.cm^{-2}) and b representing Tafel slope (mV.dec^{-1})

From the Tafel plots of Pt/TURGO and Pt/URGO in Fig. 2.21, a higher exchange current density with lower Tafel slope of $239.4 \text{ mV.dec}^{-1}$ is observed with Pt/URGO while a lower exchange current density with higher Tafel slope of 397 mV.dec^{-1} is obtained with Pt/TURGO. The contradictory result hints towards a higher intrinsic rate of reaction at equilibrium with Pt/TURGO due to large number of N, S active site and defects causing uniform and higher Pt dispersion leading to a higher ECSA. However, a higher Tafel slope

indicates less number of surface Pt atoms due to poor binding ability of N,S co-doped graphene and stronger adsorption of carbonaceous intermediates like CO on the existing Pt surface, which arises from altered electronic properties of Pt due to S doping, inhibiting oxidative removal of CO intermediate, thus quickly blocking the limited available Pt sites. As a result, a larger overpotential is needed to achieve a tenfold increase in current, leading to the high Tafel slope. While a lower exchange current density in Pt/URGO suggests a lower density of active sites due to fewer and only N heteroatoms and larger quantity of Pt clusters, which on the contrary enhanced reaction kinetics arising from an optimal electronic environment created by favourable pyridinic-N configuration that weakens the adsorption of poisoning intermediates, making them easier to oxidize and remove from the catalyst surface as evident from lower Tafel slope. The high current density and exchange current density (j_0) in Pt/TURGO stemmed from its high surface area, but its high Tafel slope shows kinetically inefficient reaction. The S-doping on graphene, while potentially beneficial for other reactions, may not be ideal for the specific mechanism of methanol oxidation on Pt, leading to a slower kinetic pathway. In contrast, Pt/URGO has a kinetically superior reaction (low Tafel slope) despite a lower surface area and j_0 . This means Pt/TURGO despite minimum Pt loading is better for high power output, while Pt/URGO with more Pt content is more promising material for high-efficiency applications from a practical perspective.

In conclusion, the Tafel slope analysis provides quantitative evidence that the N-doped graphene support (URGO) is more effective than the N,S-co-doped support (TURGO) in enhancing the intrinsic electrocatalytic kinetics of platinum for methanol oxidation reaction. This finding highlights the critical role of support engineering in optimizing catalyst performance.

IV. Electrochemical Impedance spectroscopy

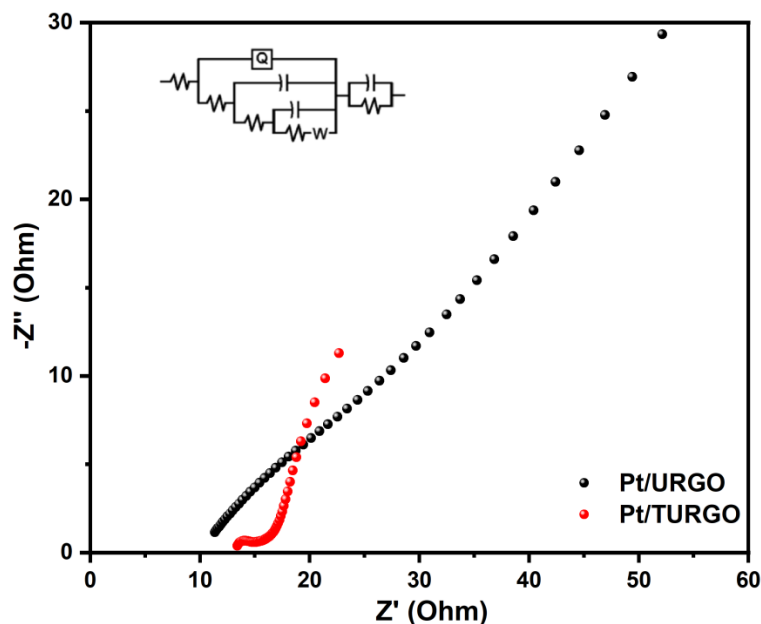


Figure 2.22: Nyquist plots of Pt/TURGO and Pt/URGO

The Nyquist plots of Pt/TURGO and Pt/URGO as represented in Fig. 2.22 provide valuable insights into their electrochemical behaviour in agreement with previous results. The charge transfer resistance (R_{ct}) measured from the diameter of the semicircle formed at the low frequency region showed a lowest charge transfer resistance of $3.418 \, \Omega$ in Pt/TURGO supporting higher current density (CV) and exchange current density results (Tafel plot) despite a higher Tafel slope suggesting kinetically less efficient reaction at high potentials. This result is due to the presence of large number of active sites from N and S co-doping in graphene, which enhanced conductivity and electron transfer rate at the electrode-electrolyte interface with superior utilisation of each Pt atom. The sheer quantity of these active sites overcomes the kinetic drawback of each individual site. Thus, the lower resistance is due to a higher density of active sites rather than a more efficient reaction mechanism. In contrast, a higher R_{ct} of $34.38 \, \Omega$ is observed with Pt/URGO evident from larger diameter of the semicircle due to lower conductivity and less number of active sites with less favourable electronic environment for the reaction. Finally, the low-frequency linear region (Warburg impedance) signifies mass transport. A short, steeper, more vertical line for Pt/TURGO suggests superior diffusion of methanol reactant molecules to its active sites due to porous nature of the support, which further contributes to its better overall performance. While a less steep and longer linear region in Pt/URGO indicates more pronounced mass transport limitations.

The Pt/TURGO catalyst achieved a lowest charge transfer resistance (R_{ct}) and 1.92 times higher current density with only 3.07% platinum loading vs. 35.21% for Pt/URGO and 54.47 times higher than commercial Pt/C. This performance, despite a kinetic compromise shown by its higher Tafel slope, is driven by the ability of N,S-co-doped support to dramatically increase platinum utilization efficiency and improve mass transport outperforming the Pt/URGO catalyst. However, it is also important to note that presence of S on graphene support is not very beneficial for loading Pt in its catalytically active metallic state, a prerequisite for driving MOR due to its incomplete reduction caused by sulphur, which is responsible for the kinetic limitations of the catalyst.

V. Chronoamperometry

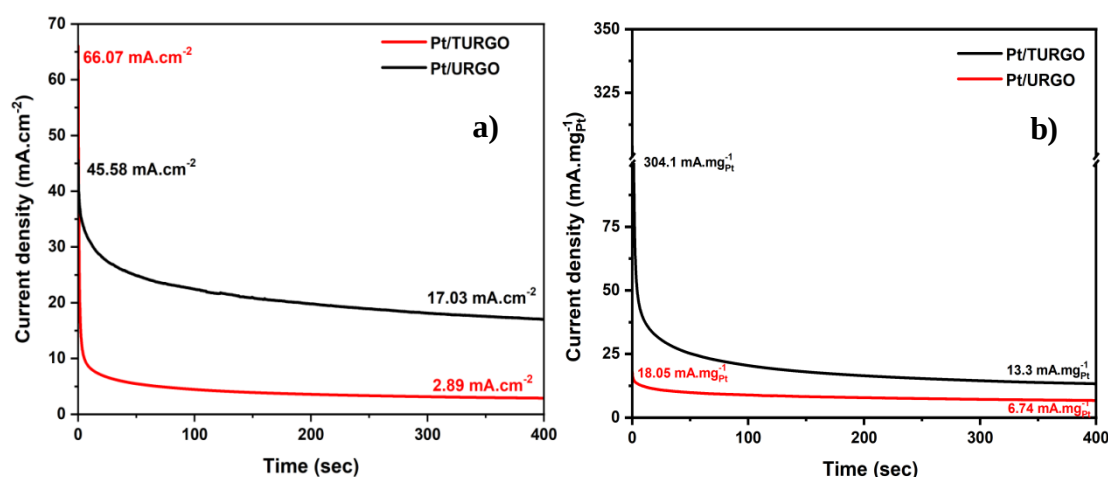


Figure 2.23: Chronoamperometric stability test plots of Pt/TURGO and Pt/URGO in terms of (a) geometric current density (b) Platinum mass activity

The chronoamperometry results provide a critical assessment of the long-term electrocatalytic stability and poisoning resistance of the catalysts during the methanol oxidation reaction. While the geometric current density plot in Fig. 2.23(a) shows higher sustained values for Pt/URGO due to its significantly higher platinum loading (35.21% vs. 3.07%), the mass activity plot Fig. 2.23(b) reveals the true intrinsic efficiency of the materials. Pt/TURGO exhibits a remarkably superior initial mass activity of 304.1 mA.mg_{Pt}⁻¹ which is approximately 17 times higher than that of Pt/URGO. Furthermore, after 400 seconds of continuous operation, Pt/TURGO retains a steady-state mass activity of 13.3 mA.mg_{Pt}⁻¹, effectively doubling the performance of Pt/URGO (6.74 mA.mg_{Pt}⁻¹). This enhanced stability and higher retention rate in the Pt/TURGO catalyst confirm that the synergistic N,S co-doping of the TURGO support creates a more robust electronic environment by preventing the Platinum sites from being blocked as quickly as the N-doped (URGO) support, which effectively mitigates the poisoning effects of carbonaceous intermediates like CO, allowing for superior catalytic performance with minimal precious metal usage.

Table 2.9: Comparative electrochemical parameters of Pt/TURGO and Pt/URGO against reported Pt based anode catalysts

Sample	Pt (Wt. %)	Electrolyte	Scan rate (mV.s ⁻¹)	MOR Onset Potential (V)	Anodic peak current density (i _{pa}) (mA.cm ⁻²)	Anodic peak current density (i _{pa}) mA. mg _{Pt} ⁻¹	Anodic peak potential (V _{pa})	i _f /i _b	ECSA cm ² .mg ⁻¹	Ref.
Pt/TURGO	3.072	1M CH ₃ OH + 1M H ₂ SO ₄	50	0.486	70.81	325.91	0.719	19.4	114.54	This work
Pt/URGO	35.21	1M CH ₃ OH + 1M H ₂ SO ₄	50	0.378	36.79	14.57	0.740	1.20	0.306	
Pt/S-RGO	2	1M CH ₃ OH + 1M NaOH	50	-0.55	NR	644	-0.24	15	220	[26]
Pt/N-RGO	46.9	0.5 M CH ₃ OH + 0.5 M H ₂ SO ₄	20	0.3	NR	160.8	0.625	1.16	45.2	[27]
Pt/Graphene	--	0.5 M CH ₃ OH + 0.5 M H ₂ SO ₄	20	0.4	NR	134.2	0.6	0.87	68.7	[27]
Pt/C	20	2 M CH ₃ OH + 0.5 M H ₂ SO ₄	20	0.5	4.2	NR	0.93	0.75	12.6 cm ²	[25]

N.R. : 'Not Reported' in the cited literature.

2.4 Conclusion

1. A simple and less toxic reflux method using thiourea as a dual precursor was successfully employed to synthesize N,S co-doped reduced graphene oxide (N,S-RGO). This process effectively reduced graphene oxide (GO) while simultaneously incorporating nitrogen and sulfur heteroatoms into the graphene lattice.
2. The study established a direct correlation between the amount of thiourea used and the final N and S content in the RGO. The optimal ratio of 1:8 of GO/ thiourea was identified to produce best material (1:8rGO or TURGO), as it achieved a balanced structure with optimal oxygen removal and favorable I_D/I_G ratio.
3. The optimal N,S-RGO demonstrated significantly enhanced thermal stability compared to GO, and a highly reduced structure with a C/O ratio of 74.4%, indicating successful elimination of oxygen functionalities.
4. The N,S-RGO material exhibited exceptional supercapacitive performance, with the optimized TURGO sample achieving a high specific capacitance of 488.20 $F \cdot g^{-1}$. This superior performance is attributed to a synergistic effect of electrical double-layer capacitance derived from large surface area and pseudocapacitance from the N and S heteroatoms.
5. The inclusion of the sulfur atom had a profound effect on the structure and performance in terms of highest energy density of 54.96 $Wh \cdot kg^{-1}$ at a power density of 100 $W \cdot kg^{-1}$ compared to an energy density of N-doped RGO (URGO) with 15.09 $Wh \cdot kg^{-1}$ at 200 $W \cdot kg^{-1}$ power density. The larger sulfur atom in TURGO introduced greater steric hindrance, which increased the interlayer distance between graphene sheets, a key factor for improved ion transport.
6. XPS analysis revealed a more diverse set of nitrogen configurations in TURGO, including a predominant amount (38.31%) of Graphitic-N, and thiophenic S (82.92%) which enhanced conductivity. In contrast, the sulfur-free URGO contained fewer active sites and a less favorable N configuration.
7. The strong electronic interaction between the highly polarising sulfur atoms in the N,S-co-doped RGO and the platinum precursors created a less effective binding environment, which inhibited complete reduction of Pt to metallic state and resulted in a significantly lower platinum loading.

8. Despite its significantly lower Pt loading (3.07% vs. 35.21% for URGO), the Pt/TURGO catalyst showed superior intrinsic activity, with an anodic current density 1.92 times higher than Pt/URGO and 54.47 times higher than commercial Pt/C. This is due to the formation of smaller, more dispersed Pt nanoparticles and a strong electronic interaction between Pt and the N and S heteroatoms on the TURGO support.
9. The research demonstrates that Pt/TURGO outperforms Pt/URGO in both intrinsic activity and long-term stability. Although Pt/URGO shows higher bulk current due to excessive loading (35.21% Pt), its mass-normalized performance reveals rapid poisoning and poor site utilization. Conversely, the N,S co-doping in TURGO provides a superior anchoring effect, maintaining a steady-state mass activity 1.97 times higher than Pt/URGO. This proves that synergistic doping, rather than high Pt loading, is the key to sustained and cost-effective electrochemical operation.

2.5 References

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CHAPTER III

CERIUM INCORPORATED MANGANESE OXIDE – NS-RGO NANOCOMPOSITE: SYNTHESIS, STRUCTURAL ANALYSIS AND SUPERCAPACITOR PERFORMANCE

Chapter 3

Cerium Incorporated Manganese Oxide – NS-RGO Nanocomposite: Synthesis, Structural Analysis and Supercapacitor Performance

3.1 Introduction

The global energy crisis, driven by the depletion of fossil fuels and escalating environmental concerns, has underscored the urgent need for advanced energy storage solutions. Among the various electrochemical energy storage technologies, supercapacitors (SCs) have emerged as a highly promising alternative due to their rapid charge-discharge kinetics, high power density and exceptional cycle stability. While their energy density is a key limitation, significant research efforts have focused on developing novel electrode materials to bridge this gap.

While carbon-based materials are widely used in EDLCs, their charge storage is limited to the surface, resulting in lower energy density. To overcome this, researchers have focused on transition metal oxides (TMOs) as pseudocapacitive electrode materials. TMOs, such as MnO_2 , RuO_2 , Co_3O_4 , MoO_3 , and V_2O_5 are favored for their high theoretical capacitance, multiple oxidation states, and superior charge storage capability [1]. Among these, manganese dioxide (MnO_2) stands out as an exceptionally promising candidate due to its abundant reserves, low cost, environmental friendliness, and a high theoretical specific capacitance of 1370 F.g^{-1} . The pseudocapacitance of MnO_2 is attributed to reversible redox reactions involving the transition between its multiple oxidation states (e.g., $\text{Mn}^{3+}/\text{Mn}^{2+}$, $\text{Mn}^{4+}/\text{Mn}^{3+}$), which facilitates the exchange of protons and/or cations from the electrolyte [2]. Despite its impressive theoretical potential, pure MnO_2 suffers from critical limitations that hinder its practical application. The primary challenges are its poor electrical conductivity (10^{-5} to 10^{-6} Scm^{-1}), lower diffusion coefficient and structural instability during prolonged charge-discharge cycles. These drawbacks lead to reduced electrochemical performance, including low specific capacitance and poor cyclic stability [3].

To unlock the full potential of MnO_2 , extensive research has been conducted to address these issues through various strategies. These include controlling synthetic approaches to develop specific polymorphs (α , β , γ , and δ), which have varying tunnel or layered architectures. For instance, the large tunnel structure of α - MnO_2 (Octahedral Molecular Sieves, OMS-2) and the 2D layered δ - MnO_2 are ideal for the movement of large ions like K^+ [4]. This is a crucial factor in optimizing supercapacitor performance. Further, modifying the nanostructure of MnO_2 into forms like nanowires, nanosheets, or nanorods can enhance the specific surface area and shorten ion diffusion pathways, thereby improving performance [4]. Moreover, integrating MnO_2 with highly conductive materials like graphene, carbon nanotubes (CNTs), and conductive polymers creates synergistic effects [5,6]. The conductive matrix improves electron transport, while the MnO_2 provides a high-capacity charge storage medium. Another effective strategy involves doping the MnO_2 lattice with metal ions like Fe, Ag, Ni, Cu, V, Pd, or Co. This process creates crystal defects and oxygen vacancies, significantly boosting the material's electrical conductivity. The dopant ions also tune the electronic structure, enhancing the kinetics of redox reactions. Furthermore, these metal ions can support and extend layer spacing in the material, preventing structural collapse and significantly improving cycling stability, which leads to a better specific capacitance and durability [3].

In this context, Cerium (Ce) emerges as a particularly compelling choice due to its unique and powerful properties. As a key member of the rare earth family, Cerium is abundant and readily available. More importantly, its ability to easily switch between its Ce^{4+} and Ce^{3+} oxidation states provides a strong pseudocapacitive contribution, introducing additional redox-active sites within the host lattice [7]. This redox activity directly contributes to the overall charge storage capacity of the electrode, making it an excellent dopant for supercapacitor applications. Ce doping has shown remarkable success in enhancing the performance of various metal oxides for supercapacitor applications. For instance, doping MoO_3 with Ce at a molar ratio of 30 achieved an ultrahigh energy density of 150.0 Wh kg^{-1} and a specific capacitance of 1446 F.g^{-1} . These significant improvements were attributed to increased oxygen vacancies and a larger specific surface area, which enhanced ionic diffusion and electrical conductivity for asymmetric supercapacitors (ASC) [8]. Similarly, introducing 1.5 mole% Ce into WO_3 resulted in a superior specific capacitance of 493 F.g^{-1} compared to the pristine material, primarily due to increased porosity and oxygen vacancies that facilitate efficient charge transfer [9]. The large ionic

size of cerium is also crucial, as it helps to extend and support the layered structure of host material, preventing structural collapse and dramatically improving long-term cycling stability. These benefits have been observed in other metal oxides, including NiO, CdO, and spinel ferrite CoFe_2O_4 , confirming that Ce doping is a versatile and effective method for improving not only specific capacitance but also the structural stability and conductivity of host materials [10–12]. By leveraging these proven, multifaceted properties of cerium doping, its incorporation into $\alpha\text{-MnO}_2$ (OMS-2) and combining with a conductive matrix of multiple heteroatom decorated reduced graphene oxide (RGO) presents a promising strategy. This approach aims to create a high performance electrode material that combines the advantages of a robust host with a highly effective dopant and superior conductivity of support, directly addressing the persistent challenges of low electrical conductivity and poor cyclic stability in MnO_2 based supercapacitors.

This chapter details the synthesis and characterization of a novel ternary nanocomposite of Ce doped OMS-2 supported on N, S co-doped reduced graphene oxide (NS-RGO). We address the limitations of previous literature, which often used a high concentration of Ce and simple unmodified RGO synthesized via less scalable hydrothermal methods [13]. Our approach is distinguished by its focus on cost-effectiveness and scalability, employing a simple reflux method with a minimal quantity of Ce, which is more scalable and accessible technique compared to typical hydro/solvothermal method requiring specialized equipment, high pressures, and high temperatures, which are less suitable for large-scale production [8,9,12,14]. This work leverages the synergistic effect of N and S co-doped RGO, a strategy not previously reported for this material system, to create defects, enhance conductivity and prevent nanosheet restacking.

Through comprehensive characterisation by FTIR, XRD, SEM, BET, XPS, ICP-MS, TG-DTA and electrochemical evaluation by CV, GCD, EIS, the superior performance of the composite has been demonstrated. While bare Ce-doped OMS-2 and NS-RGO showed higher capacitance in different electrolytes individually, their optimised synergistic combination exhibits exceptional specific capacitance and stability, particularly in an acidic medium. These findings provide crucial insights into the rational design of high-performance, cost-effective electrode materials, paving the way for next-generation supercapacitors.

3.2 Methodology

All chemicals and reagents used in this study were of analytical grade. Detailed information regarding the purity and suppliers of these materials is documented in the Appendix following the final chapter.

3.2.1 Synthesis of $\text{Ce}_x\text{OMS-2}$ ($x = 1.5$ mmoles)

The synthesis of $\text{Ce}_x\text{OMS-2}$ nanorods was accomplished via a reflux-based precipitation method. Initially, an oxidant solution was prepared by dissolving 0.6064 g (1.5 mmoles) of Cerium sulfate tetrahydrate, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and 2.945 g (0.0186 moles) of Potassium permanganate, KMnO_4 , in 50 mL of distilled water. This mixture was heated to 80°C to ensure complete dissolution. Concurrently, a reactant mixture was prepared in a round-bottom flask, consisting of 4.4 g (0.026 moles) of Manganese sulfate monohydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 1.5 mL of concentrated nitric acid, HNO_3 , in 15 mL of distilled water. The flask was heated to 80°C and stirred continuously. The oxidant solution was then added drop wise to the reactant mixture, and the combined suspension was subjected to reflux for 24 hours under constant stirring. The resulting black solid product was then isolated and purified. It was repeatedly washed with distilled water until a qualitative test for sulphate ions showed no presence of impurities. Following this, the precipitate was rinsed with ethanol and dried in an oven at 110°C overnight, yielding the CeOMS-2 nanorods.

3.2.2 Synthesis of OMS-2

The synthesis of OMS-2 was performed following the same procedure as described for the CeOMS-2 nanorods in Section 3.2.1, with the sole modification of omitting the cerium precursor to yield pure OMS-2 nanorods.

3.2.3 Synthesis of NS-RGO

The experimental procedure for the synthesis of NS-RGO was performed as outlined in detail in Section 2.2 (Chapter II).

3.2.4 Synthesis of $\text{Ce}_x\text{OMS-2/NS-RGO}$ nanocomposite ($x = 1.5$ mmoles)

A dispersion of NS-RGO was prepared by suspending 150 mg of the material in 100 mL of distilled water, followed by sonication for 45 minutes. To this dispersion, 50 mg of CeOMS-2 sample was added in order to obtain a 25:75 mass percent ratio of CeOMS-2 and

NS-RGO, and the resulting mixture was sonicated for an additional 5 minutes to ensure uniform dispersion. The mixture was then stirred continuously for 1 hour before being transferred to an hot air oven for drying at 80°C. The final product of the composite, was designated as the CeOMS-2/NS-RGO nanocomposite. Similarly, other composite ratios of 10:90, 50:50 and 75:25 were synthesised for optimising the nanocomposite composition.

3.2.5 Materials Characterisation

A suite of analytical techniques was employed to fully characterize the synthesized samples. Fourier Transform Infrared (FTIR) spectra were obtained using an IRAffinity – 1S SHIMADZU 00822 spectrophotometer in the range of 400–4000 cm^{-1} . X-ray Diffraction (XRD) patterns were recorded on a Bruker D8Advance diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) to study the crystal structure. For thermal analysis, simultaneous Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out using a SHIMADZU DTG-60 analyser. Samples were heated from 25°C to 800°C at a rate of 10°C/min under a nitrogen atmosphere to assess thermal stability. The surface morphology were examined using Scanning Electron Microscopy (SEM) on JEOL JSM-7610F FEG-SEM. The oxidation states and elemental composition were further investigated via X-ray Photoelectron Spectroscopy (XPS) using a Kratos Analytical Ltd. Axis Supra, FEI Inc. model, with an Al $K\alpha$ X-ray source (1486.6 eV). All spectra were first charge-corrected by referencing the adventitious carbon C1s peak to 284.8 eV to account for electronic shifts and surface charging. Finally, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was performed on the ICP-MS system, Agilent 7900 to determine the elemental composition in each sample. The surface area, pore volume, and pore size distribution of the samples were characterized using N_2 adsorption-desorption isotherms at 77 K. The measurements were performed using a volumetric gas adsorption analyser (BELSORP-mini II, Bel Japan Inc., Japan). The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method, while the pore size distribution and pore volume were calculated using the Barrett–Joyner–Halenda (BJH) method.

3.2.6 Electrochemical Measurements

The electrochemical properties of all samples were systematically investigated using a three-electrode CHI6081E electrochemical workstation. This setup consisted of a modified glassy carbon electrode (GCE, 3 mm diameter) as the working electrode, a graphite rod as

the counter electrode and an aqueous silver/silver chloride (Ag/AgCl) electrode as the reference electrode for H_2SO_4 and Na_2SO_4 electrolyte. While Mercury mercurous oxide (Hg/HgO) electrode was used as a reference electrode in KOH medium. The GCE was meticulously prepared by sequentially polishing with 1, 0.3 and 0.05 μm alumina slurry, followed by sonication in ethanol for 2 minutes. The working electrode was fabricated by drop-casting sample ink onto the dried GCE, which was prepared by dispersing 2 mg of the sample in 40 μL isopropyl alcohol for 10 minutes, following which 20 μL Nafion binder was added and dispersed for another 5 minutes. The modified electrode was then air-dried overnight. For electrochemical evaluation, Cyclic voltammetry (CV) was performed at scan rates of 2, 5, 10, 20, 30, 40 and 50 $\text{mV}\cdot\text{s}^{-1}$ within an optimised potential range of -0.3 V to 0.6 V to assess the effect of scan rate on the charge storage capacity of the materials. Galvanostatic charge-discharge (GCD) curves were recorded in the same potential window of -0.3 V to 0.6 V at various current densities for comparative analysis of specific capacitance. The studies were performed in 1M H_2SO_4 , 1M Na_2SO_4 and 1M KOH to assess the influence of pH on charge storage capacity of samples. Furthermore, the cyclic stability of the nanocomposite was evaluated in 1M H_2SO_4 alongwith electrochemical impedance spectroscopy (EIS) conducted from 100 kHz to 1 Hz to evaluate charge transfer characteristics of the electrode.

3.3 Results & discussion

3.3.1 Structural and morphological analysis of CeOMS-2/NS-RGO nanocomposite

I. FTIR spectral analysis

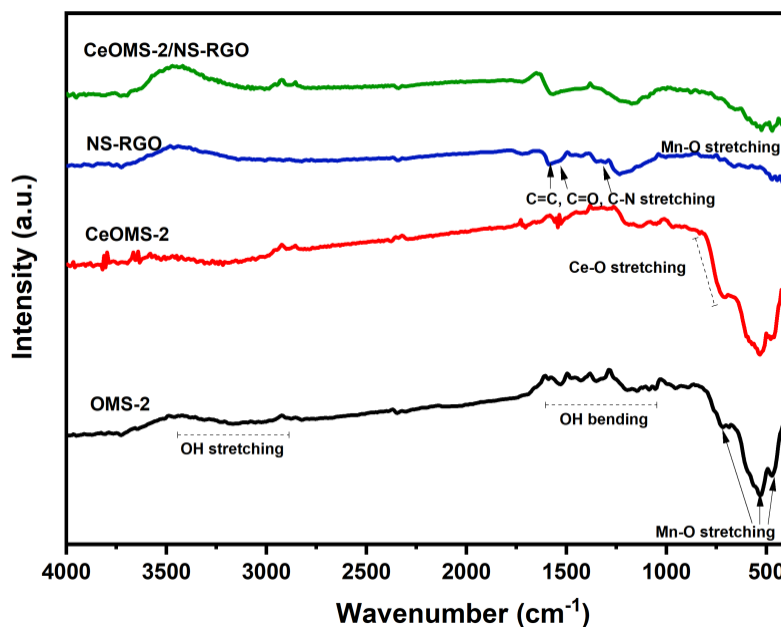


Figure 3.1: FTIR spectra of (a) OMS-2 (b) CeOMS-2 (c) NS-RGO (d) CeOMS-2/NS-RGO

The FTIR spectral analysis in Fig. 3.1 confirms the successful synthesis of each component and the final composite. The OMS-2 spectrum is defined by a broad absorption band at $\sim 3400\text{ cm}^{-1}$ and a peak in the frequency range of $1250\text{ to }1600\text{ cm}^{-1}$, which are characteristic of the O-H stretching and bending vibrations, respectively, of surface hydroxyl groups and physically adsorbed water molecules. The four characteristic bands in the fingerprint region below 1000 cm^{-1} corresponding to Mn-O vibrational modes in $[\text{MnO}_6]$ octahedra are exhibited at around 708.9 cm^{-1} , 528.5 cm^{-1} , 472 cm^{-1} and 440 cm^{-1} . The CeOMS-2 spectrum showed an increase in intensity of shoulder band of OMS-2 at 708.9 cm^{-1} due to integrated Ce-O stretching vibration, confirming the successful incorporation of cerium into the OMS-2 lattice. In contrast, the NS-RGO spectrum showed a strong peak at $\sim 1581\text{ cm}^{-1}$ associated with the C=C stretching of the graphitic backbone with feeble O-H stretching vibrations, as well as distinct peaks around 1226 cm^{-1} , 1041 cm^{-1} , 1180 cm^{-1} and $825, 725\text{ cm}^{-1}$ corresponding to C-N, S=O and C-S stretching

vibrations, which proved the successful doping of nitrogen and sulfur into the reduced graphene oxide sheets. Finally, the CeOMS-2/NS-RGO composite spectrum demonstrated a clear superposition of the characteristic peaks from both the CeOMS-2 and NS-RGO components. The simultaneous presence of peaks for Mn-O, Ce-O, C=C, and C-N/C-S bonds validates the successful fabrication of the composite.

II. Structural Analysis by X-ray Diffraction

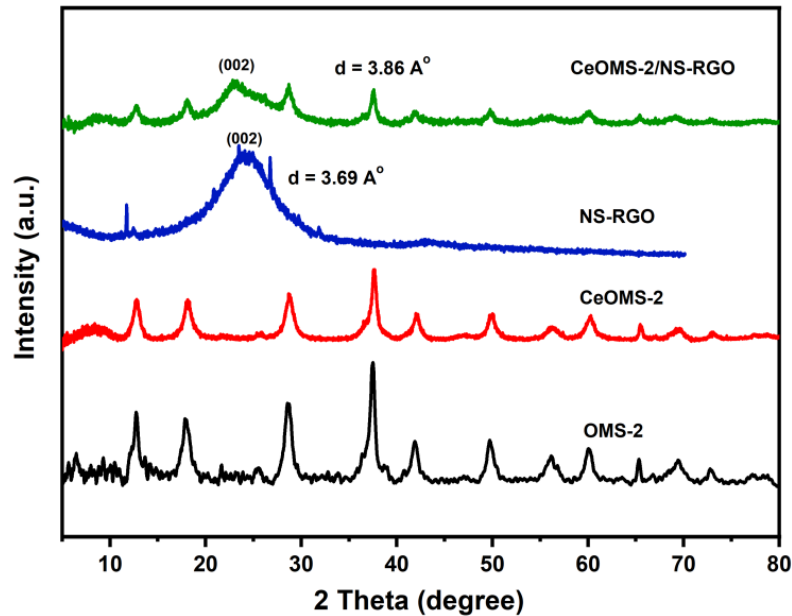


Figure 3.2: X-ray diffraction patterns of OMS-2, CeOMS-2, NS-RGO and CeOMS-2/NS-RGO

Table 3.1: Particle size and interplanar spacing of samples derived from XRD data

Sample	Crystallite size (nm)	Interplanar spacing (nm)
OMS-2	10.01	2.4
CeOMS-2	8.47	2.39
NS-RGO	0.98	3.69
CeOMS-2/ NS-RGO	7.97	3.86

The XRD diffraction patterns represented in Fig. 3.2 indicate highly crystalline nature of OMS-2 and CeOMS-2 nanorods, from sharp diffraction peaks. The introduction of Ce in OMS-2 framework led to a reduced intensity and broader peaks causing reduction in particle size from 10.01nm to 8.47 nm along with reduced interplanar spacing as shown in

Table 3.1. In contrast, the NS-RGO sample showed amorphous nature with a single, broad peak of (002) plane revealing a d-spacing of 3.69 Å, a characteristic of its disordered graphene structure due to N and bulky S heteroatom incorporation within its framework. The very small crystallite size of 0.98 nm further confirms the low degree of crystallinity and the highly disordered nature of the NS-RGO sheets. The CeOMS-2/NS-RGO nanocomposite successfully combines these two distinct structures; with its XRD pattern displaying both, the sharp peaks of the CeOMS-2 component and the broad peak of the NS-RGO. A key finding is the increase in the NS-RGO interplanar spacing from 3.69 Å to 3.86 Å within the composite, which demonstrates successful intercalation of CeOMS-2 nanorods between the graphene layers, leading to a larger separation and confirming the formation of the nanocomposite with a reduced diffracting domain size as the presence of the RGO sheets hinders the growth of the CeOMS-2 nanocrystallites. The observed changes in peak position of NS-RGO and crystallite size provide strong evidence for the successful formation of the composite material, with a strong interaction between the two components.

III. Thermal analysis

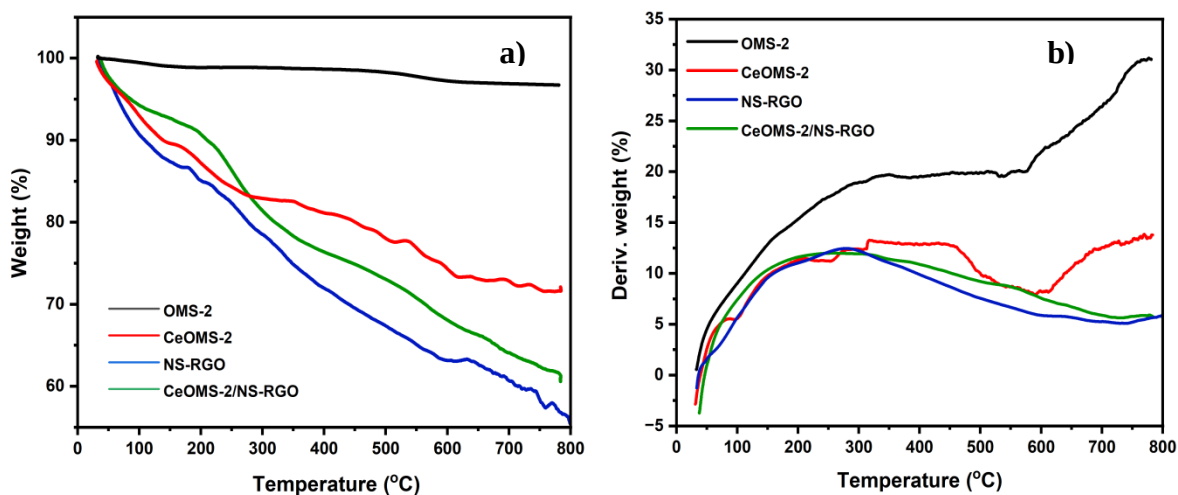


Figure 3.3: (a) Thermogram (b) Differential thermogram of OMS-2, CeOMS-2, NS-RGO, CeOMS-2/NS-RGO

The thermogravimetric analysis of samples in Fig. 3.3(a) reveal distinct thermal stability profiles. The OMS-2 sample displayed exceptional thermal stability with only 1.14% initial weight loss upto 200°C for physisorbed water molecules, with a total weight loss of 3.26% at 780°C, due to decomposition of Mn to lower oxidation states accompanying phase changes within the structure forming Mn_2O_3 as represented by a minor endotherm in

DTA plot in Fig. 3.3(b). Doping 1.5 mmol of Ce in OMS-2 caused a subtle change in thermal stability with a higher weight loss of 16.93% up to 285°C with the loss of thermally unstable oxygen groups from its structure, forming minor endotherms in the DTA plot. The higher weight loss is a clear indication of increased oxygen affinity of CeOMS-2, upon Ce doping. A further substantial weight loss with a major endotherm in the higher temperature region between 500 – 600°C was observed, accounting to decomposition or phase change in CeOMS-2 to a stable product, with 72.1% total residual weight indicating lower stability of CeOMS-2 over OMS-2. In NS-RGO, an initial major loss of 12.98% up to 160°C is observed, confirming the presence of sufficient labile oxygen groups on its surface following a gradual weight loss of 30.22%, due to thermal degradation of residual oxygen-containing functional groups (such as hydroxyl, carboxyl, and epoxy groups) and the pyrolytic decomposition of carbon framework, seen as a broad exotherm at initial temperatures followed by weak and broad endotherm at higher temperature in differential thermogram. However, the thermal stability of the nanocomposite of CeOMS-2/NS-RGO was found to be intermediate between the individual counterparts, maintaining a final residue of 61.27%. The increase in stability of the composite can be accounted to the synergistic effect of the stable CeOMS-2 framework on NS-RGO.

IV. SEM imaging

The SEM images illustrated distinct morphologies for the synthesised samples. The morphology of OMS-2 in Fig. 3.4(a) revealed one-dimensional nanorods with a relatively uniform shape and size, a characteristic of well-synthesised OMS-2 with a tunnelled structure. The nanorods appeared to be aggregated, forming larger clusters. The individual nanorods appear to have lengths of 100 to 200 nanometers with an average width of ~ 30 nm. The image in Fig. 3.4(b) displayed a potentially more agglomerated nanorods with partly bent and rough surface morphology caused by lattice distortion with incorporation of Ce in OMS-2 framework in CeOMS2 material with a reduced average width of 19.87 nm than its undoped counterpart. The morphology of CeOMS-2/NS-RGO in Fig. 3.4(c) and (d) represented large, crumpled and thin nanosheets of high surface area of RGO with uniformly anchored CeOMS-2 nanorods. While the bright spots on the surface of RGO in (c) indicate successful intercalation of CeOMS-2 nanorods which increased its interplanar spacing, confirmed from XRD results. Image (d) confirmed strong interaction between the

two components with fewer agglomerations. This composite morphology suggests a successful synthesis process that combines the properties of both components, leading to a synergistic effect for promising functional properties.

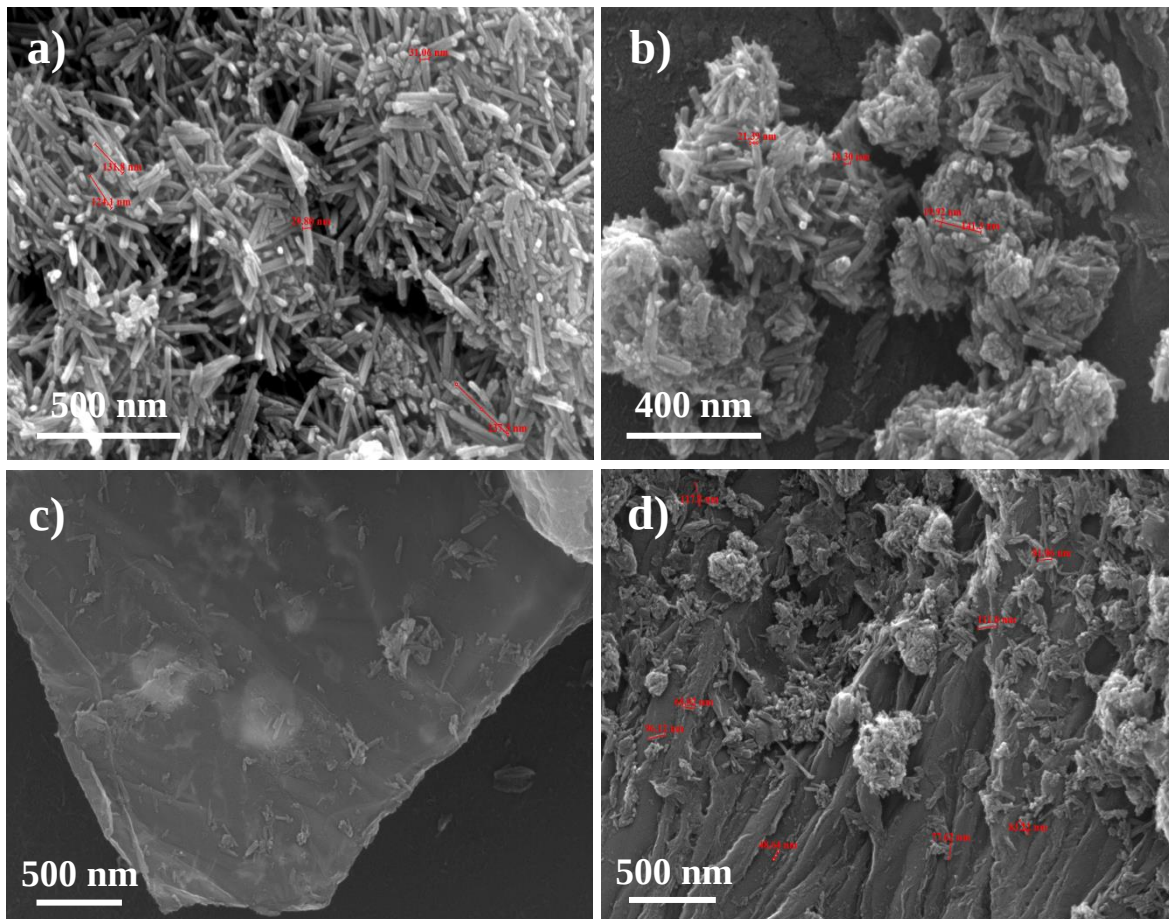


Figure 3.4: Scanning electron micrographs of (a) OMS-2 (b) CeOMS-2 (c) and (d) CeOMS-2/NS-RGO

V. N₂ Adsorption–Desorption Isotherms and Pore Structure Analysis

The N₂ adsorption–desorption isotherms for all three samples, OMS-2, CeOMS-2, and CeOMS-2/NS-RGO, in Fig. 3.5(a), (c) and (e) represent Type IV isotherm which are characteristic of mesoporous materials with pore sizes between 2 and 50 nm. However, the isotherms differ in terms of hysteresis loop obtained. The H1 type hysteresis loop in OMS-2 and CeOMS-2 indicate narrow distribution of uniform and well-defined cylindrical pores of mesoporous material. While CeOMS-2/NS-RGO nanocomposite exhibited H3 hysteresis loop, for mesoporous materials with slit-shaped pores, a characteristic of layered graphene oxide materials. This change in loop shape from H1 to H3 confirms the successful generation of slit-like porous network.

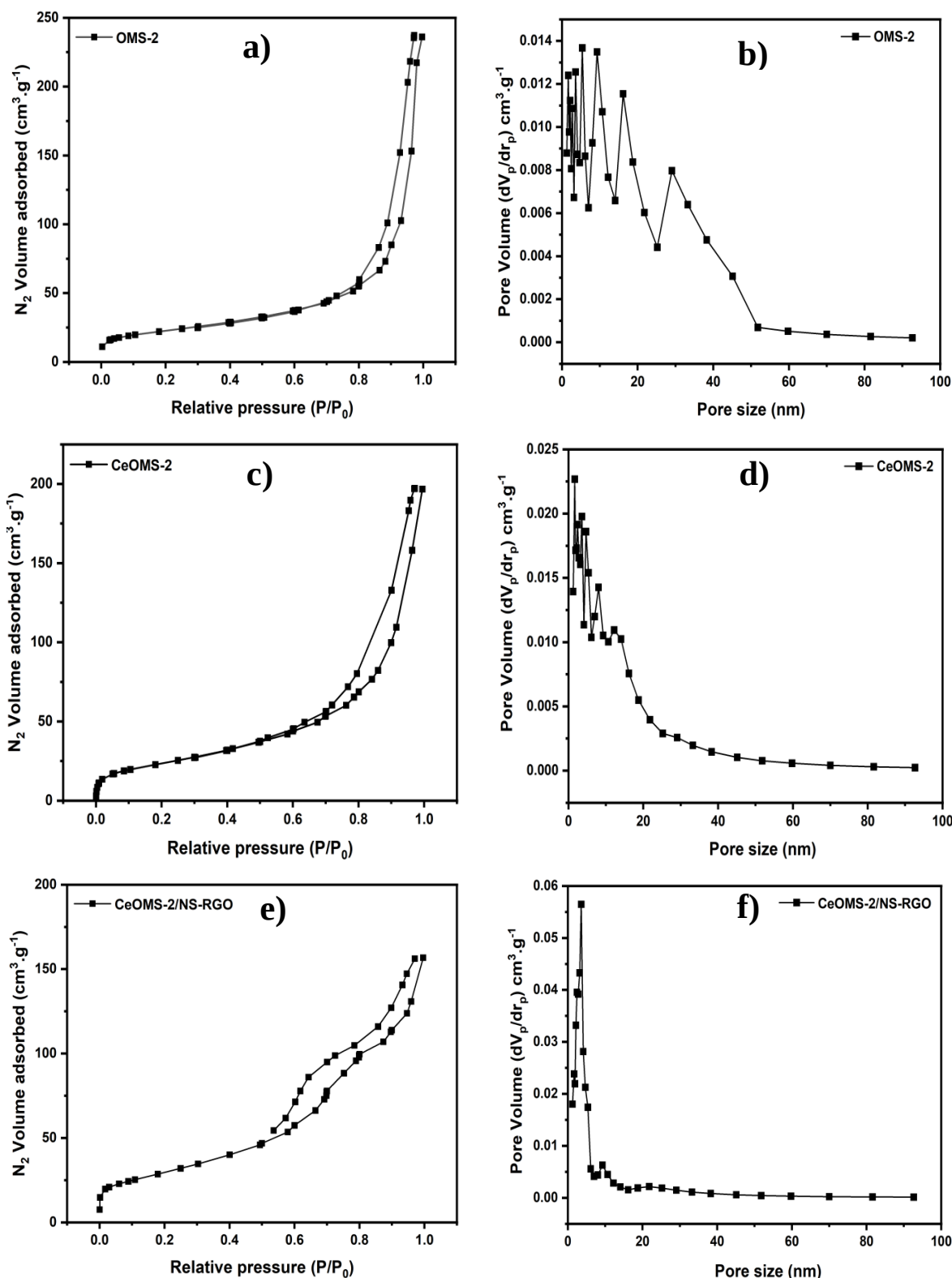


Figure 3.5: N_2 adsorption–desorption isotherms and BJH pore size distribution curves for (a) & (b) OMS-2, (c) & (d) CeOMS-2 , (e) & (f) CeOMS-2/NS-RGO, respectively.

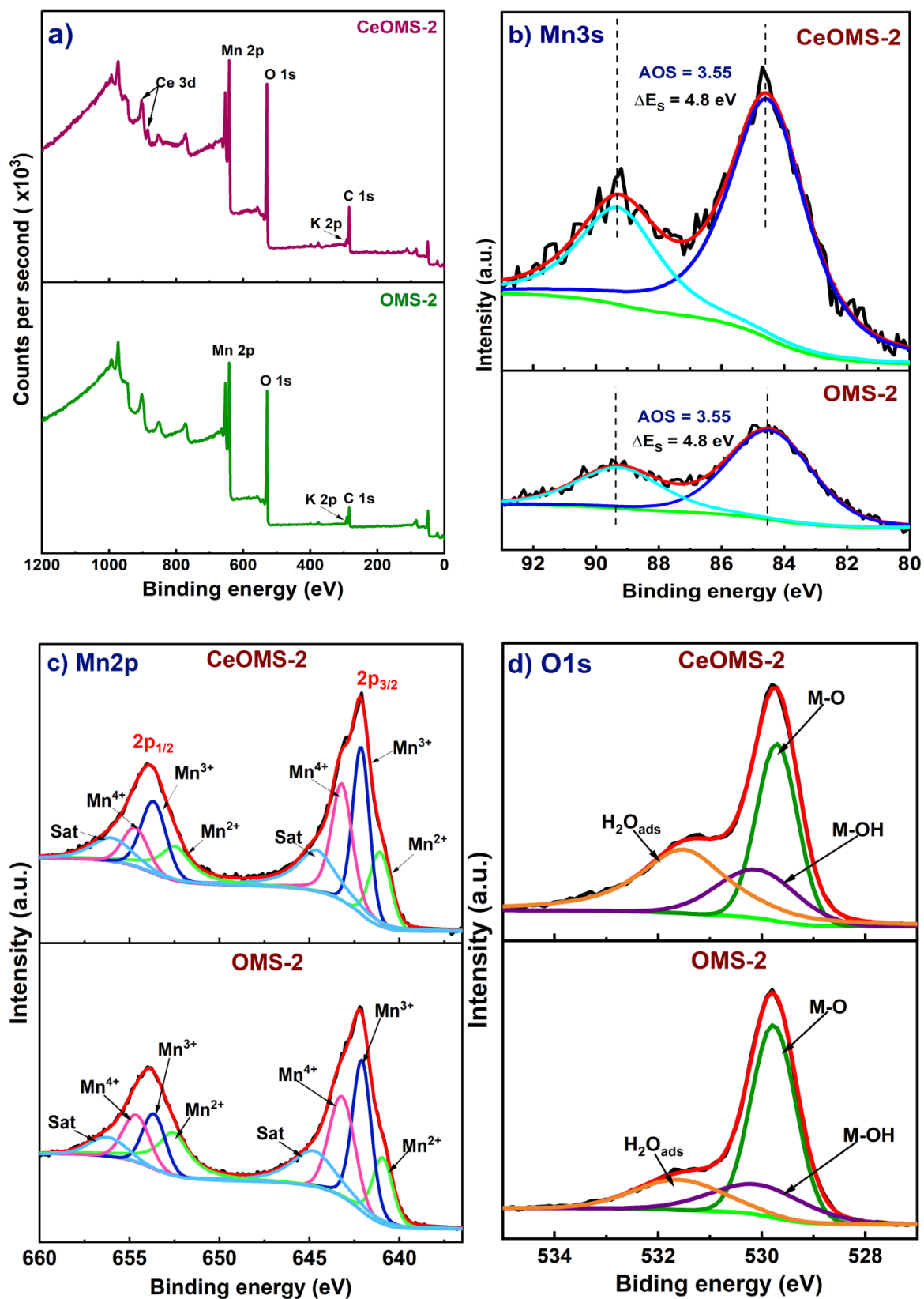
Moreover, the type IV isotherm signifies that N_2 gas adsorption involves multilayer formation and capillary condensation within the pores at higher relative pressures ($P/P_0 >$

0.4). The sharp rise in the isotherm at pressures approaching 1.0 suggests the presence of some larger inter-particle voids or macropores. This analysis is essential for understanding how the porous structure changes with material modifications. The Brunauer-Emmett-Teller (BET) surface area of OMS-2 ($79.63 \text{ m}^2.\text{g}^{-1}$) slightly increases to $82.80 \text{ m}^2.\text{g}^{-1}$ after cerium doping. In stark contrast, the addition of NS-RGO to form the CeOMS-2/NS-RGO nanocomposite leads to a dramatic increase in the BET surface area to $105.34 \text{ m}^2.\text{g}^{-1}$. This is attributed to the high surface area of the NS-RGO sheets and the creation of a new, highly accessible porous network. The N_2 adsorption-desorption isotherm for the CeOMS-2/NS-RGO composite confirms its mesoporous nature, with a pore structure of plate-like particle aggregates. The Barrett-Joyner-Halenda (BJH) pore size distribution analysis in Fig. 3.5(b), (d) and (f) provides further insights. While OMS-2 has a broad pore distribution with a primary peak at 5-10 nm, the CeOMS-2 sample shows a shift to smaller pores, confirming that cerium doping reduces pore size, with the total pore volume and pore radius decreasing significantly, from $0.3541 \text{ cm}^3.\text{g}^{-1}$ and 5.35 nm to $0.2954 \text{ cm}^3.\text{g}^{-1}$ and 1.66 nm, respectively, indicating that cerium occupies the existing pores in OMS-2. For the nanocomposite material, the BJH curve reveals a distinct change with a highly pronounced peak at 2-5 nm, demonstrating that the addition of NS-RGO primarily creates a larger number of smaller pores. Although the surface area of nanocomposite increases substantially, the total pore volume further decreases to $0.2359 \text{ cm}^3.\text{g}^{-1}$, suggesting that the NS-RGO creates a more compact structure with a high density of small pores, which is consistent with the observed H3 hysteresis loop. The pore radius for the nanocomposite is 3.59 nm, which is larger than CeOMS-2 but smaller than OMS-2, reflecting a pore size distribution influenced by the inter-particle spaces created by the NS-RGO sheets. This significant increase in density of small pores is responsible for the dramatic rise in the BET specific surface area, highlighting the successful synthesis of a highly porous material suitable for applications in energy storage.

Table 3.2: : Surface area and porosity analysis from BET and BJH plots

Sample	BET surface area [$\text{m}^2.\text{g}^{-1}$]	Pore radius [$\text{cm}^3.\text{g}^{-1}$]	Total pore volume [nm]
OMS-2	79.63	5.35	0.3541
CeOMS-2	82.80	1.66	0.2954
CeOMS-2/NS-RGO	105.34	3.59	0.2359

VI. Surface chemistry and bulk composition analysis : XPS and ICP-MS study



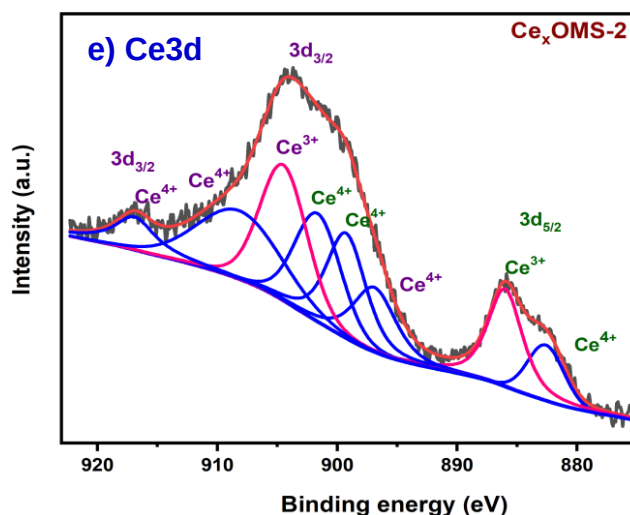


Figure 3.6: (a) XPS survey scan of OMS-2 and CeOMS-2 (b) XPS core level spectra of Mn3s (c) Mn2p (d) O1s in OMS-2 and CeOMS-2 (e) XPS core level spectra of Ce3d in CeOMS-2

The XPS survey scans in the Fig. 3.6(a) provide a comprehensive elemental analysis of the samples. The OMS-2 and CeOMS-2 show prominent peaks for manganese (Mn2p), oxygen (O1s) and potassium (K2p), confirming its composition with CeOMS-2 sample displaying distinct peaks at around 900 eV that are characteristic of cerium (Ce3d) confirming successful incorporation of Ce. The doping of Ce into OMS-2 increased intensity of the oxygen peak suggesting an increase in the surface concentration of oxygen species, likely a result of the formation of new Ce-O bonds and an increase in surface oxygen vacancies, crucial for its higher activity.

The average oxidation state (AOS) of Mn in all analyzed samples was quantified by calculating the difference in binding energy (ΔE_s) between the main and satellite peaks observed in the Mn3s core level spectra as shown in Fig. 3.6(b). The relation between ΔE_s and AOS is given by the following relation [15]:

$$\text{AOS} = 8.956 - 1.126\Delta E_s \quad \text{----- (1)}$$

The AOS of manganese in OMS-2 was determined to be 3.55 and this state was observed to remain unchanged despite Ce doping. This high AOS is attributed to the predominant presence of Mn^{4+} over Mn^{3+} . The high resolution core level Mn2p spectra in Fig. 3.6(c), represented two predominant peaks at 642.1 eV and 653.8 eV, corresponding to Mn 2p_{3/2} and Mn 2p_{1/2} sub-levels, respectively, due to spin orbit coupling in both OMS-2 and CeOMS-2. Each peak could be further deconvoluted into 4 peaks corresponding to Mn^{2+} ,

Mn^{3+} , Mn^{4+} and satellite peak at binding energy values of 640.93, 642.08, 643.19 and 644.77 eV for $2p_{3/2}$ peak and 652.57, 653.64, 654.62 and 656.21 eV for $2p_{1/2}$ peak, with slight shift in peak positions to lower energy upon Ce doping due to altered chemical environment of Mn. However, the presence of peaks for Mn^{4+} , Mn^{3+} , and Mn^{2+} indicates a mixed-valence state for manganese in both materials. The significant increase in $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio from 1.02 to 1.07, upon Ce doping as shown in Table 3.3, indicates the formation of more vacancies within OMS-2 framework. Moreover, an increase in K/Mn atomic ratio in CeOMS-2 reveals Ce occupying framework via substitution of Mn and interstices, over the tunnel sites through replacement of K^+ ions.

The O1s XPS spectra in Fig. 3.6(d) provides crucial information on the surface oxygen species, which are critical for the electrochemical performance of the samples. Each O1s spectrum is deconvoluted into three distinct components, namely lattice oxygen (O_{lat}) at 529.8 eV, oxygen vacancies (O_{vac}) at 530.2 eV and adsorbed oxygen (O_{ads}) at 531.6 eV. The Table 3.3 data confirms a notable increase in the percentage of vacancy oxygen or hydroxyl oxygen from 21.18% in pristine OMS-2 to 24.07% in CeOMS-2. This is a direct consequence of the significant ionic radius mismatch between Mn^{4+} (~53 pm) and Ce^{4+} (~97 pm), which induces lattice distortion and creates these defects. These oxygen vacancies serve as active sites that enhance the interaction with the electrolyte, facilitating faster ion diffusion and promoting the redox reactions essential for supercapacitor operation. Additionally, the higher percentage of O_{ads} in CeOMS-2 (34.77%) further indicates higher affinity towards oxygen and increase in catalytically active surface sites, collectively leading to the superior charge storage capacity and improved performance of the cerium-doped material.

The complex high resolution Ce3d XPS core spectrum for CeOMS-2 in Fig. 3.6(e) is composed of multiple peaks attributed to the spin-orbit splitting of the Ce3d core level into $3d_{5/2}$ and $3d_{3/2}$ components, as well as distinct features associated with its two dominant oxidation states, Ce^{3+} and Ce^{4+} . The $3d_{5/2}$ peak is deconvoluted into 4 peaks confirming 3+ and 4+ state of Ce, with peaks appearing at 882 eV for Ce^{3+} and at 885.4, 898.66, 901.03 eV for Ce^{4+} . Similarly, $3d_{3/2}$ peak is deconvoluted into another 4 peaks at 903.9 eV (Ce^{3+}) and 896.29, 907.57, 916.29 eV (Ce^{4+}). The peak at approximately 916 eV is a key indicator for the presence of the Ce^{4+} oxidation state. The deconvolution of the spectrum allows for the quantification of the relative concentrations of Ce^{3+} and Ce^{4+} on the material surface, which is crucial for understanding its charge storage properties, as the redox pair

of $\text{Ce}^{3+}/\text{Ce}^{4+}$ facilitates the storage and release of electrical charge through a reversible reaction, known as a pseudocapacitive mechanism. The ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$ is often correlated with the performance of the material, as the presence of Ce^{3+} ions is typically associated with the creation of oxygen vacancies, essential for ion diffusion and charge transfer. A higher $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio typically indicates a greater number of these oxygen vacancies and a higher degree of non-stoichiometry, which leads to improved ionic conductivity and more active sites for the electrochemical reactions.

Table 3.3: Elemental and Oxidation State Analysis from ICP-MS and XPS analysis

Sample	K/Mn		Ce/Mn		$\frac{\text{Mn}^{3+}}{\text{Mn}^{4+}}$	$\frac{\text{Ce}^{3+}}{\text{Ce}^{4+}}$	O_{ads}	O_{vac}	O_{lat}
	ICP-MS	XPS	ICP-MS	XPS					
OMS-2	0.0778	0.0331	--	--	1.02	--	22.78	21.18	56.04
CeOMS-2	0.1067	0.039	0.031	0.1688	1.07	0.4092	34.77	24.07	41.16

3.3.2 Electrochemical evaluation of charge storage capacity of CeOMS-2/NS-RGO nanocomposite as a hybrid supercapacitor

I. Effect of electrolyte

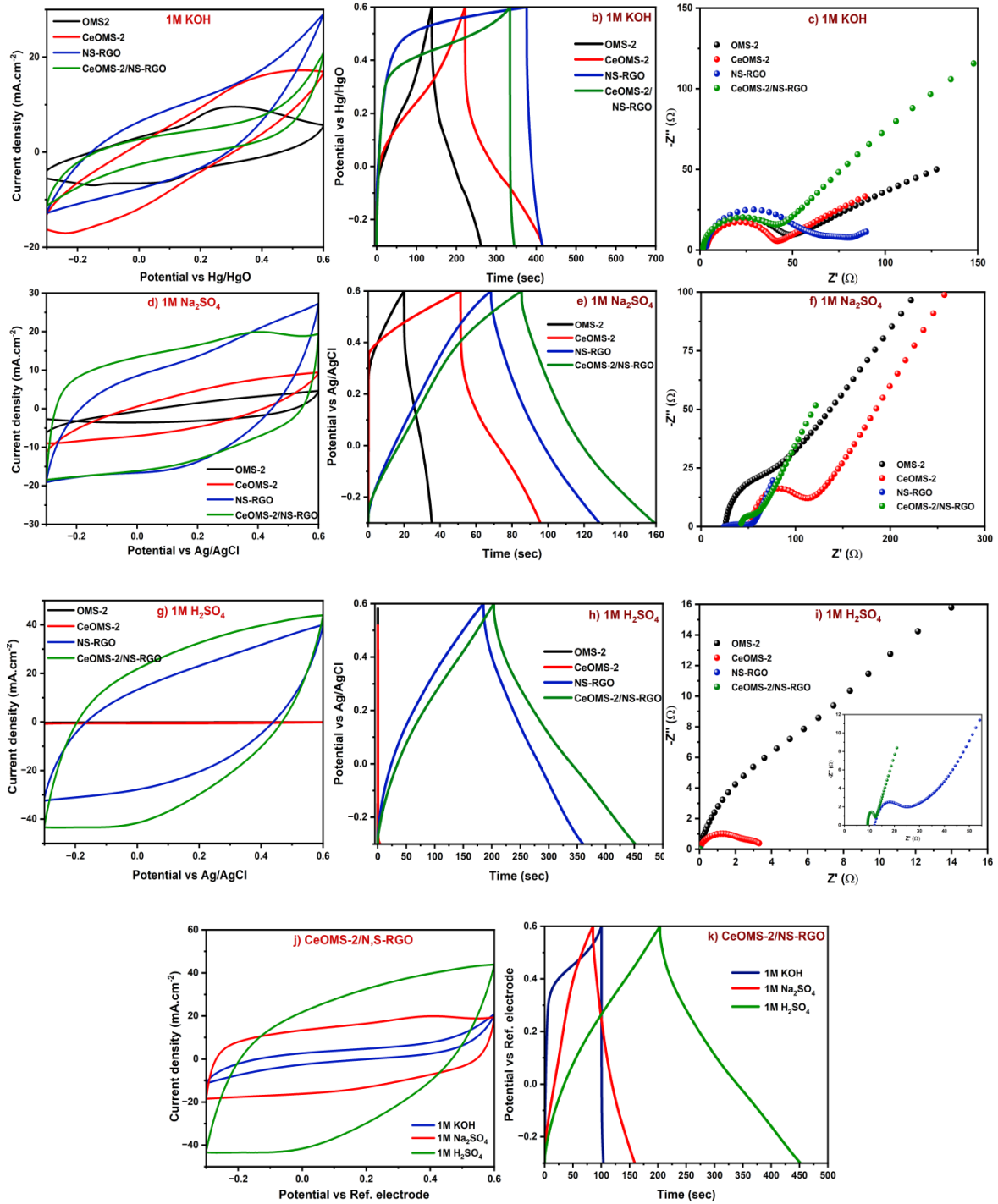


Figure 3.7: (a) CV at 50 mV.s⁻¹ (b) GCD at 1A.g⁻¹ (c) Nyquist plot recorded in 1M KOH electrolyte, (d) CV at 50 mV.s⁻¹ (e) GCD at 1A.g⁻¹ (f) Nyquist plot recorded in 1M Na₂SO₄ electrolyte, (g) CV at 50 mV.s⁻¹ (h) GCD at 1A.g⁻¹ (i) Nyquist plots recorded in 1M H₂SO₄

electrolyte of OMS-2, CeOMS-2, NS-RGO and CeOMS-2/NS-RGO, (Inset : Magnified Nyquist plot of NS-RGO and CeOMS-2/NS-RGO) (j) Comparative CV and (k) Comparative GCD profile of CeOMS-2/NS-RGO in 1M H₂SO₄, 1M Na₂SO₄ and 1M KOH electrolyte.

The supercapacitive performance of the OMS-2 family of materials and nanocomposite (OMS-2, CeOMS-2, NS-RGO, and CeOMS-2/NS-RGO) was rigorously evaluated across three distinct electrolytes (1M KOH, 1M Na₂SO₄ and 1M H₂SO₄) within a fixed potential window of -0.3 to 0.6V to elucidate the role of Ce doping, NS-RGO composite formation, electrolyte effects and kinetic factors on the charge storage mechanism through CV, GCD and EIS techniques.

i. Performance in alkaline electrolyte (1M KOH)

The comparative assessment of cyclic voltammograms at 50 mV.s⁻¹ and their respective galvanostatic charge – discharge profiles at 1A.g⁻¹ recorded within a potential window of -0.3 to 0.6V are shown in Fig. 3.7(a) and (b), respectively and their graphical evaluation in Table 3.4, which revealed the favourability of alkaline environment towards pseudocapacitive behaviour of OMS-2 and CeOMS-2 over their NS-RGO supported forms, due to mixed-valence state for both manganese (Mn³⁺/Mn⁴⁺) and cerium (Ce³⁺/Ce⁴⁺) represented by redox peaks in CV and quasi- linear shaped GCD curve which facilitated easier electron transport within the electrode material, reducing its internal resistance and allowing for faster charge-discharge rates. Moreover, the ability of K⁺ ions from electrolyte to intercalate within the tunnelled structure of OMS-2 also serves as a charge storage mechanism with less structural disruption as shown in below equation:



The incorporation of Ce in OMS-2 led to an enhanced surface redox pseudocapacitance arising from increased lattice defects due to differences in ionic sizes of Mn (0.53 Å) and Ce ions (0.97 Å). The Ce ions created oxygen vacancies (from XPS) and higher surface area (from BET), which facilitated easy K⁺ ion mobility and reaction kinetics with lowered charge transfer resistance in Fig. 3.7(c). In contrast, the charge storage capacity of NS-RGO and nanocomposite of CeOMS-2/NS-RGO reduced in such high pH environment due to deprotonation of nitrogen and sulfur functional groups on the RGO surface which created a negatively charged surface that electrostatically repelled the negatively charged

OH^- anions in the electrolyte, hindering the efficient formation of the electrical double layer and impeding the access of electrolyte ions (K^+) to the CeOMS-2 active sites. The lowest charge transfer resistance in nanocomposite indicates kinetic superiority with limited storage.

ii. Performance in neutral electrolyte (1M Na_2SO_4)

The electrochemical performance of the synthesised materials in 1M Na_2SO_4 is generally characterized by lower charge storage capacity but potentially greater stability compared to the alkaline (KOH) electrolyte due to the lower intrinsic ionic conductivity and the presence of larger, less kinetically active ions (Na^+ and SO_4^{2-}) being less favourable for pseudocapacitance than K^+ and OH^- ions, which is evident from comparatively smaller CV integral area and shorter discharge times in GCD in Fig. 3.7(d) and (e) and Table 3.4 data. These ions with larger hydrated radii and lower ionic mobility makes ion insertion/adsorption into the mesoporous OMS-2 and CeOMS-2 more difficult and slower, resulting in a significantly lower diffusion rate, thereby reducing their capacitance and rate capability. This kinetic impediment is quantitatively observed in the Nyquist plots with a higher charge transfer resistance (in Fig. 3.7(f)) than in KOH. However the NS-RGO supported CeOMS-2 nanocomposite exhibited a lowest R_{ct} of $15.89\ \Omega$ and a steep low-frequency slope indicating rapid diffusion of the Na^+ electrolyte ions within the porous structure, leading to favorable rate capability. Despite an overall performance drop in the neutral medium the CeOMS-2/NS-RGO composite maintains its rank as the best-performing material with a gravimetric specific capacitance of $82\ \text{F.g}^{-1}$, over 55.78 and $39.38\ \text{F.g}^{-1}$ in NS-RGO and CeOMS-2, respectively, validating the structural and synergistic advantages afforded by the metal oxide/ NS-RGO combination, irrespective of the less favorable electrolyte environment.

iii. Performance in acidic electrolyte (1M H_2SO_4)

The supercapacitance of the materials measured in 1M H_2SO_4 displayed a stark difference in their charge storage mechanism in CV and GCD profile in Fig. 3.7 (g) and (h) and Table 3.4. The OMS-2 and CeOMS-2 exhibited much lower specific capacitance and stability in acidic electrolytes (H_2SO_4) compared to neutral (Na_2SO_4) or alkaline (KOH) electrolyte. As in acidic media, the potential window for OMS-2 is severely limited due to the corrosion or dissolution of the oxide material, which ultimately reduced the stored energy and its capacitance. The metal reduction and dissolution in strong acid, forming soluble

Mn^{2+} ions, degrades the electrode thus limiting its long-term stability. While the high conductivity of high surface area NS-RGO, the faradaic reactions at the heteroatom sites and its excellent compatibility with H^+ ions boosts the total capacitance of RGO. In an acidic electrolyte, the nitrogen and sulfur atoms on the RGO surface can become protonated (e.g., forming $-\text{NH}_3^+$, $-\text{SH}_2^+$) which creates a positively charged surface that can attract anions (e.g., SO_4^{2-}) from the electrolyte, enhancing the double-layer capacitance and also act as redox active centres contributing towards pseudocapacitance.

The H_2SO_4 electrolyte provides superior ionic conductivity, leveraging small H^+ ions for rapid ion transport and penetration. The N,S-RGO support is critical, overcoming the poor native conductivity of CeOMS-2 to accelerate electron transfer. This synergy promotes optimal kinetic control, favoring the desired reversible pseudocapacitive reaction ($\text{MnO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{MnOOH}$) while simultaneously mitigating MnO_2 dissolution. The excellent conductivity ensures that charge transfer occurs rapidly across the entire active surface, preventing localized accumulation of charge or potential, which can trigger the unwanted degradation reactions. Electrochemical impedance spectroscopy validates these kinetics, showing an extremely low R_{ct} of $7.292 \, \Omega$ (Fig. 3.7(i)), signifying fast charge transfer and high active material accessibility. This performance leads to the longer discharge time yielding maximum specific capacitance of $275.56 \, \text{F} \cdot \text{g}^{-1}$, a substantial improvement over the highly resistive ($R_{\text{ct}} > 2000 \, \Omega$) unsupported material.

Reportedly, Carlson et al. [16] showed a highly selective response of the $\alpha\text{-MnO}_2$ structure to charge-carrying ions, which is also clearly seen when comparing H^+ , Na^+ , and K^+ ions in above observations. The H^+ ion is optimal because it participates in a stable pseudocapacitive redox reaction (Mn-OH bond formation), providing a strong thermodynamic driving force that is highly efficient, and avoids the need for transporting large solvation shells, and ensures the best structural stability. Conversely, the larger Na^+ and K^+ ions must intercalate into the $[2 \times 2]$ tunnels via a mechanism that involves the transport of large, solvated ions. For these larger cations, co-inserted water molecules cause significant destabilization by crowding and physically displacing the ions from their favorable crystallographic sites [16]. This steric and kinetic hindrance results in poor ion mobility and reduced accessible capacity, along with the high structural stress that ultimately leads to the rapid capacity fade as observed in electrodes operating in Na^+/K^+ -based electrolytes. This analysis definitively establishes the critical role of electrolyte chemistry in governing the energy storage mechanism within the OMS-2 architecture (Fig.

3.8). While the native and Ce-doped OMS-2 rely on K^+ intercalation for charge storage in alkaline media, the introduction of N,S-RGO fundamentally engineers the electrode-electrolyte interface. This strategic modification optimally promotes H^+ -based pseudocapacitance in an acidic environment, a stark contrast to the sluggish ion kinetics and unfavorable surface interactions observed in KOH (Fig. 3.7(j) and (k)). Consequently, the CeOMS-2/N,S-RGO nanocomposite based hybrid supercapacitor harnesses a synergistic mechanism from Ce-enhanced Mn redox-based pseudocapacitance providing high energy density, while the N,S-RGO contributing excellent power density through heteroatom-induced pseudocapacitance and EDLC properties. This mechanistic optimization in acidic electrolyte yields a high-performance material with significant practical applicability for advanced energy storage solutions.

Table 3.4: Electrochemical performance metrics in different electrolytic conditions

	Cs (1M KOH)			Cs (1M Na ₂ SO ₄)			Cs (1M H ₂ SO ₄)		
Sample	CV at 50 mV.s ⁻¹	GCD at 1 A.g ⁻¹	R _{ct} (Ω)	CV at 50 mV.s ⁻¹	GCD at 1A.g ⁻¹	R _{ct} (Ω)	CV at 50 mV.s ⁻¹	GCD at 1A.g ⁻¹	R _{ct} (Ω)
OMS-2	134.78	137.34	37.86	36.67	17.52	58.25	2.59	2.91	5794.39
CeOMS-2	267.78	216.89	33.53	101.04	39.38	54.12	11.47	2.34	2024
NS-RGO	57.86	44.22	61.64	75.56	66.93	28.58	201.71	194.28	10
CeOMS- 2/NS- RGO	3.76	4.75	37.79	128.44	82	15.89	275.56	275.56	7.292

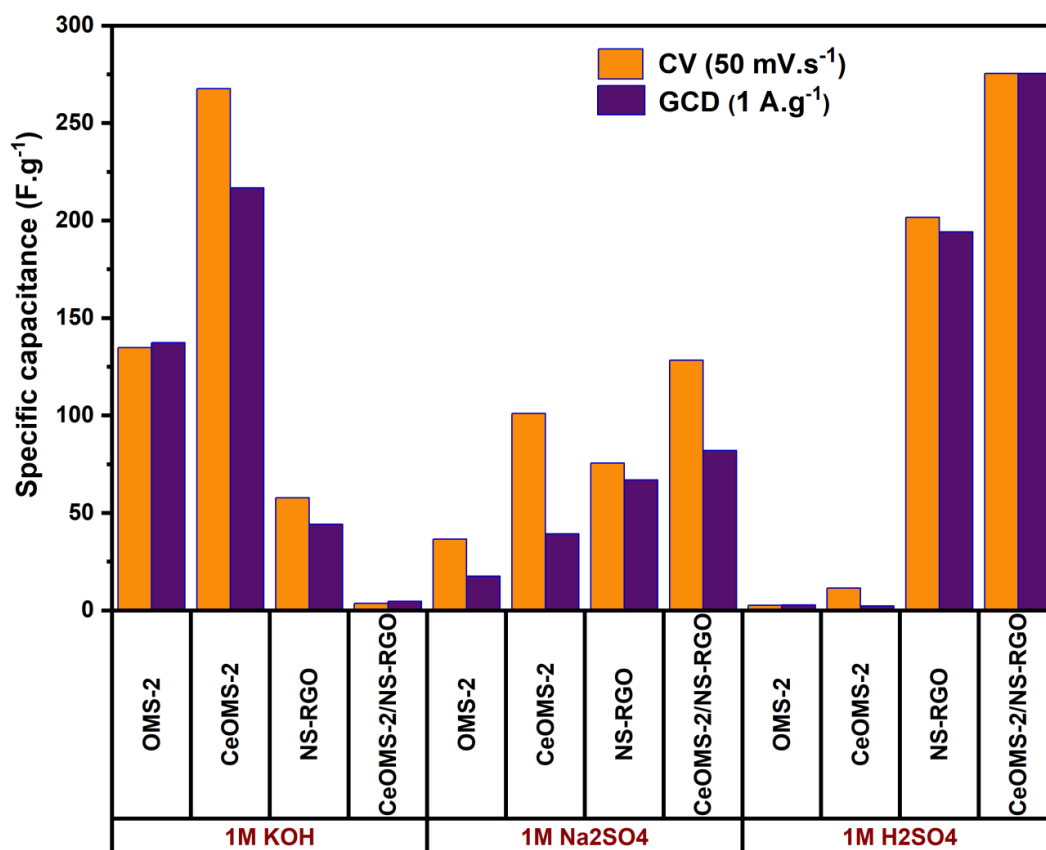


Figure 3.8: Comparison of specific capacitance results, displaying the dramatic electrolyte-dependent performance shift for the synthesised materials

II. Effect of scan rate and current density on supercapacitive performance of CeOMS-2/NS-RGO nanocomposite

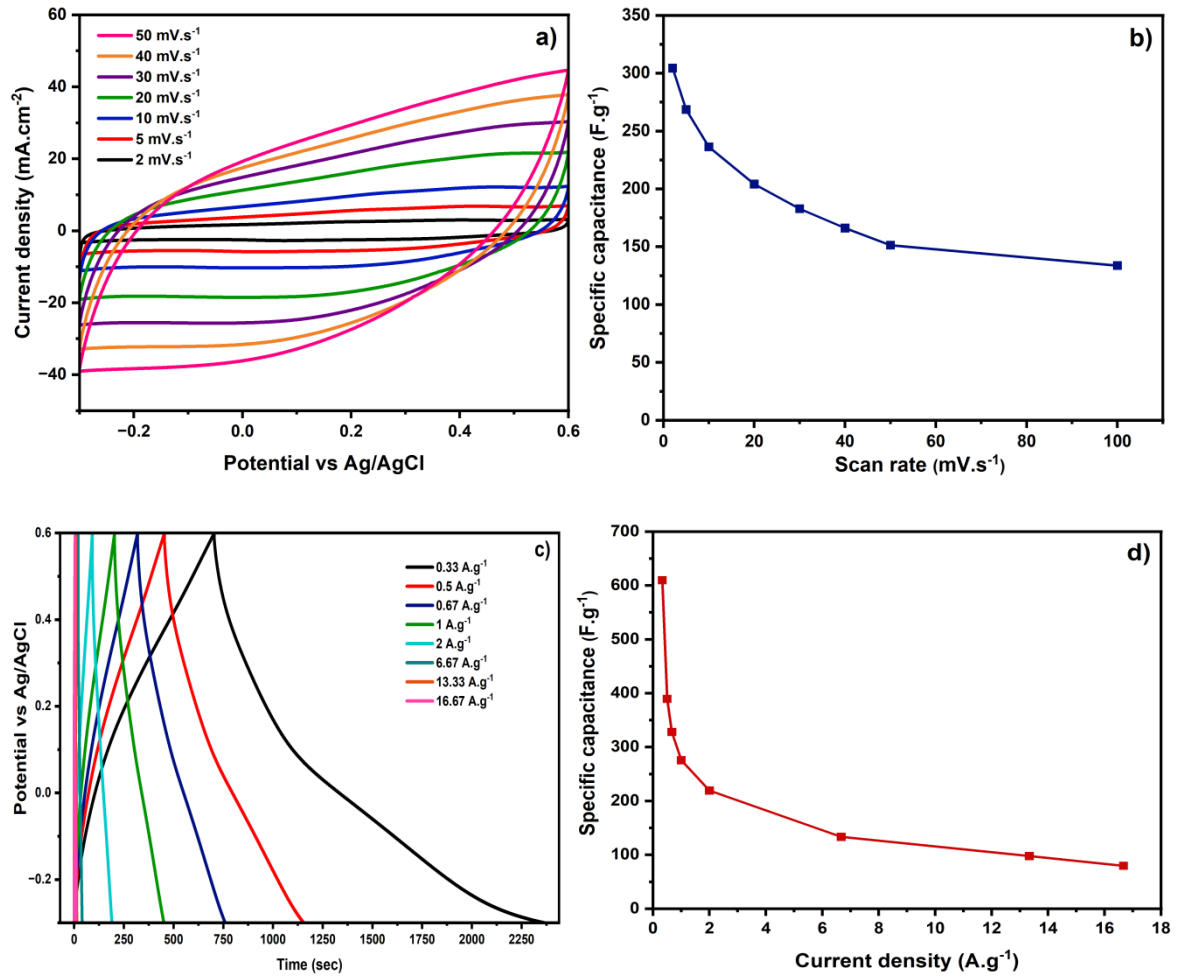


Figure 3.9: (a) CV of CeOMS-2/NS-RGO recorded at varying scan rates in 1M H₂SO₄ electrolyte between -0.3 to 0.6 V (b) Specific capacitance as a function of scan rate (c) GCD profile of CeOMS-2/NS-RGO recorded in 1M H₂SO₄ at varying current densities between 0.3 to 0.6 V (d) Specific capacitance as a function of current density

The supercapacitance of CeOMS-2/NS-RGO was analysed by recording CV at multiple scan rates from 2 to 50 mV.s⁻¹ within a potential window of -0.3V to 0.6V in 1M H₂SO₄. The specific capacitance (C_s) of the samples in F.g⁻¹ was calculated from the integral area of obtained CV using the formula:

$$C_s = \frac{\int Idv}{\Delta V * m * v} \quad \text{----- (3)}$$

Here, the integral ($\int Idv$) represents the area of the CV curve, which corresponds to the total charge stored. This value is then normalized by dividing it by the product of the mass

of active material on working electrode (m) in g, the potential scan rate (v) in $V.s^{-1}$, and the working potential window (ΔV) in volts.

The Fig. 3.9(a) demonstrated excellent rate capability with the CV curves maintaining a quasi-rectangular shape and discernible redox features even at the highest scan rates, signifying a highly reversible and kinetically fast charge storage mechanism. From Fig. 3.9 (b), a maximum specific capacitance of $304.33 F.g^{-1}$ is recorded at the slowest scan rate ($2 mV.s^{-1}$). This low rate allows optimal ion diffusion, maximizing the contribution from bulk pseudocapacitance. Despite increasing the scan rate to $50 mV.s^{-1}$, the electrode retains a significant suercapacitance of $151.33 F.g^{-1}$ ($\sim 50\%$ retention). This robust performance at high rates is a testament to the synergistic effect of the conductive N,S-RGO scaffold, which minimizes kinetic limitations and ensures the storage mechanism is dominated by fast surface-controlled pseudocapacitance and EDLC, enabling high-power operation.

Similarly the GCD curves were recorded within the identical potential window in 1M H_2SO_4 at varying current densities of 0.33, 0.5, 0.67, 1, 2, 6.67, 13.33, 16.67 $A.g^{-1}$. The specific capacitance of each electrode was calculated from the GCD curves using the relation:

$$C_s = \frac{I \times \Delta t}{\Delta V * m} \text{ ----- (4)}$$

Here, I is the discharge current density ($mA.cm^{-2}$), Δt is the discharge time (s), ΔV is the potential window (V) and m is the mass of the electroactive material (g). This formula enabled the quantitative analysis of the charge storage capacity of the material.

The profiles in Fig. 3.9 (c) confirmed the high reversibility and efficient capacitive storage, exhibiting near-linear, symmetric triangular shapes with minimal IR drop and longer discharge times across all rates. The rate capability plot in Fig. 3.9(d) showed a maximum specific capacitance of $609.62 F.g^{-1}$ at the lowest current density ($0.33 A.g^{-1}$), where full utilization of pseudocapacitive sites is achieved. At the very high rate of $16.67 A.g^{-1}$, it reduced to $79.64 F.g^{-1}$. This retention in specific capacitance, even at extreme rates, highlights the robust power density of the nanocomposite. The N,S-RGO scaffold lowered resistance for rapid electron transport and minimized kinetic limitations, which sustained performance even under high-rate operation.

III. Optimisation of CeOMS-2/NS-RGO nanocomposite for high performance hybrid supercapacitor

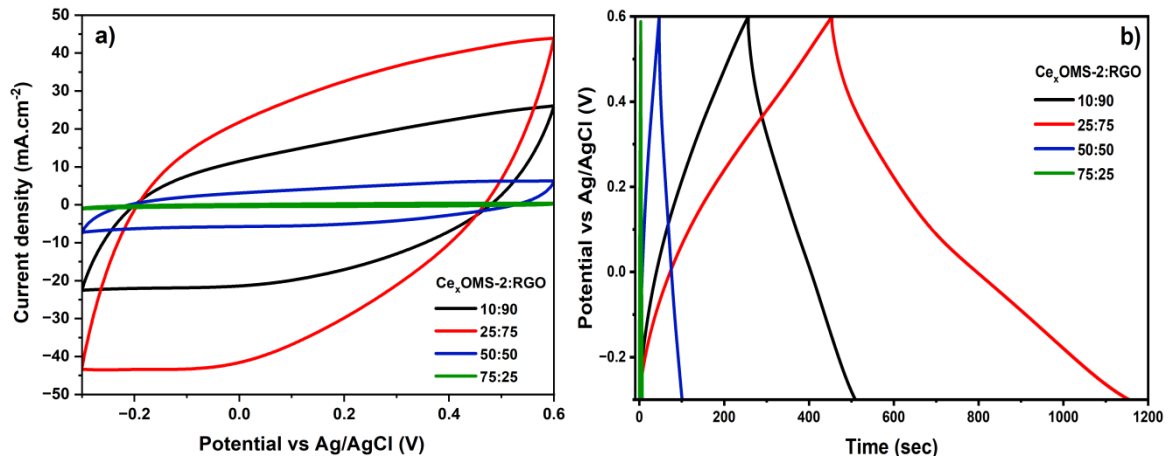


Figure 3.10: (a) CV (b) GCD profile of CeOMS-2/NS-RGO at varying optimisation ratio

The optimisation of the nanocomposite as a hybrid capacitor is essential to harness the pseudocapacitance of energy dense CeOMS-2 nanorods with NS-RGO of high power density in order to overcome the conductivity and kinetic limitations of CeOMS-2 while maximizing the total active mass for charge storage. To identify the ideal synergistic proportions of CeOMS-2 and NS-RGO for fabricating this hybrid supercapacitor, electrochemical evaluation of the nanocomposites with varying ratio of CeOMS-2 and NS-RGO (10:90, 25:75, 50:50, 75:50) was performed by analysing their CV and GCD patterns.

Table 3.5: Summary of electrochemical optimization results showing specific capacitance values for CeOMS-2:NS-RGO composites across four mass ratios of CeOMS-2 and NS-RGO.

CeOMS-2:NS-RGO (x:y)	Specific capacitance (F.g^{-1})	
	CV (50 mV.s^{-1})	GCD (0.5 A.g^{-1})
0:100	201.71	259.42
10:90	149.63	140.39
25:75	275.56	389.33
50:50	42.25	30.06
75:25	10.24	4.05
100:0	11.47	4.27

The analysis of the CV (Fig. 3.10(a)) and GCD (Fig. 3.10(b)) curves and the derived specific capacitance from Table 3.5 conclusively identifies the 25:75 ratio as the optimal composition, as it uniquely provides the largest CV area and the longest discharge time (1155 seconds), directly correlating to the maximum specific capacitance. While the 10:90 ratio also exhibits good reversibility and low iR drop due to its high NS-RGO content, its overall capacity is limited because it lacks sufficient CeOMS-2 active material. Conversely, composites rich in CeOMS-2 (e.g., 50:50 and 75:25) suffer from high internal resistance and poor ion kinetics, which causes a drastic drop in the CV area and discharge time. Thus, the 25:75 ratio successfully maximizes the utilization of the pseudocapacitive active material while providing sufficient NS-RGO to overcome the kinetic bottleneck of the metal oxide.

IV. Durability test

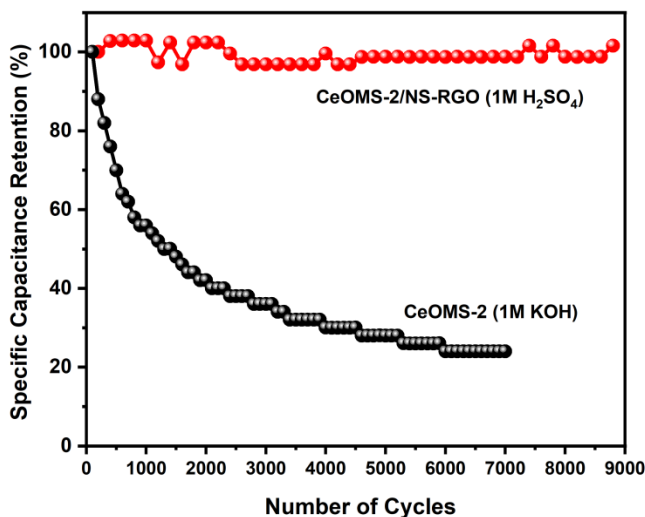


Figure 3.11: Durability test of CeOMS-2/NS-RGO in 1M H₂SO₄ and CeOMS-2 in 1M KOH

The graph in Fig. 3.11 effectively displays the cyclic stability of the pristine CeOMS-2 material in 1M KOH against the optimized CeOMS-2/N,S-RGO composite in 1M H₂SO₄. The CeOMS-2/N,S-RGO composite in 1M H₂SO₄ exhibits outstanding stability, retaining consistently above 95% (101.6%) capacity over 8000 cycles. This near-perfect retention is achieved because the N,S-RGO scaffold provides structural support, inhibiting active material dissolution, while the acidic electrolyte facilitates a highly reversible H⁺-based

pseudocapacitance mechanism. Conversely, the pristine CeOMS-2 electrode in 1M KOH shows catastrophic decay, retaining only 24% capacitance after 7000 cycles. This poor performance is due to the compromised stability of the metal oxide in the alkaline environment upon prolonged cycling, which promotes active material dissolution and irreversible structural degradation from K^+ intercalation. Thus, the data conclusively proves that both, conductive optimised composite structure and the acidic electrolyte are critical for achieving long-term operational stability for its practical application.

V. Ragone plot

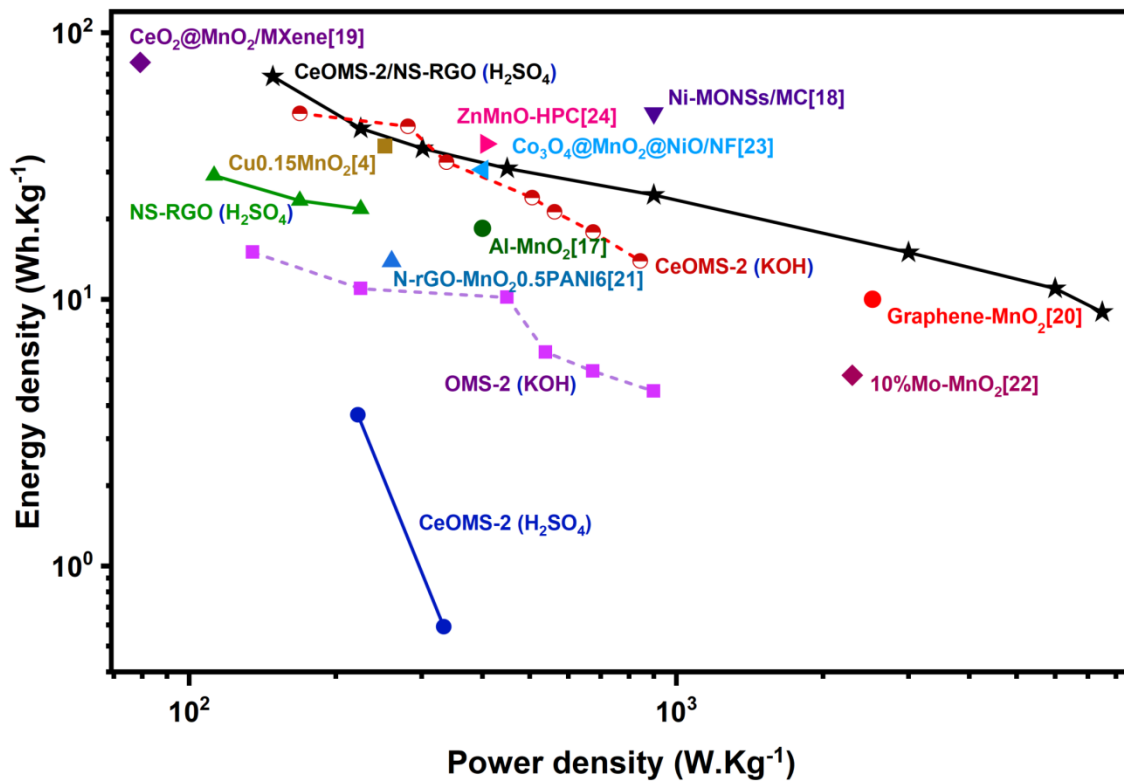


Figure 3.12: Ragone plot of energy density vs. power density under acidic and alkaline electrolytic conditions

The practical viability of the supercapacitor electrodes is determined by the relationship between their deliverable energy density and power density, as summarized in the Ragone plot in Fig. 3.12. In this study, these metrics were determined using a three-electrode cell assembly to establish the intrinsic performance limits of the active materials across various discharge rates, providing a primary benchmark for their viability in future device fabrication.

The CeOMS-2/NS-RGO nanocomposite emerged as the optimal material in H₂SO₄ electrolyte, demonstrating a peak specific energy of 68.58 Whkg⁻¹ at a power density of 148.5 W.kg⁻¹ with a superior rate capability and maintaining a superior specific energy up to 8.96 Whkg⁻¹ with a power density of 7.5 kW.kg⁻¹ due to its rich pseudocapacitive contribution from the Ce modified OMS-2 phase, facilitated by an open, porous structure and the highly conductive NS-RGO scaffold, which acts as a robust, low-resistance electron pathway, simultaneously minimizing ion diffusion distances to the active material.

This excellent performance stemmed from a synergistic architecture confirmed from the results significantly surpassing those of the individual components, such as NS-RGO, a high-power EDLC and bare OMS-2, a moderate-power pseudocapacitor. The key to its high energy density is the Ce-doping in OMS-2, which introduced structural defects and introduced a higher ratio of the active Mn³⁺/Mn⁴⁺ redox pair with a greater concentration of oxygen vacancies which enhanced the metal oxide's intrinsic charge storage capacity. The influence of the electrolyte reveals a complex interplay, wherein bare CeOMS-2 achieves a 13.6 times higher energy density of 50 Whkg⁻¹ at a power density of 168.75 W.kg⁻¹ in KOH than in H₂SO₄ suggesting a better kinetic interaction of OH⁻ ions with the bare oxide. While, the incorporation of the highly conductive NS-RGO network dramatically shifts the advantage to the acidic electrolyte. This dramatic change validates the NS-RGO's crucial role in rapidly channelling electrons through its high BET surface area and optimized pore structure along with its efficient ion accessibility in the acidic medium which ultimately outweighs the OH⁻ ions kinetic advantage on the bare oxide, resulting in the overall best-in-class performance of CeOMS-2/NS-RGO composite.

Collectively, the data confirms that the CeOMS-2/NS-RGO material effectively bridges the performance gap between high-energy batteries and high-power conventional capacitors. While full-cell device fabrication remains a subject for future study, the obtained results validate its potential as a high-performance electrode being highly competitive with various reported hybrid materials [4,17–24] and occupying a significantly higher region in Ragone plot, for advanced energy storage applications.

3.4 Conclusions

1. A novel CeOMS-2/NS-RGO nanocomposite hybrid supercapacitor was successfully synthesized using a cost-effective and scalable reflux-based precipitation method, followed by simple solution mixing of the two components, thus overcoming the limitations of less scalable solvothermal techniques in previous studies.
2. Comprehensive structural analysis confirmed the successful incorporation of cerium into OMS-2 lattice creating more redox centres and vacancies alongwith the formation of its composite with NS-RGO.
3. X-ray Diffraction and Scanning Electron Microscopy confirmed a synergistic morphology where CeOMS-2 nanorods were successfully anchored onto and between the crumpled NS-RGO nanosheets, resulting in an increased interplanar spacing of NS-RGO from 3.69 to 3.86 Å.
4. The unique structure led to a dramatic improvement in material properties, including a high BET surface area of 105.34 m².g⁻¹ and the creation of a slit-like mesoporous network (H3 hysteresis loop), which is ideal for efficient electrolyte ion transport.
5. XPS analysis confirmed a higher ratio of the active Mn³⁺/Mn⁴⁺ redox pair and a greater concentration of oxygen vacancies upon Ce doping which are essential for enhanced pseudocapacitive kinetics.
6. Electrochemical evaluation demonstrated that the incorporation of the highly conductive NS-RGO network dramatically shifted the optimal performance of the material to the acidic (1M H₂SO₄) electrolyte.
7. The optimized CeOMS-2/NS-RGO composite achieved a highest energy density of 68.58 W.h.kg⁻¹ at 148.5 W.kg⁻¹ power density with superior rate capability and excellent cyclic stability in 1M H₂SO₄, significantly outperforming the individual CeOMS-2 (a moderate-power pseudocapacitor) and NS-RGO (a high-power EDLC) components in a three-electrode cell assembly.
8. This work provides a successful framework for the rational design of high-performance, cost-effective hybrid electrode material for next-generation supercapacitors by leveraging the synergistic effects of metal oxide doping and heteroatom-decorated carbon supports.

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CHAPTER IV

STRATEGIES FOR Ni DOPING TOWARDS BIFUNCTIONAL AND ENHANCED CATALYTIC ACTIVITY OF OMS-2 FOR ELECTROCHEMICAL ENERGY CONVERSION

Chapter 4

Strategies for Ni Doping Towards Bifunctional and Enhanced Catalytic Activity of OMS-2 for Electrochemical Energy Conversion

4.1 Introduction

The escalating global demand for sustainable energy, driven by the imperative to mitigate CO₂ emissions and the subsequent calamitic changes associated with global warming, has spurred intensive research into high-efficiency electrochemical systems [1–4]. Among the promising candidates, Fuel Cells and Electrolytic Water Splitting stand out as key technologies for energy conversion and storage. The efficiency and widespread adoption of both systems, however, are fundamentally limited by the sluggish kinetics of their core electrochemical reactions like the Methanol Oxidation Reaction (MOR) at the anode of Direct Methanol Fuel Cells (DMFC), and the Oxygen Evolution Reaction (OER) at the anode of water electrolyzers [5,6].

Methanol being an attractive biomass fuel for energy storage and conversion, is safer than gasoline and natural gas. It is easy to store and transport, and can be sustainably produced (including via CO₂ reduction). With a very high energy density, it is a competitive new energy source. Its energy is released through its oxidation reaction, a key anodic process in DMFC [7]. This anodic methanol oxidation reaction requires a robust catalyst, typically Pt/C, being the benchmark catalyst. Unfortunately, this system is inherently flawed as the Pt active sites are blocked by carbon monoxide (CO) intermediates of MOR, diminishing its performance, while the carbon support corrodes at high voltages, leading to catalyst detachment and stability failure. Achieving successful DMFC commercialization necessitates the urgent exploration of cost-effective electrocatalysts offering both high performance and exceptional operational stability for MOR [8]. Alloying Pt with other diverse metal elements like Ru, Pd, Au, Ni, Co, Cu have been found to be a fruitful solution in improving its efficiency for MOR by modulating electronic structure of Pt for

reducing CO adsorption strength and facilitating its oxidation by oxygenated species (OH^-) produced via dissociative adsorption of water molecules at a lower potential via ligand and strain effect [8]. Moreover to attain maximum utilization efficiency and minimum platinum usage, various carbon and non-carbon based functionalised conductive supports have been utilised to obtain higher catalytic activity with long term stability [9]. However, its high cost and scarcity invokes a pressing need for low-cost alternative catalysts. Transition metals and their oxides are attractive replacements though less competitive than Pt, being abundant, inexpensive, and easily available. Their use is further motivated by their favorable stability, dynamic active sites and large surface area, which enhance catalytic activity in various energy-related reactions [10–18]. While methanol oxidation is easier to initiate in acidic media, it strictly requires expensive noble metal catalysts. Non-noble metal catalysts are unstable and easily dissolve in acid. Conversely, MOR in alkaline media is highly advantageous as it offers better oxidation kinetics, less toxicity and easier polarization. Crucially, the favorable deprotonation kinetics in alkaline conditions enables the effective use of non-noble metal-based catalysts.

Similarly, water electrolysis, driven by renewable energy, is the preferred route for CO_2 free hydrogen production; however, its efficiency is severely restricted by the kinetically sluggish oxygen evolution at the anode. The high energy barrier for OER necessitates highly active catalysts. While precious metal oxides like IrO_2 and RuO_2 are the current benchmarks, their high cost, low abundance and poor stability limits widespread adoption. Thus, the urgent challenge is to develop efficient, stable and low-cost non-noble metal electrocatalysts for sustainable alkaline water electrolysis [19]. Various other transition metal oxide, spinel, inverse spinel oxide, perovskite based OER catalysts have been reported, namely, CeO_2 , Co-Ni-Fe oxides, NiO , CuO , VO_2 , NiCo_2O_4 , NiFe_2O_4 , CoFe_2O_4 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ [15,17,20–25].

Manganese oxides (MnO_x) represent a highly attractive, earth-abundant alternative to noble metal catalysts, showcasing excellent electrocatalytic performance across various reactions. Specifically, MnO_2 is favored for its diverse valence states and crystal structures, which ensures its sustainability and renewability (as manganese is the only transition metal vital to the natural photosynthetic cycle). While MnO_2 generally has lower intrinsic activity than metals like nickel, its structure is highly advantageous for electrocatalysis. The diversity of MnO_2 arises from the variable stacking of its $[\text{MnO}_6]$ octahedra, enabling tunable electronic structures and morphologies. Among its various

diverse forms, the α - MnO_2 with its unique (2×2) tunnelled morphology referred as Octahedral Molecular Sieve-2, OMS-2 (Cryptomelane) with abundant defect edges provides essential sites that enhance catalytic performance and facilitate strategic modification. Its 0.46 nm × 0.46 nm dimensioned tunnel size provides geometric confinement, and its mixed valence state ($\text{Mn}^{3+}/\text{Mn}^{4+}$) contributes to excellent redox properties and high lattice oxygen mobility. For MOR/OER, the catalytic process critically involves the redox cycle of Mn species; the presence of unstable Mn^{3+} is considered as the highly active site that boosts OH^- adsorption and reaction kinetics, necessitating stabilization strategies to realize optimal performance. However, its intrinsic activity and electronic conductivity often require enhancement. To address these shortcomings, doping OMS-2 with other transition metals has proven to be a highly effective strategy in tuning its intrinsic properties, which has grabbed extensive research interests in the field of electrocatalysis, energy storage and conversion [26–29]. Among various transition metals, Nickel (Ni) is a highly advantageous and economical dopant in the electrochemical field, known for its abundant reserves and excellent corrosion resistance, particularly in alkaline media [30]. Doping metal oxides with Ni offers a viable strategy to significantly tune and enhance catalytic performance. The primary benefit stems from the synergistic effect created by Ni doping, which effectively modulates the geometric and electronic structure of the host material, thus improving its electrical conductivity and creating surface oxygen vacancies which served as catalytically active sites, leading to a superior increase in activity via oxidative removal of CO intermediates in MOR and by optimising the adsorption energy of oxygenated intermediates for reactions like the OER often surpassing that of the undoped parent material [31–33]. Furthermore, Ni serves to introduce additional catalytic active sites for processes like MOR, and structurally, a small amount of Ni can enhance stability in layer structured materials and reduce charge transfer impedance [34]. The ability of Ni to reorganize electronic structure, even modifying properties like charge carrier concentration and hole mobility in materials, highlights its versatile role in maximizing the efficiency, stability and longevity of various electrocatalysts and energy storage components [35].

The compelling need to overcome the intrinsic activity and stability limitations of MnO_2 in alkaline media, particularly by stabilizing the key Mn^{3+} active sites through low-cost Ni modification, forms the core rationale for the experimental work detailed in this chapter. This research is unified by the Ni-substitution strategy but is structurally divided into two

distinct synthesis and application studies. This research commences with in-situ synthesis of Nickel-substituted Octahedral Molecular Sieves ($\text{Ni}_x\text{OMS-2}$) nanostructures via a facile reflux method and precise thermal engineering with systematic optimisation of Ni loading. This material is subjected to comprehensive characterization by FTIR, XRD, SEM, BET, XPS, ICP-MS and TG-DTA to confirm the successful incorporation of Ni into the lattice and its resulting electronic modifications, followed by a rigorous evaluation of its bifunctional electrocatalytic potential toward both MOR and OER, providing the essential mechanistic and performance foundation for the subsequent systematic study.

The study then transitions to another detailed and systematic investigation centered on ex-situ synthesized $\text{Ni}_x\text{OMS-2}$ nanostructures. To establish a robust structure-property-performance correlation, these materials are synthesized across a range of varying Ni percentages and also undergo comprehensive structural, morphological, and electronic characterization to precisely track the influence of increasing Ni content on the physical and electronic properties of the catalyst. Critically, the subsequent electrochemical application of this series of ex-situ-prepared $\text{Ni}_x\text{OMS-2}$ nanostructures is focused on the methanol oxidation activity due to its negligible performance in catalysing oxygen evolution. This systematic evaluation aims to directly correlate the location of Ni dopants and its concentration with electrocatalytic applications and stability, ultimately allowing for the identification of an optimal Ni loading and fabrication method that maximizes the efficiency of the $\text{Ni}_x\text{OMS-2}$ catalyst for use in non-precious-metal-based alkaline fuel cell and water splitting technology.

4.2 Methodology

All chemicals and reagents used in this study were of analytical grade. Detailed information regarding the purity and suppliers of these materials is documented in the Appendix following the final chapter.

4.2.1 In-situ Synthesis of $\text{Ni}_x\text{OMS-2}$ nanorods ($x = 0.01, 0.03, 0.05$ moles)

The synthesis of $\text{Ni}_x\text{OMS-2}$ nanorods was accomplished via a reflux-based precipitation method. Initially, the Potassium permanganate, KMnO_4 oxidant solution was prepared by dissolving 2.945 g (0.0187 moles) of KMnO_4 in 50 mL of distilled water. This mixture was heated to 80°C to ensure complete dissolution. Concurrently, a reactant mixture was prepared in a round-bottom flask, consisting of 4.4 g (0.026 moles) of Manganese sulfate monohydrate, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 1.244 g of Nickel acetate tetrahydrate, $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.01 mole) and 1.5 mL of concentrated nitric acid, HNO_3 , in 15 mL of distilled water. The flask was heated to 80°C and stirred continuously. The oxidant solution was then added drop wise to the reactant mixture, and the combined suspension was subjected to reflux for 24 hours under constant stirring. The resulting black solid product was then isolated and purified. It was repeatedly washed with distilled water until a qualitative test for sulphate ions showed no presence of impurities. Following this, the precipitate was rinsed with ethanol and dried in an oven at 110°C overnight, yielding the $\text{Ni}_{0.01}\text{OMS-2}$ nanorods referred as NMA. Similarly, $\text{Ni}_{0.03}\text{OMS-2}$ (NMB), $\text{Ni}_{0.05}\text{OMS-2}$ (NMC) was synthesized by varying Ni concentration to 0.03 and 0.05 moles, respectively.

An undoped OMS-2 sample was also synthesized by omitting the addition of the Ni precursor to the process described above.

4.2.2 Synthesis of calcined $\text{Ni}_{0.03}\text{OMS-2}$

The synthesized $\text{Ni}_x\text{OMS-2}$ nanostructures were calcined at 200, 400 and 600°C for 3 hours in air atmosphere to investigate the relationship between calcination temperature and the resulting structure and catalytic performance. These thermally treated materials were labelled as NMB200, NMB400 and NMB600.

4.2.3 Ex-situ Synthesis of NiOMS-2 nanorods

The ex-situ synthesis of NiOMS-2 was achieved by wet impregnation method. In a typical procedure, 2 g of undoped OMS-2 was added to a 20 mL aqueous solution containing 2

wt% $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.01696 g). The required mass of the nickel salt precursor was calculated to yield a 2 wt% Ni content relative to the weight of host OMS-2. The mixture was first subjected to bath sonication for 30 minutes for complete dispersion of OMS-2 nanorods and then magnetically stirred for an additional 1 hour. The mixture was subsequently dried in hot air oven at 120°C. The resultant solid product was calcined at 200°C for 2 hours, yielding the product designated as 2%NMO.

Following the same procedure, 5%NMO, 10%NMO and 20%NMO were synthesised using the corresponding amount of $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ precursor necessary to achieve 5 wt%, 10 wt% and 20 wt% nominal Ni loadings.

4.2.4 Materials characterisation

A suite of analytical techniques was employed to fully characterize the synthesized samples. Fourier Transform Infrared (FTIR) spectra were obtained using an IRAffinity – 1S SHIMADZU 00822 spectrophotometer in the range of 400–4000 cm^{-1} . X-ray Diffraction (XRD) patterns were recorded on a Bruker D8Advance diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) to study the crystal structure. For thermal analysis, simultaneous Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out using a SHIMADZU DTG-60 analyser. Samples were heated from 25°C to 800°C at a rate of 10°C/min under a nitrogen atmosphere to assess thermal stability. The surface morphologies were examined using Scanning Electron Microscopy (SEM) on JEOL JSM-7610F FEG-SEM. The oxidation states and elemental composition were further investigated via X-ray Photoelectron Spectroscopy (XPS) using a Kratos Analytical Ltd. Axis Supra, FEI Inc. model, with an $\text{Al K}\alpha$ X-ray source (1486.6 eV). All spectra were first charge-corrected by referencing the adventitious carbon C1s peak to 284.8 eV to account for electronic shifts and surface charging. Finally, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was performed on the ICP-MS system, Agilent 7900 to determine the elemental composition in each sample. The surface area, pore volume, and pore size distribution of the samples were characterized using N_2 adsorption-desorption isotherms at 77 K. The measurements were performed using a volumetric gas adsorption analyser (BELSORP-mini II, Bel Japan Inc., Japan). The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method, while the pore size distribution and pore volume were calculated using the Barrett–Joyner–Halenda (BJH) method.

4.2.5 Electrochemical Measurements

The electrocatalytic performance of the synthesized nanostructures was studied using a CHI6081E electrochemical workstation in a standard three-electrode glass cell. The standard setup utilized a mercury/mercurous oxide (Hg/HgO) electrode as the reference and a graphite rod as the counter electrode. The working electrode was a 3mm diameter Glassy Carbon Electrode (GCE) and 1cm × 1cm glassy carbon plate. Prior to use, GCE surface was meticulously cleaned by sequential polishing with 1, 0.3 and 0.05 micron alumina slurries, followed by 2 minutes of sonication in ethanol.

The catalyst ink was prepared by ultrasonic dispersion of 2 mg of the catalyst material in 40 μL of isopropyl alcohol for 10 minutes, followed by the addition of 20 μL of Nafion binder and subjecting the mixture to an additional 5 minutes of sonication. The polished GCE was modified by drop-casting 5 μL of this prepared ink twice onto its surface to obtain a total ink loading of 10 μL . To ensure proper adhesion and drying, the modified electrode was then dried in an oven at 50°C for 20 minutes. The electrode with an average catalyst mass loading of 0.99 $\text{mg}\cdot\text{cm}^{-2}$ was further used for electrochemical studies.

The methanol oxidation studies were carried out by recording cyclic voltammograms (CV), within a potential window of -0.1 to 0.95V (vs. Hg/HgO) at varying scan rates from 2 to 50 $\text{mV}\cdot\text{s}^{-1}$ using a mixture of 1M methanol and 1M NaOH as an electrolyte. The OER studies were carried out in N_2 -saturated 1M NaOH electrolyte. The linear sweep voltammograms (LSV) for OER were obtained by scanning potential from 1.3V to 1.8V (vs. RHE) at 1 $\text{mV}\cdot\text{s}^{-1}$ scan rate. All polarization curves were 100% iR-corrected using the software enabled auto iR compensation function and converted to the Reversible Hydrogen Electrode (RHE) scale. The stability of samples for MOR was assessed via chronoamperometry (CA) at 0.85 V (vs. Hg/HgO) for 1000 sec. For OER the constant potential stability test was performed at 1.627 V (vs. RHE) for 6 hours. The Electrochemical Impedance Spectroscopy (EIS) was performed in the frequency range of 100 kHz to 1 Hz at a fixed potential. The resulting data was further fitted to an equivalent circuit using ZSimpWin 3.21 software. The various electrochemical parameters mentioned in the subsequent section were calculated to evaluate and compare the kinetics of the MOR and OER on the synthesised samples.

Evaluation of kinetic parameters

a) Tafel Slope: The Tafel polarization curves were generated to understand the electrode kinetics of methanol oxidation and oxygen evolution. This was done by plotting the logarithmic current density against the potential relative to Hg/HgO reference electrode. The reaction kinetics for different samples were analyzed by fitting the resulting linear plots to the Tafel equation, given as:

$$\eta = a + b \log (j) \quad \text{-----} (1)$$

In this equation, η is the overpotential (V), a is the intercept, j is the current density ($\text{mA}\cdot\text{cm}^{-2}$), and b is the Tafel slope ($\text{mV}\cdot\text{dec}^{-1}$). A smaller Tafel slope indicates more efficient charge transfer at the interface between the catalyst and the electrolyte.

b) Electrochemical active Surface Area (ECSA): The Electrochemical active surface area of the catalysts were determined through a comparative analysis of their electrochemical double-layer capacitance (C_{dl}). The C_{dl} values were obtained by recording CV within a non-faradaic potential range (0 to 0.1 V vs. Hg/HgO) at multiple scan rates (10, 20, 40, 60, 80, and 100 mV/s) in 1M NaOH electrolyte solution. The ECSA was then calculated using the ratio of each samples double-layer capacitance to the specific capacitance (C_s), as shown in the subsequent formula [36]:

$$\text{ECSA} = C_{dl} / C_s \quad \text{-----} (2)$$

To obtain C_{dl} , the difference (Δj) between the anodic and cathodic current densities, j_a and j_c , respectively, were measured from cyclic voltammograms at a fixed potential of 0.05V, against the scan rate. The slope of this linear plot is equivalent to two times the double-layer capacitance. The specific capacitance (C_s) is the capacitance value normalized to the actual surface area of a standard, planar electrode. For idealized planar interfaces, C_s typically ranges from 20 to 60 $\mu\text{F}\cdot\text{cm}^{-2}$. In this study, a value of 40 $\mu\text{F}\cdot\text{cm}^{-2}$ was used, which is commonly cited for mixed manganese or other transition metal-based oxides [37–40]. The ECSA was then calculated by dividing the determined double-layer capacitance (C_{dl}) by this assumed specific capacitance of 40 $\mu\text{F}\cdot\text{cm}^{-2}$.

c) Surface Active Sites Concentration (Γ): Determining the exact surface concentration (Γ) of active catalytic sites in dynamically reconstructing 3d transition metal oxyhydroxides is methodologically challenging. The most appropriate and widely accepted established

method for this measurement involves integrating the area under the redox peak associated with the transformation between the oxide/hydroxide and oxyhydroxide forms [41]. To quantify this surface concentration of active sites (in mol.cm⁻²), cyclic voltammograms of the different samples were recorded. The measurements were taken within a potential range of 0.0 to 0.4 V relative to a Hg/HgO reference electrode, at a scan rate of 5 mV.s⁻¹ in a 1 M NaOH electrolyte. The surface concentration (Γ) in moles.cm⁻², was calculated using the subsequent formula [42]:

$$\Gamma = \frac{Q}{nFA} \quad \text{-----} \quad (3)$$

Wherein, F indicates Faraday's constant, A represents the geometric surface area of the glassy carbon electrode. Q is the charge corresponding to distinct anodic oxidation peak in CV quantified by integrating area under the metal ion oxidation peak in the first anodic scan segment before catalytic oxidation of the reactant, n is the number of electrons transferred during the redox transition.

d) Turnover Frequency (TOF): The Turnover Frequency in OER is a crucial electrochemical metric used to quantify the number of reaction cycles completed by a single active site per unit time under specific experimental conditions. It is determined using the following equation [43]:

$$\text{TOF} = \frac{jA}{4nF} \quad \text{-----} \quad (4)$$

In this equation, j represents the current density in mA.cm⁻² measured at a specific OER overpotential. A is the geometric surface area of the working electrode, F is Faraday's constant and n denotes the total number of active sites in moles.

4.3 Results & discussion

4.3.1 Structural and morphological analysis of in-situ $\text{Ni}_x\text{OMS-2}$ nanostructures

I. Structural Analysis by X-ray Diffraction

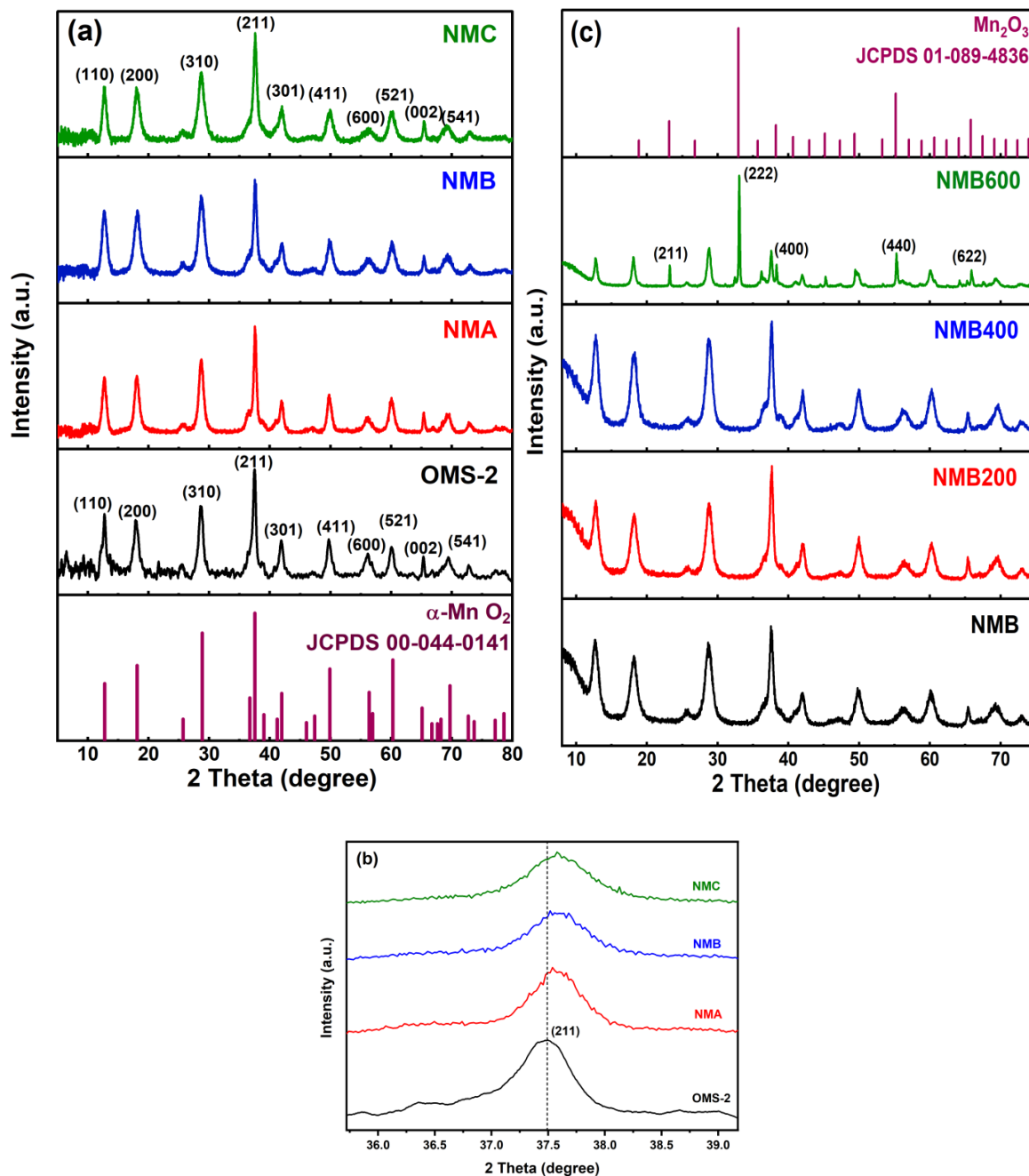


Figure 4.1: (a) XRD patterns of OMS-2 and Ni substituted forms of OMS-2 with varying Ni concentration (b) Magnified view of peak shift in plane (211) (c) XRD patterns of NMB, NMB200, NMB400 and NMB600

Table 4.1: Particle size and interplanar spacing of samples

Sample	Average particle size (nm)	$d_{(211)}$ Å	Sample	Average particle size (nm)	$d_{(211)}$ Å
OMS-2	10.01	2.399	NMB	7.32	2.391
NMA	8.73	2.392	NMB200	7.96	2.389
NMB	7.32	2.391	NMB400	8.01	2.391
NMC	7.33	2.391	NMB600	22.16	2.467

The X-ray diffraction patterns for all in-situ nickel-doped samples are displayed in Figure 4.1(a). These patterns confirm the characteristic diffraction profile of the OMS-2 material, demonstrating that the structural integrity of the OMS-2 framework remains intact regardless of the nickel concentration introduced. The distinct diffraction peaks of the OMS-2 phase, corresponding to 2 theta values of 12.80, 18.10, 28.79, 37.52, 41.94, 49.86, 56.31, 60.12, 65.28 and 69.58, are indexed to the (110), (200), (310), (211), (301), (411), (600), (521), (002), and (541) planes, respectively, of the cryptomelane-type α -MnO₂ phase (JCPDS card no. 00-044-0141). As the nickel content increases, a noticeable shift of these peaks toward a higher 2 theta value is observed, accompanied by successive peak broadening, as detailed in Fig. 4.1(b). This change is the cumulative result of the reduction in crystalline domain size, along with possible micro strain, lattice defects and structural disorder induced by the nickel doping, which arises from the differences in the oxidation states of nickel and manganese, as indicated in Table 4.1. Importantly, no peaks indicative of the segregation or formation of nickel oxide impurity phases were detected. Upon calcination of the NMB sample to 200°C (as shown in Fig. 4.1(c)), an increase in peak intensities, resulting in sharper peaks, and a gradual growth in particle size were observed, attributed to reduced strain and a more ordered structure. Similarly, calcination at 400°C yielded a slight increase in average crystallite size according to Scherrer analysis. This exhibited apparent peak broadening and raised shoulders on the (211) plane, which is explained by the fragmentation of larger OMS-2 crystals and the initial formation of small nuclei of the stable Mn₂O₃ phase, while the fundamental cryptomelane base structure was maintained. Finally, at 600°C, a partial decomposition of the α -MnO₂ phase into the Mn₂O₃ phase occurred, evidenced by the appearance of additional peaks in the NMB600 pattern that match the bixbyite structure of Mn₂O₃ (JCPDS card no. 01-089-4836).

Substantial particle growth was concurrent with this phase change to a lower oxidation state of manganese.

II. FTIR spectral analysis

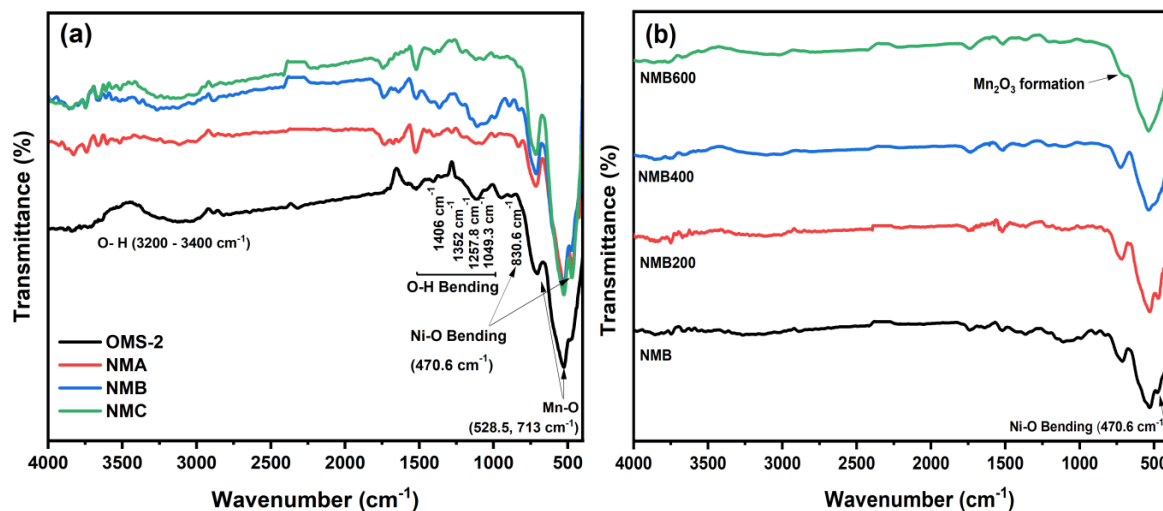


Figure 4.2: FTIR spectra of (a) OMS-2 and Ni substituted forms of OMS-2 with varying Ni concentration (b) NMB, NMB200, NMB400 and NMB600

The FTIR shown in Figure 4.2(a) were analysed to investigate the lattice vibrational characteristics and impacts of substitution of nickel on the structure of OMS-2. The samples displayed four characteristic bands stemming from the Mn-O vibrational modes within the $[\text{MnO}_6]$ octahedra, which appeared at approximately 713 cm^{-1} , 528.5 cm^{-1} , 472 cm^{-1} and 440 cm^{-1} . The bands observed at 470.6 cm^{-1} and 832 cm^{-1} are notably intense only in the NMA and NMC samples, which is attributed to Ni-O bending vibrations. Conversely, the less intense band at 470.6 cm^{-1} in the NMB sample suggests that the OMS-2 framework structure is well-preserved in this particular sample. Bands at 1406 cm^{-1} , 1352 cm^{-1} , 1257.8 cm^{-1} , 1119.8 cm^{-1} and 1049.3 cm^{-1} correspond to the bending vibrations of Ni-O-H and Mn-O-H groups within the lattice. The high intensity of these bands in NMB contribute to its enhanced catalytic activity for MOR and OER, benefiting from both lattice and adsorbed oxygen. A broad band extending from 3200 to 3400 cm^{-1} represents the O-H stretching vibrations. The sequential calcination of the NMB sample at increasing temperatures, as depicted in Fig. 4.2(b), leads to the removal of adsorbed water molecules and OH groups and consequently, the disappearance of their corresponding bands. As the temperature is raised, the intensity of the bands at 470.6 cm^{-1} and 723 cm^{-1}

diminishes. The band at 470.6 cm^{-1} completely vanishes at 600°C , which indicates a gradual phase transformation in the OMS-2 material from the $\alpha\text{-MnO}_2$ structure to Mn_2O_3 .

III. Morphological and textural analysis

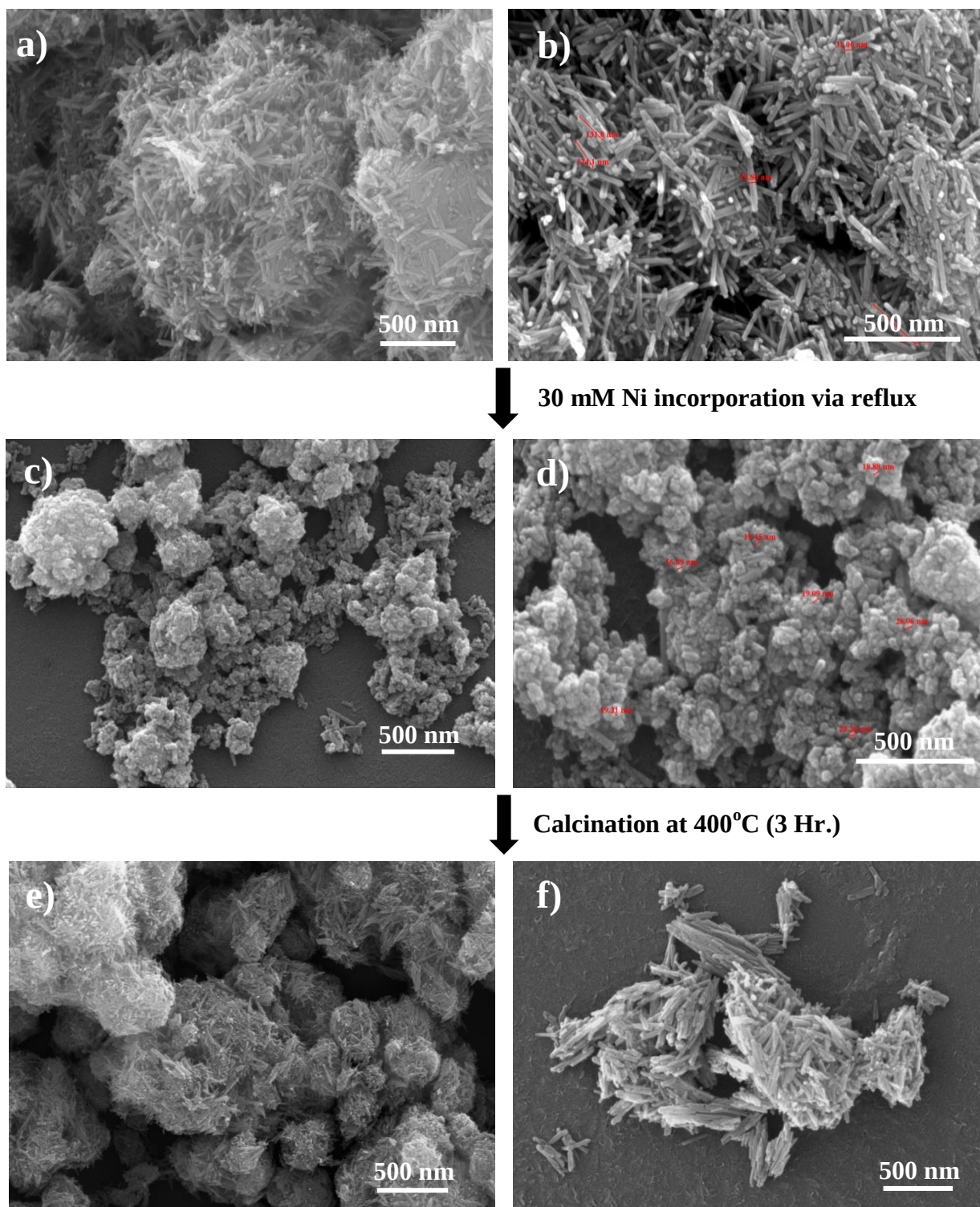


Figure 4.3: SEM images of (a)-(b) OMS-2 (c)-(d) NMB (e)-(f) NMB400 at low and high magnification

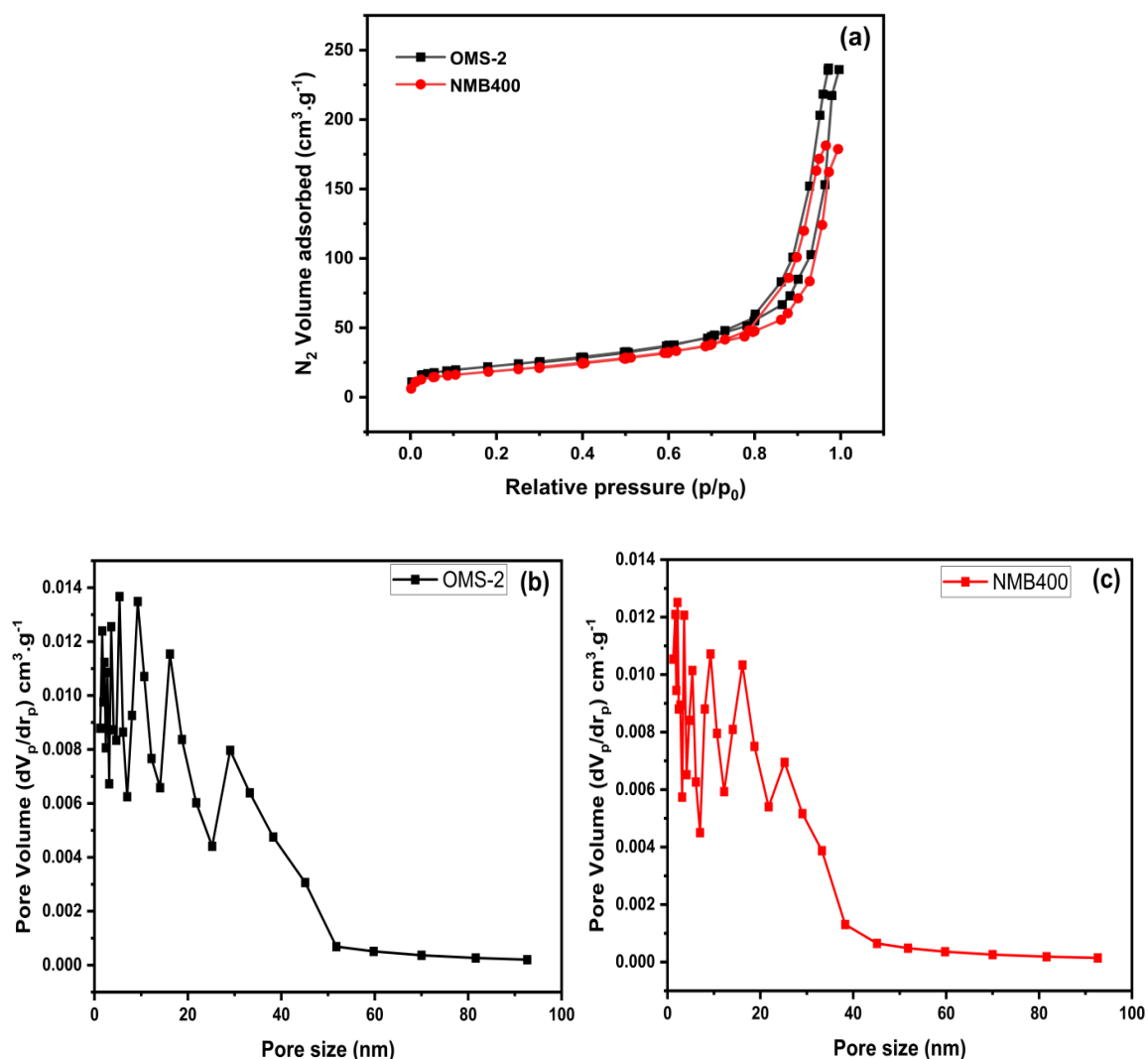


Figure 4.4: (a) N_2 adsorption–desorption isotherms of OMS-2 and NMB400 (b) Pore size distribution curve of OMS-2 (c) NMB400

The surface morphology analysis, based on the Scanning Electron Microscopy (SEM) images presented in Fig. 4.3(a)-(b), revealed that the initial OMS-2 particles possessed a distinct nanorod morphology with an average aspect ratio (length/width) of 4.42. The incorporation of 30 mM Ni into the OMS-2 structure significantly altered this surface morphology from Fig. 4.3(c)-(d), causing the NMB nanorod grains to become densely packed and aggregated, which coincided with a substantial reduction and increased variation in their aspect ratio. Subsequently, when the NMB sample was subjected to calcination at 400°C, the particle shape underwent a recovery in Fig. 4.3(e)-(f), as the nanorods re-established their original morphology. This heating process also led to a substantial increase in the aspect ratio to 4.15 than that in NMB and a reduction in the overall clustering of the particles.

The analyses of surface area and porosity, conducted using nitrogen adsorption-desorption isotherms in Fig. 4.4(a) demonstrated distinct textural properties of the synthesized materials. The pristine OMS-2 material was found to have a specific BET surface area of $79.629 \text{ m}^2.\text{g}^{-1}$ and a total pore volume of $0.3541 \text{ cm}^3.\text{g}^{-1}$. These values were higher than those measured for the Ni-substituted analogue, NMB400, which displayed a BET surface area of $66.631 \text{ m}^2.\text{g}^{-1}$ and a total pore volume of $0.2715 \text{ cm}^3.\text{g}^{-1}$. More importantly, the pore size distribution, determined using the Barrett-Joyner-Halenda (BJH) method, revealed a substantial difference in the most frequent pore size. The OMS-2 sample in Fig. 4.4(b) showed a peak pore radius of 5.35 nm, while the NMB400 material in Fig. 4.4(c) exhibited a considerably narrower peak pore radius of 2.14 nm. Collectively, this data suggests that although nickel incorporation causes a minor decrease in overall surface area and porosity, its primary effect is a fundamental modification of the pore architecture. This change results in NMB400 being dominated by a higher concentration of finer, narrower mesopores. However, despite these diminished textural parameters, NMB400 consistently exhibited outstanding catalytic performance in both the methanol oxidation reaction and the oxygen evolution reaction. This enhanced activity is therefore primarily attributed not to the sheer quantity of surface area, but rather to the qualitative enhancement of the active sites and the favorable reaction mechanism introduced by the presence of nickel.

IV. Surface and Bulk Compositional Analysis

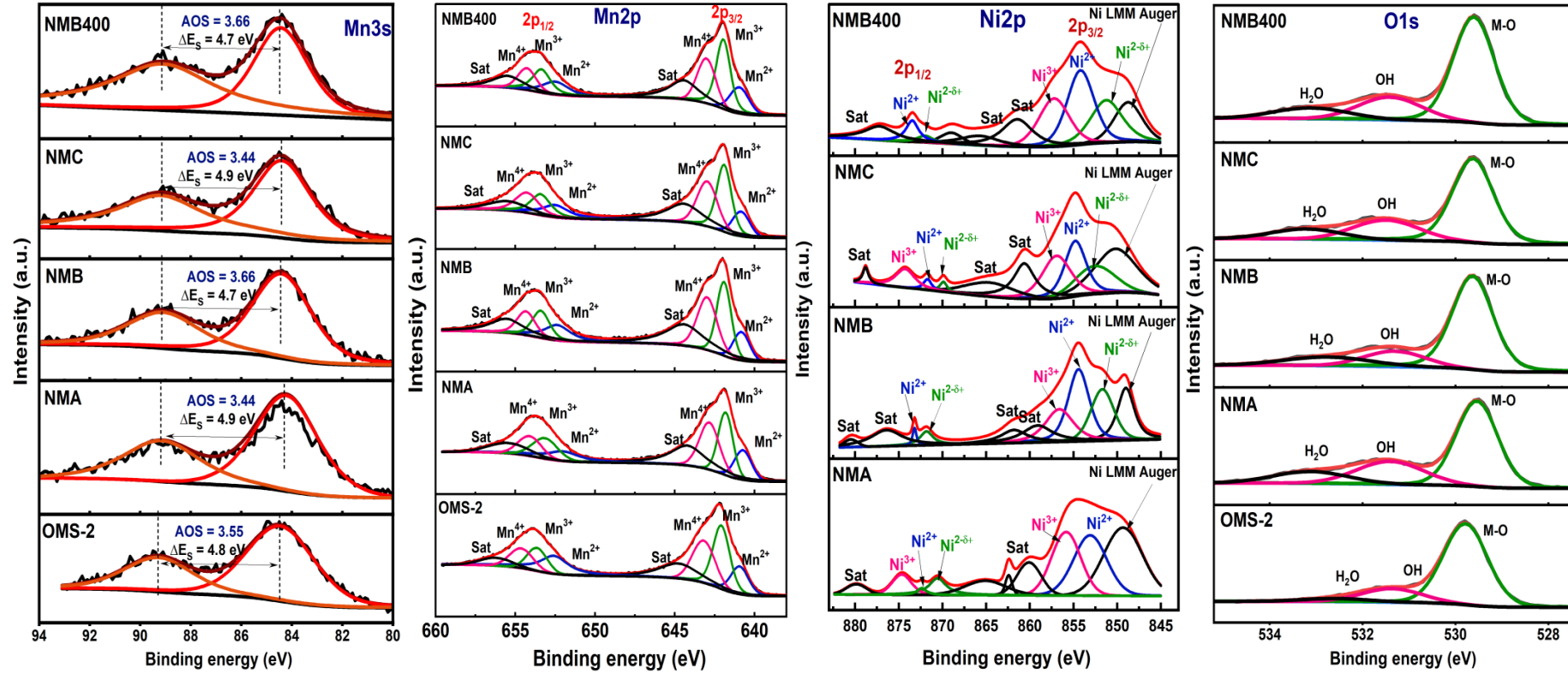


Figure 4.5: Core level XPS spectra of (a) Mn 3s (b) Mn 2p (c) Ni 2p (d) O 1s in OMS-2, NMA, NMB, NMC and NMB400

Table 4.2: Surface composition and chemical state analysis from ICP-MS and XPS measurements

Sample	K/Mn		Ni/Mn		$\frac{Mn^{3+}}{Mn^{4+}+Mn^{3+}+Mn^{2+}}$	Mn (AOS)	$\frac{Ni^{2+}}{Ni^{3+}}$	O_{ads}	O_{vac}	O_{lat}
	ICP-MS	XPS	ICP-MS	XPS	(%)					
OMS-2	0.0778	0.0331	--	--	35.55	3.55		10.69	21.29	68.02
NMA	0.1016	0.0396	0.0031	0.1416	35.90	3.44	1.087	16.91	26.98	56.11
NMB	0.1444	0.0466	0.0128	0.1646	36.28	3.66	1.614	16.90	20.00	63.10
NMC	0.0971	0.0414	0.0194	0.1670	36.14	3.44	1.211	15.29	25.30	59.41
NMB400		0.0311		0.1347	36.80	3.66	1.493	15.12	23.53	61.35

The elemental composition of the samples and the oxidation state of manganese on each sample surface were determined through X-ray photoelectron spectroscopy (XPS). Specifically, the average oxidation state (AOS) of Mn in all analysed samples was quantified. This quantification was achieved by calculating the difference in binding energy (ΔE_s) between the main and satellite peaks observed in the Mn3s core level spectra as shown in Fig. 4.5(a), and subsequently inputting this ΔE_s value into the reported formula for calculation of AOS [44]:

$$\text{AOS} = 8.956 - 1.126\Delta E_s \quad \text{----- (5)}$$

The highest average oxidation state of manganese at 3.66 was found in NMB and NMB400 samples. This high AOS is attributed to the predominant presence of Mn^{4+} over Mn^{3+} . Further in Mn2p core level XPS spectra in Fig. 4.5(b) the Mn^{3+} oxidation state was identified by deconvoluting the spectra of OMS-2 consisting of two primary peaks at 642.1 eV for $\text{Mn}2p_{3/2}$ and 653.7 eV for $\text{Mn}2p_{1/2}$. While a minor shift of these peaks to a lower energy of 641.8 eV and 653.2 eV is observed upon Ni doping in Ni substituted OMS-2 analogues. The negative shift is a consequence of Ni incorporation within OMS-2 framework by replacing Mn, while altering electronic environment of other Mn species in $[\text{MnO}_6]$ octahedra [26]. Additionally, the presence of Mn^{2+} was indicated by peaks near 641 eV and 652.6 eV, while Mn^{4+} was indicated by peaks near 643 eV and 654.3 eV across all four samples. The $\text{Mn}^{3+}/(\text{Mn}^{3+} + \text{Mn}^{4+} + \text{Mn}^{2+})$ ratio was highest for NMB400 and NMB and lower for the other samples as shown in Table 4.2. The results indicated highest proportion of catalytically active Mn^{3+} in NMB400 sample. The incorporation of the Ni dopant into the $[\text{MnO}_6]$ framework was confirmed to occur via Mn substitution rather than K^+ ion substitution in the tunnels, as evidenced by the highest K/Mn ratio in NMB. However, this ratio decreased after calcination at 400°C; this reduction is potentially due to the fragmentation of the OMS-2 base, which causes the partial loss of K^+ ions from the structure. This result aligned with the ICP-MS findings presented in Table 4.2.

Furthermore, the Ni2p core scan XPS spectra in Fig. 4.5(c) displayed two main peaks at 854.4 eV for $\text{Ni}2p_{3/2}$ and 873.2 eV for $\text{Ni}2p_{1/2}$, representing the predominance of Ni^{2+} state. Accompanying these were a shake-up satellite peak and a Ni LMM Auger peak at higher and lower binding energies, respectively. A detailed deconvolution of the Ni2p peaks across all samples revealed the presence of three distinct states:

$\text{Ni}^{2-\delta+}$ due to formation of intimate, non-stoichiometric Ni-O-Mn structure (i.e., Ni-O bonds within the MnO_2 framework) at 851.3 eV and 872 eV.

Ni^{2+} as $\text{Ni}(\text{OH})_2$ at approximately 854.4 eV and 873.2 eV.

Ni^{3+} as NiOOH at approximately 856.9 eV and 874.4 eV.

Crucially, the catalytically active redox couple ratio ($\text{Ni}^{2+}/\text{Ni}^{3+}$) was 1.614 in NMB, which decreased to 1.493 after calcination. This reduction indicates a higher concentration of the active Ni^{3+} state in NMB400.

The O1s core scan spectra, as displayed in Fig. 4.5(d), was successfully deconvoluted into three distinct peaks, each representing a different oxygen species. A peak corresponding to lattice oxygen involved in the M-O-M (Mn-O-Mn or Ni-O-Mn) bonding within the α - MnO_2 and Ni doped α - MnO_2 crystal lattice was obtained at 529.5 eV. A peak at 531.4 eV was attributed to hydroxyl groups (Mn-O-H / Ni-O-H) that arise from the vacancy defects created as a result of Ni substitution. A peak at 533.1 eV signifies hydroxyl functionalities (H-O-H) on the MnO_2 surface, originating from adsorbed water molecules. The data from Table 4.2 makes it clear that the calcination of NMB led to the creation of a greater number of vacancy defects without compromising the structural integrity of the OMS-2 framework. Furthermore, NMB initially maintained a higher proportion of lattice oxygen (63.1%), which only slightly decreased to 61.35% after calcination. This minor reduction is a consequence of vacancy defects being formed within the structure at the elevated temperature, ultimately contributing to the enhanced catalytic properties observed in NMB400.

V. Thermal Analysis

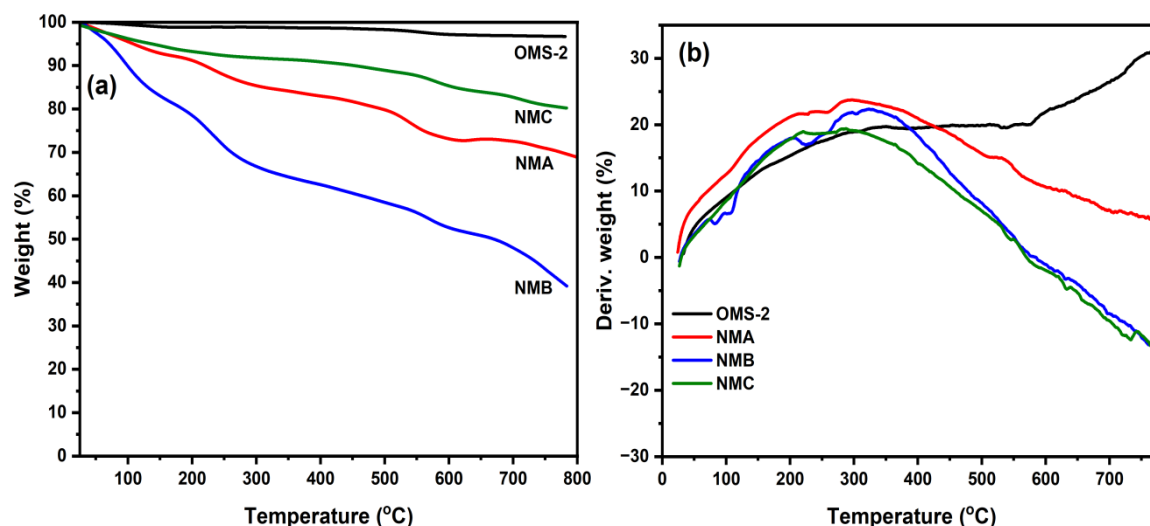


Figure 4.6: (a) Thermogram (b) DTA profile of OMS-2 and in-situ Ni doped forms

Thermogravimetric (TGA) and Differential Thermal analysis (DTA) of OMS-2 material and its Ni-doped variants are shown in Fig. 4.6(a) and (b), respectively. Up to 150°C, the OMS-2 sample exhibited a minor weight loss of only 1.13%, which is attributed to the release of physisorbed water molecules. In contrast, among the Ni-doped forms, the NMB sample displayed the most significant mass loss of 17%, which is due to a higher quantity of adsorbed water molecules, a result that is consistent with the XPS analysis. Both of these initial weight changes corresponded to an endothermic event visible in the DTA profile.

Upon continued heating up to 300°C, the NMA, NMB and NMC samples showed substantial weight losses of 14.64%, 33.25% and 8.21%, respectively. During this same interval, OMS-2 demonstrated only a negligible mass loss, increasing slightly to 1.18%. This second stage of weight reduction is attributed to the desorption of chemisorbed water molecules and the loss of some surface lattice oxygen. A third mass loss was observed in the temperature range of 500°C to 620°C. This final, major decomposition is caused by the transformation of the α - MnO_2 phase into Mn_2O_3 , resulting from the elution of bulk lattice oxygen and corresponding reduction in the Mn oxidation state. Beyond 675°C, all samples (doped and undoped OMS-2 forms) underwent further decomposition to the final phase, Mn_3O_4 , with NMB recording the highest overall weight loss of 60.73%.

4.3.2 Electrocatalytic assessment of In-situ NixOMS-2 nanorods : Methanol Oxidation Reaction

I) Effect of Ni concentration on catalytic activity

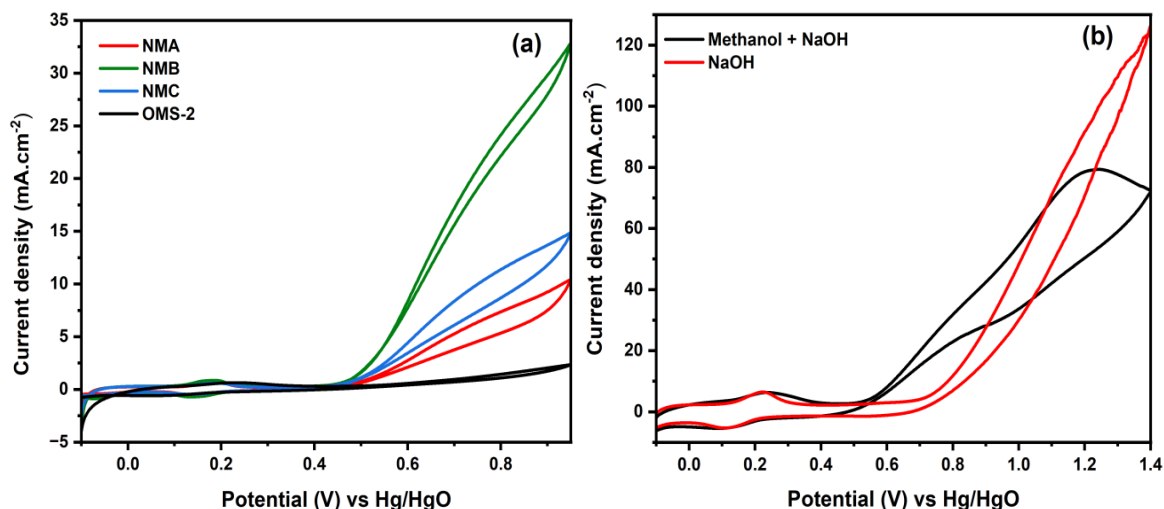
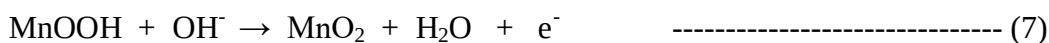
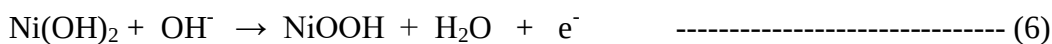


Figure 4.7: Cyclic voltammograms of (a) OMS-2 and Ni substituted OMS-2 catalysts (b) CV of NMB in 1M NaOH before and after addition of 1M methanol

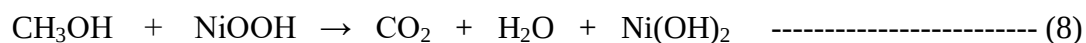
The evaluation of the electrocatalytic efficiency of the prepared catalysts for methanol oxidation was carried out by recording their cyclic voltammograms (CVs) in an alkaline solution containing a 1M concentration of both methanol and NaOH, with the potential scanned from -0.1 to 0.95 V at a low scan rate of 2 mV.s⁻¹, as illustrated in Fig. 4.7(a). From the cyclic voltammograms of all the nickel substituted OMS-2 variants it was observed that each CV exhibited a reversible Faradaic redox signal before appearance of methanol oxidation signal, between 0.1V to 0.24V vs. Hg/HgO. This observation is attributed to the simultaneous redox transitions of the nickel ions from Ni²⁺ to the highly active Ni³⁺ state and the manganese ions from Mn³⁺ to Mn⁴⁺ oxidation state, corresponding to reaction (6) and reaction (7). This collective oxidation appears as a single, broad peak in the voltammograms, which suggests a robust electronic coupling between the two metal species.



However, the OMS-2 catalyst displayed a redox peak that was less intense, broader, and shifted to a more positive potential. This characteristic indicates that the conversion

involving only Mn^{3+} to Mn^{4+} in pure OMS-2 is a sluggish reversible transition requiring a high overpotential. Conversely, when nickel was substituted into the catalyst structure, this specific redox peak experienced a negative potential shift. This negative shift is an evidence of improved reaction kinetics for the sluggish Mn^{3+} conversion to the Mn^{4+} species. This enhancement is attributed to a reduction in the energy barrier required for the reaction, which arises from the altered electronic environment of the manganese centers due to the presence of nickel. The initial electrooxidation of $\text{Ni}(\text{OH})_2$ to the active NiOOH species, being a necessary step in many nickel-based catalysts, typically requires a high potential, reportedly exceeding 1.35V vs. RHE, which is equivalent to 0.38V vs. Hg/HgO [7]. This high potential requirement is recognized as a significant limiting factor in the overall methanol oxidation reaction as it subsequently raises the MOR potential to a value substantially higher than the potential of the oxygen reduction reaction (ORR) occurring at the cathode of a DMFC, which in turn leads to a diminished current output from the fuel cell. Despite this common limitation, this research has shown that when OMS-2 is synthesized with 30 mM incorporation of Ni within its crystal lattice, the potential necessary for this crucial $\text{Ni}(\text{OH})_2$ electrooxidation step is lowered by 0.2V.

Further, a sharp increase in current density with rising potentials was observed in NMB catalyst indicating a superior methanol oxidation performance, achieving the lowest onset potential of 0.45 V and a highest anodic forward peak current density of $27.02 \text{ mA}\cdot\text{cm}^{-2}$. In contrast, the other catalysts NMA, NMC, and OMS-2 showed considerably lower current densities at 0.85 V vs. Hg/HgO reference electrode, recording values of 8.27, 12.58 and $1.73 \text{ mA}\cdot\text{cm}^{-2}$, respectively. The enhanced methanol electrooxidation on NMB is primarily catalysed by the highly active nickel oxy-hydroxide (NiOOH) sites on the surface of catalyst, according to the following reaction:



The highly active species, specifically Ni^{3+} , plays a primary role in the subsequent cleavage of the C-H bond and the oxidation of the adsorbed methanol intermediates. Simultaneously, the high-valent Mn^{4+} sites present on the catalyst surface are typically coordinated with surface hydroxyl groups (OH^-). These coordinated OH^- groups are essential for the complete oxidation of the methanol intermediates (such as CHO_{ads} , COOH_{ads}) that are bound to the active nickel sites. They achieve this by supplying the required nucleophiles for both the deprotonation steps and the addition of oxygen. This is

further facilitated by nickel-induced activated lattice oxygen within the $[\text{MnO}_6]$ framework. This entire cooperative mechanism contributes to both the electronic synergy and the structural stability of the overall catalyst framework. Furthermore, the material NMB possesses a surface that is rich in Mn^{3+} and more proportion of lattice oxygen (as confirmed from XPS results). This composition optimizes the local electronic environment, resulting in superior charge transfer kinetics and, importantly, helps to stabilize the transient, high-valent Ni^{3+} species.

Previous studies have established that on certain nickel-based catalysts in alkaline solutions, the methanol oxidation reaction and the oxygen evolution reaction are the two competing processes that often begin at nearly identical onset potentials [42]. To rule out any potential interference or ambiguity stemming from this competition, the cyclic voltammograms of the NMB catalyst were recorded under two distinct conditions. First, in the presence of 1M methanol in the alkaline electrolyte, and secondly without methanol in the electrolyte (as presented in Fig. 4.7(b)). These CVs were obtained within a broad potential window ranging from -0.1 to 1.4V, using a scan rate of 50 mV.s^{-1} . The resulting data revealed a significantly delayed onset potential for the oxidation of electrolyte in the absence of methanol. This observation strongly suggests that the NMB catalyst preferentially promotes methanol oxidation over the competing oxygen evolution reaction with sufficient potential lag to prevent interference of OER.

II) Effect of NaOH and methanol concentration on catalytic activity of NMB

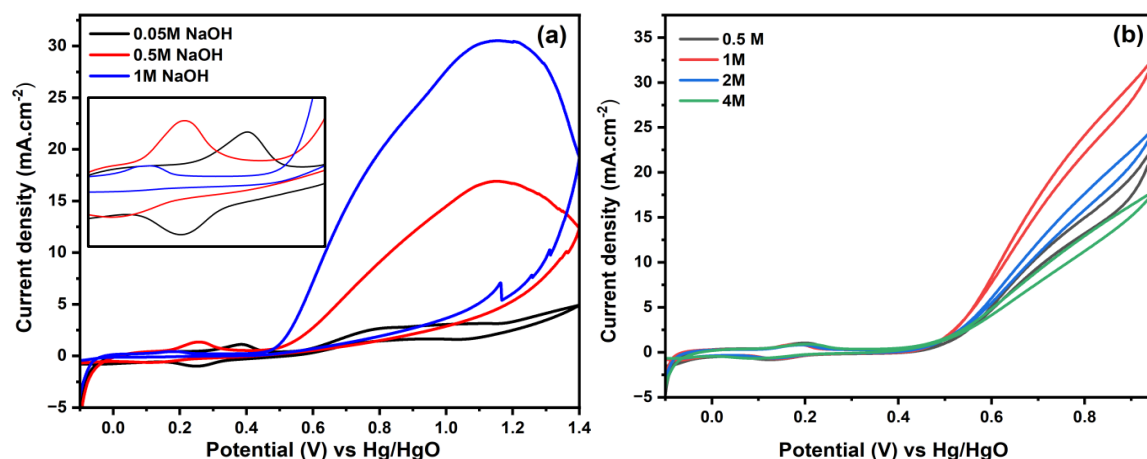


Figure 4.8: Cyclic voltammograms of NMB at 2 mV.s^{-1} scan rate in (a) 1M CH₃OH and varying concentration of NaOH. (Inset : Ni(II) to Ni(III) redox peaks) (b) 1M NaOH and varying concentrations of CH₃OH

The effect of NaOH concentration on the electrocatalytic activity of NMB was investigated by recording CV, as displayed in Fig. 4.8(a), under varying concentrations of NaOH (0.05, 0.5 and 1M), while keeping the methanol concentration constant. In a separate experiment, CVs were recorded on NMB by varying the methanol concentration to 0.5M, 1M, 2M and 4M, with a fixed 1M NaOH concentration, as shown in Fig. 4.8(b).

Analysis of the CVs in Fig. 4.8(a) and its inset revealed that an increase in the alkali concentration leads to a decrease in the onset potential for both, the oxidation of Ni(OH)₂ to NiOOH and the subsequent methanol oxidation. This lowering of potential is hypothesized to be due to a shift in the reaction equilibrium, caused by enhanced hydroxyl ion adsorption onto the nickel sites. This adsorption, in turn, facilitates the production of the active NiOOH sites via oxidation [7]. Methanol is more readily adsorbed onto these active NiOOH sites compared to the less adsorbing Mn sites. Furthermore, at elevated anodic potentials, the adsorption of OH⁻ ions on both the Ni and Mn sites helps in oxidative removal of methanol oxidation intermediates, thereby regenerating the sites for the adsorption of new methanol molecules. This process is corroborated by the observation of a reduced area under the reduction peak of NiOOH to Ni(OH)₂ during the backward scan, which signifies the partial consumption of NiOOH sites in the process of methanol oxidation with its conversion to Ni(OH)₂.

In contrast, in Fig. 4.8(b) the kinetics of methanol oxidation were apparently improved as the methanol concentration was increased from 0.5M to an optimum 1M concentration. However, when the concentration of methanol was raised above 1M, the resulting methanol oxidation current density declined. This observed decrease in activity is likely caused by methanol poisoning, a phenomenon where a disproportionately high ratio of methanol to hydroxide ions hinders the necessary formation rate of the active NiOOH species. This inhibition occurs because methanol molecules occupy the Ni^{2+} sites, and deleterious intermediate species derived from methanol oxidation become adsorbed onto the NiOOH surface. Further evidence for this poisoning effect at high methanol concentration is provided by a delayed oxidation peak corresponding to the $\text{Ni}(\text{OH})_2$ to NiOOH transition, which signifies a higher energy barrier needed to initiate the oxidation due to the increased methanol adsorption. Therefore, an equimolar concentration of 1M for both NaOH and methanol is determined to be the most favorable condition for achieving efficient methanol oxidation on the synthesized NMB catalyst.

III) Effect of calcination temperature

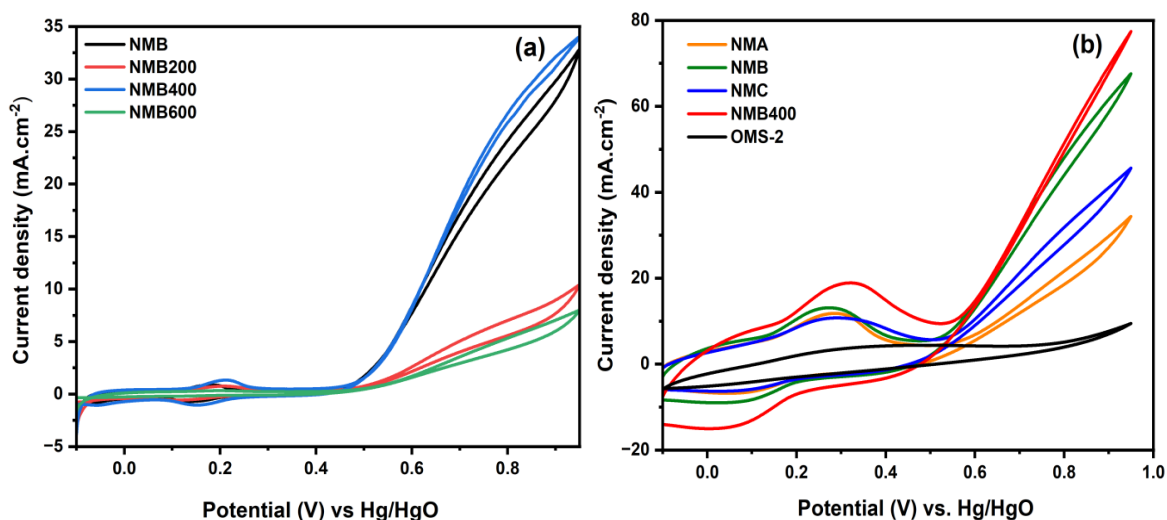


Figure 4.9: (a) CV of NMB, NMB200, NMB400 and NMB600 recorded at 2 mV.s⁻¹ scan rate in a mixture of 1M CH₃OH and 1M NaOH (b) Comparative CV of NMA, NMB, NMB400, NMC and OMS-2 recorded at 50 mV.s⁻¹ scan rate in the mixture of 1M CH₃OH and 1M NaOH

Considering the higher electrocatalytic activity exhibited by NMB catalyst compared to other nickel-modified forms of OMS-2, the effect of calcination at varying temperatures was studied on the catalytic performance. The post calcination NMB products were designated as NMB200, NMB400 and NMB600 depending upon the calcination temperature. The potential of the all the calcined samples in catalysing methanol oxidation was assessed by recording their CV (Fig. 4.9(a)) scanned within a potential span of -0.1V to 0.95V at a scan rate of 2 mV.s⁻¹ using a mixture of 1M methanol and 1M NaOH as an electrolyte. The findings indicated that the NMB catalyst calcined at 400°C produced the highest anodic current density for methanol oxidation. Conversely, lower catalytic activity was observed for the products calcined at 200°C and 600°C. The diminished activity at 200°C was attributed to incomplete decomposition and a larger particle size of sample. Meanwhile, the lower performance at 600°C resulted from unfavorable phase decomposition coupled with particle agglomeration, which collectively reduced both the surface area and the resulting electrochemical performance. In contrast, the 400°C calcination was effective, promoting the conversion of Ni(OH)₂ into the more catalytically active NiOOH phase. This transformation was supported by XPS data showing a reduced Ni²⁺/Ni³⁺ ratio. Furthermore, XRD analysis confirmed that NMB400 possessed the

smallest particle size, leading to higher electrical conductivity and a larger surface area. Besides, a greater concentration of oxygen vacancies induced by the 400°C calcination process, enhanced its catalytic activity. This superiority was quantified by its highest anodic peak current density of 30 mA.cm⁻², achieved at a potential of 0.85V vs Hg/HgO, at the 2 mV.s⁻¹ rate of scanning. Additionally, when the scan rate was increased to 50 mV.s⁻¹, as shown in Fig. 4.9(b), a significantly higher current density of 60.62 mA.cm⁻² was recorded for NMB400.

IV) Effect of scan rate

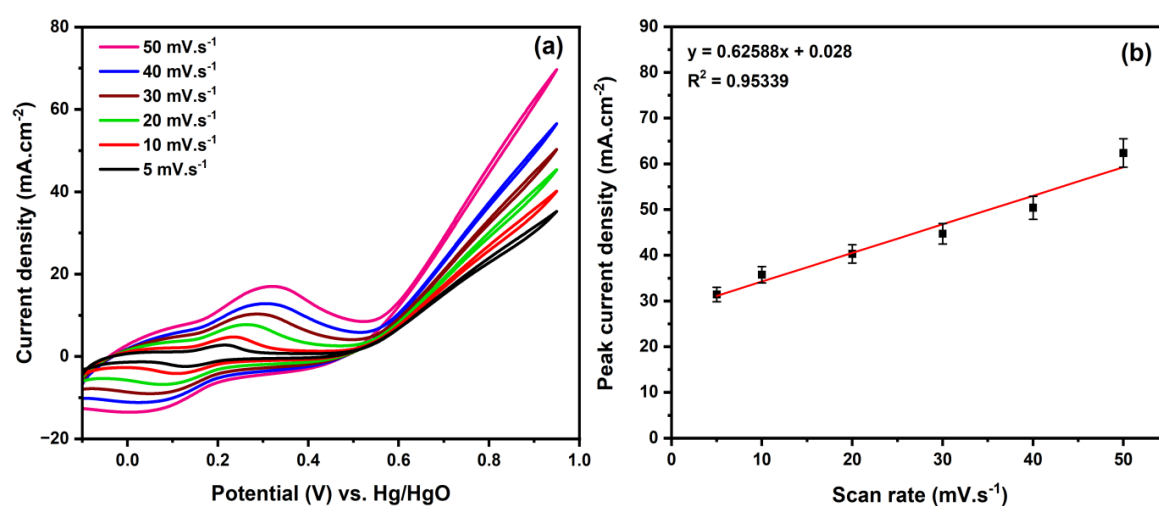


Figure 4.10: (a) Effect of scan rates on CV of NMB400 for methanol oxidation (b) Current density vs. scan rate plot of NMB400

A comprehensive electrochemical study was also conducted by recording CVs across a scan rate range of 5 to 50 mV.s⁻¹, as represented in Fig. 4.10(a) to understand the influence of the scan rates on current density of the reaction. Further plotting the peak current densities at a fixed potential of 0.85V against the corresponding scan rates, gave a linear relationship in Fig. 4.10(b). This relationship was accurately modelled by the equation $y = 0.62588x + 0.028$, ($R^2=0.953$). This linearity is the crucial evidence that confirmed the predominant surface controlled methanol oxidation kinetics on the NMB400 catalyst.

V) Evaluation of electrochemical parameters

a) *Surface concentration (Γ)* : Mechanistic studies concerning both the MOR and OER consistently underscore the fundamental importance of the in-situ oxidation and reduction processes occurring at the active sites of the catalyst during a single, full catalytic turnover cycle. Consequently, any metal site that demonstrably undergoes this particular oxidation/reduction transition immediately preceding the commencement of the main catalytic oxidation reaction is strongly considered to be participating directly in the catalysis. The quantification of such sites undergoing in-situ electrochemical change provides a vital metric for determining the accessible, MOR/OER-participating active centers. This measurement offers a highly realistic and representative assessment of the intrinsic activity of the catalyst [41]. Employing this standardized approach allows for a scientifically sound and defensible comparison of the measured performance of the NMB400 catalyst when evaluated against other modern and relevant electrocatalysts.

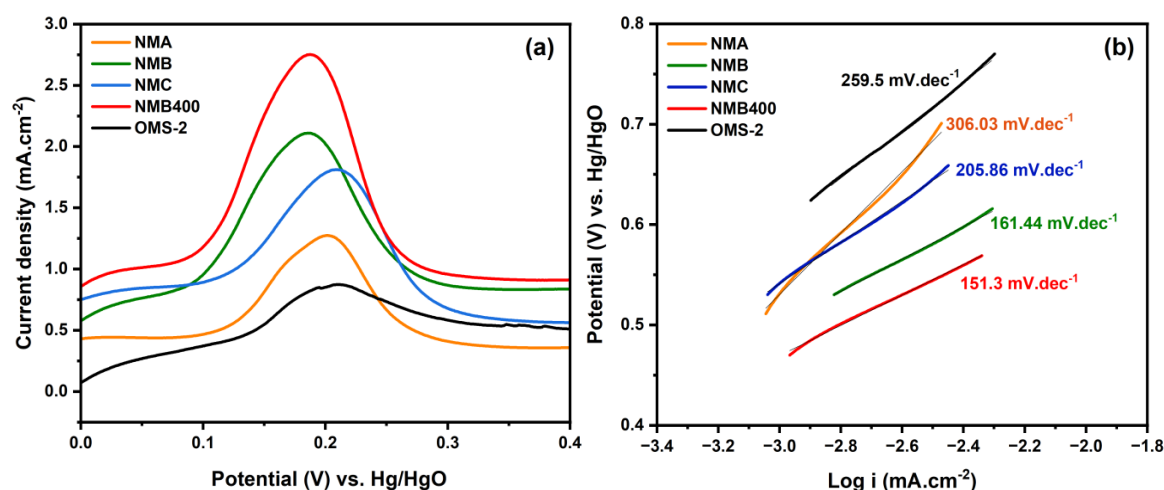


Figure 4.11: (a) Ni(II) to Ni(III) / Mn(III) to Mn(IV) transition peak during anodic scan (b) Tafel polarisation plots

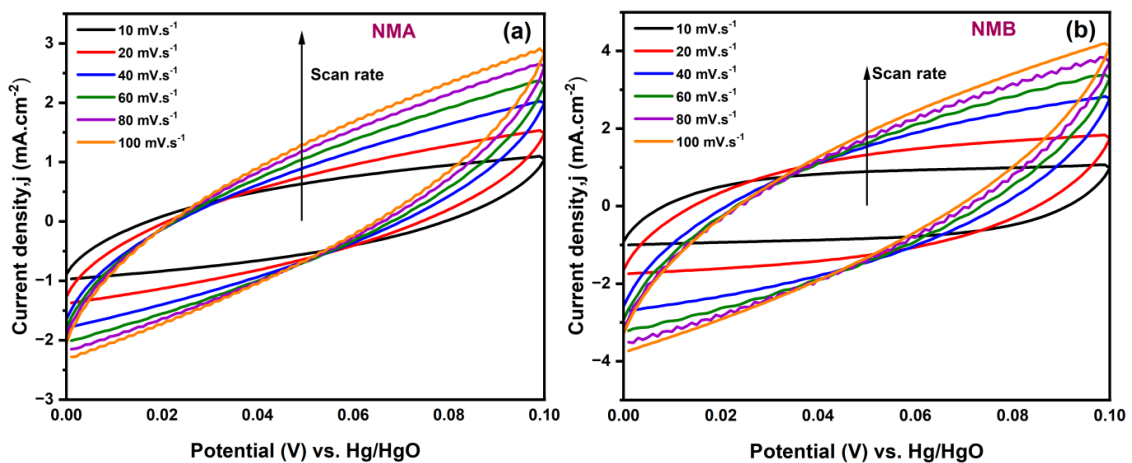
Given the established understanding that the Ni³⁺ species, in conjunction with the Mn⁴⁺ redox couple, functions as the catalytically active species for the MOR [7], its surface concentration (Γ) is an essential parameter for accurately evaluating the electrocatalytic performance of the synthesized Ni-doped OMS-2 catalyst. The single prominent peak resulting from the combined oxidation of Ni²⁺/Ni³⁺ and Mn³⁺/Mn⁴⁺ observed in the initial anodic scan segment displayed in Fig. 4.11(a) was systematically utilized to determine the number of active sites present on the catalyst surface. This was achieved by integrating the redox peak area. With an assumption of all Ni³⁺ and Mn⁴⁺ species being active for the

MOR/OER, this integrated electrical charge quantified the collective surface transition involving the highly active conversion of Ni^{2+} to Ni^{3+} and the transition of Mn^{3+} to Mn^{4+} species. This represented the estimated total, coupled active surface sites that are responsible for driving the observed enhanced oxidation kinetics. Conversely, the undoped OMS-2 sample merely displayed a broad, low-intensity oxidation feature, which corresponds to the intrinsically sluggish native Mn^{3+} to Mn^{4+} surface transition. Although its efficacy is lower, the charge derived from this specific feature in OMS-2 was nonetheless employed to quantify the accessible Mn active sites for OMS-2, ensuring the application of a consistent methodological approach. The number of electrons transferred (n) during the $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox transitions was approximated to be unity. The calculated surface concentrations, summarized in Table 4.3, clearly reveal that the NMB400 sample exhibited a significantly greater number of surface active sites, which was quantitatively evidenced by a combined Ni^{3+} and Mn^{4+} surface concentration reaching $4.966 \times 10^{-6} \text{ mol.cm}^{-2}$. This substantially elevated active site concentration is in direct correlation with its superior MOR activity when compared to other synthesized Ni-doped OMS-2 variants. Furthermore, this important finding is entirely consistent with the XPS results obtained for NMB400, which demonstrated a reduced $\text{Ni}^{2+}/\text{Ni}^{3+}$ ratio following the specific calcination process. This indicates a favorable conversion of $\text{Ni}(\text{OH})_2$ to the more electrocatalytically active NiOOH phase, which not only raised the concentration of oxygen vacancies but also increased the accessible $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. These combined effects enhanced the local conductivity and improved the synergy needed to favor charge transfer kinetics, while also facilitating the oxidative removal of methanol oxidation intermediates from the Ni active sites.

b) Tafel slope: The Tafel slope being a fundamental kinetic metric derived from the Tafel equation serves as a diagnostic tool for understanding the rate-determining step (RDS) and the charge transfer efficiency of the methanol oxidation on NiOMS-2 catalysts. The NMB400 catalyst, with its lowest Tafel slope of $151.3 \text{ mV.dec}^{-1}$, confirms its fastest intrinsic charge transfer kinetics as compared to other samples. While typical Tafel slopes for single-electron RDS are 120 mV.dec^{-1} in alkaline media, values slightly higher than this, like $151.3 \text{ mV.dec}^{-1}$ for MOR, are common for complex, multi-electron processes. This value suggests that the reaction kinetics are still predominantly under surface control but may be subject to a slight potential-dependent variation in the surface coverage of key intermediates or a minimal influence from mass transport effects at the high current

densities used. Ultimately, the low $151.3 \text{ mV.dec}^{-1}$ slope directly correlates with the optimized surface structure of NMB400 characterized by a high concentration of accessible Ni^{3+} and Mn^{4+} active sites which successfully lowers the activation energy barrier for the MOR.

c) Electrochemical active surface area : Although the geometric surface area of a catalyst is a frequently used parameter for determining current densities in various electrochemical processes, this application becomes problematic and can lead to inaccurate figures when dealing with catalysts that exhibit non-ideal planar topographies, such as porous or hollow materials. To secure a more precise and accurate quantification of the inherent catalytic performance of the material, the ECSA is the preferred method, as it better characterizes the true, accessible surface features of the catalyst [45]. As discussed in the experimental section, the ECSA was determined from C_{dl} measurement, from the cyclic voltammograms plotted in non-faradaic region for each sample as represented in Fig. 4.12(a) – (e) and the slope of derived linear plot of Δj vs. scan rate (Fig. 4.12(f)). The analysis demonstrated that the NMB400 catalyst recorded the highest ECSA value of 235 cm^2 . The NMA, NMB, NMC and the undoped OMS-2 samples yielded ECSA of 103.25, 170.38, 79 and 218.5 cm^2 , respectively. The substantial higher ECSA in NMB400 was instrumental in facilitating highly efficient methanol oxidation as represented by a higher current density and low Tafel slope, because it promoted enhanced interaction between the electrode surface and the surrounding electrolyte. This enhancement is attributed to the creation of a greater quantity of active sites resulting from the increased accessibility of the active Ni and Mn sites, coupled with a higher concentration of oxygen vacancies on the NMB400 catalyst surface, despite the fact that this material exhibited a lower overall surface area when measured by BET analysis.



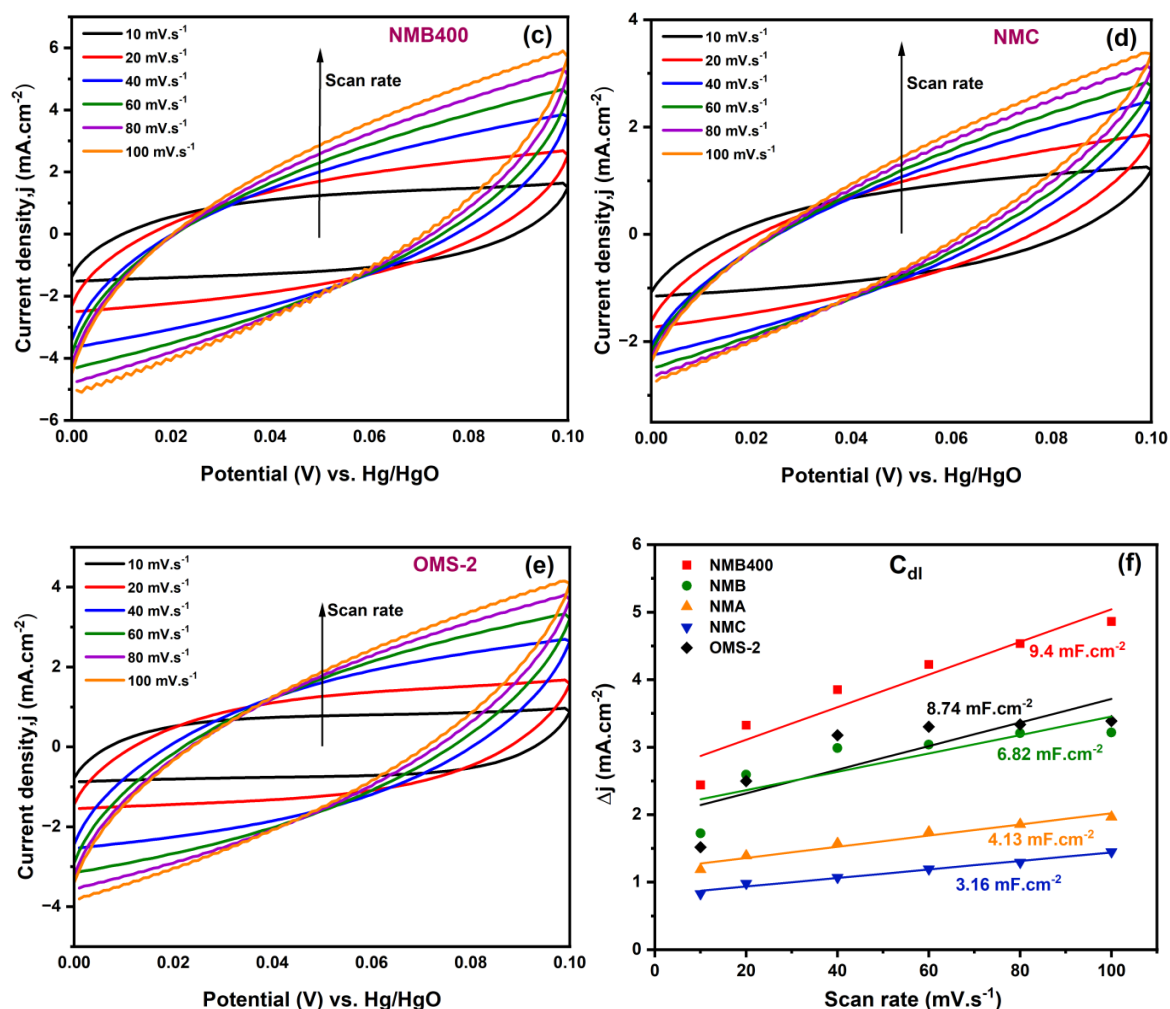


Figure 4.12: Cyclic voltammograms of (a) NMA (b) NMB (c) NMB400 (d) NMC (e) OMS-2 in non-faradaic region spanning between 0 to 0.1V vs. Hg/HgO in 1M NaOH (f) Δj vs. scan rate plot for C_{dl} measurement

d) Electrochemical impedance : The charge transfer kinetics of the catalysts were systematically evaluated by assessing the Nyquist plots obtained from EIS measurements of each sample, as shown in Fig. 4.13(a). These spectra were recorded at a fixed potential of 0.505V vs. Hg/HgO. The plots are composed of a semicircle in the high-frequency range and a linear tail in the low-frequency range. The undoped OMS-2 catalyst exhibited the largest semicircle at high frequencies. This large diameter signifies the highest charge transfer resistance (R_{ct}) and consequently, the inherently poor electrical conductivity of material. Upon the deliberate incorporation of Ni dopants, a discernible decrease in this resistance was observed. Among all the tested variants, NMB400 displayed the most favorable characteristics, consistent with all other electrochemical findings. Specifically, NMB400 showed the lowest solution resistance (R_s) and the lowest charge transfer

resistance, which was visually evident from its smallest semicircle diameter. This finding is a strong indication of significantly faster charge transfer kinetics for the methanol oxidation reaction. Furthermore, the Nyquist plot of NMB400 featured a shorter linear region at the lower-frequency end compared to the other Ni substituted forms. This shorter linear segment corresponds to a lower Warburg resistance, which suggests a faster diffusion of ions or methanol molecules to the active surface of the electrodes.

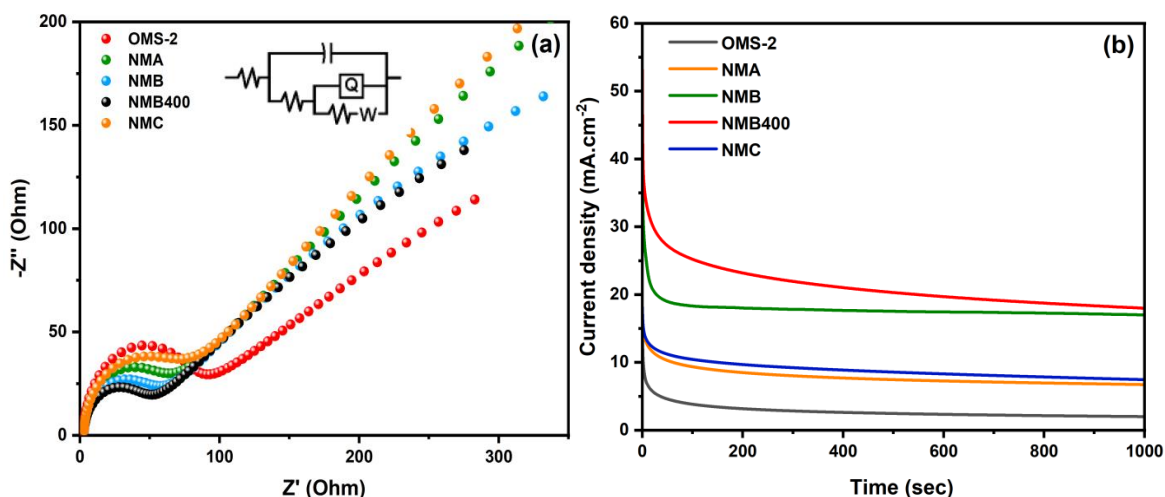


Figure 4.13: (a) Nyquist plots of NMA, NMB, NMB400, NMC and OMS-2 (b) Chronoamperometric stability tests performed at 0.85V for 1000 sec

Table 4.3: : R_s , R_{ct} , C_{dl} , ECSA and Γ values of OMS-2 and Nickel modified OMS-2 samples

Sample	R_s (Ω)	R_{ct} (Ω)	C_{dl} ($\text{mF}\cdot\text{cm}^{-2}$)	ECSA (cm^2)	Γ ($\text{mol}\cdot\text{cm}^{-2}$)
OMS-2	2.58	83.31	5.34	133.5	1.276×10^{-6}
NMA	2.847	59.78	3.60	90.0	2.318×10^{-6}
NMB	3.044	44.49	4.82	120.5	3.820×10^{-6}
NMB400	2.915	38.39	12.07	301.75	4.966×10^{-6}
NMC	2.981	61.43	3.16	79.0	3.064×10^{-6}

VI) Chronoamperometry

Chronoamperometric tests were carried out on all the synthesized samples to determine their electrocatalytic stability over time, with the measurements recorded at a fixed applied potential of 0.85V vs Hg/HgO for an extended duration of 1000 seconds (as illustrated in

Fig. 4.13(b)). The results clearly showed that the NMB400 catalyst maintained superior stability, exhibiting only a steady initial decrease in current density before stabilizing to the highest final current density of 20 mA.cm^{-2} at the 1000 sec mark. In contrast, all the other tested samples displayed a much sharper, abrupt decrease in current density during the initial 18 seconds of the test, after which they transitioned into a stable but ultimately lower current density region upon reaching 1000 seconds. This performance trend established the following stability order among all the materials : NMB400 > NMB > NMC > NMA > OMS-2. This definitive ranking not only demonstrates the enhanced electrocatalytic performance of the NMB400 catalyst but also confirms its exceptional durability and resistance to degradation during the prolonged methanol oxidation reaction.

4.3.3 Electrocatalytic assessment of In-situ NixOMS-2 nanorods : Oxygen Evolution Reaction

1) Linear Sweep Voltammetry (LSV)

The catalytic performance of all synthesized samples toward the Oxygen evolution reaction was rigorously investigated by utilizing iR-corrected LSV curves, scanned from 1.3 to 1.8V vs. RHE at a lowest scan rate of 1 mV.s^{-1} . To enable a standardized comparison against other contemporary catalysts reported in the literature, the overpotential necessary to achieve a benchmark current density of 10 mA.cm^{-2} was selected as the key metric for OER catalyst classification. Analysis of the iR corrected LSV curves (as presented in Fig. 4.14(a) showed that, among the pristine OMS-2 and its nickel-modified derivatives, the NMB sample with 30mM Ni concentration, demonstrated the most favorable initial performance, requiring an overpotential of 500 mV. The NMC derivative exhibited a slightly higher overpotential requirement of 537 mV. This initial superior activity of NMB is plausibly attributed to a higher concentration of lattice oxygen and its robust, active participation in the OER mechanism. In contrast, the NMA sample and the pristine OMS-2 material both exhibited considerably higher overpotentials, a result that signifies their diminished capability for oxygen evolution, which is likely a consequence of comparatively lesser concentration of surface active sites and lower ECSA. Significantly, the OER activity of NMB was substantially improved following the post-calcination treatment. This enhancement was clearly demonstrated by the NMB400

sample, which required a distinctly lower overpotential of only 461 mV. The prevailing theory suggests that this kinetic enhancement is a direct result of the high-temperature treatment, which effectively creates a greater number of structural vacancies and defects within the material lattice. This process, in turn, successfully increases the density of the active sites available to drive OER.

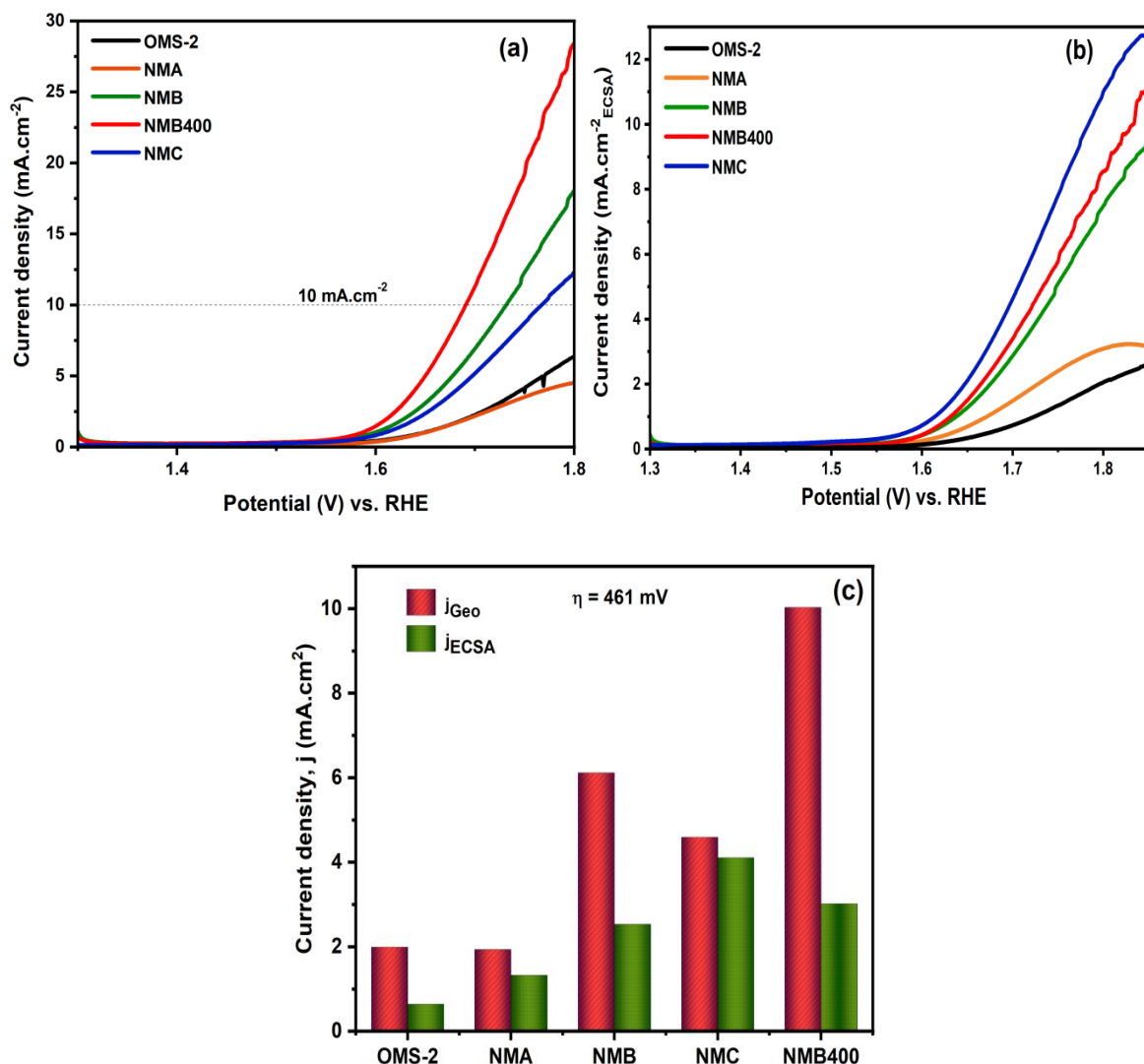


Figure 4.14: (a) iR corrected LSV curves recorded in N₂ saturated NaOH solution at 1mV.s⁻¹ scan rate (b) ECSA normalised LSV curves (c) Bar graph representing geometric and ECSA normalized current densities of various catalysts at a fixed potential of 1.691V vs. RHE

The OER activity normalized by the ECSA, as shown in Fig. 4.14(b), is a crucial metric that represents the intrinsic catalytic efficiency of the active sites themselves. This plot revealed that the NMC catalyst achieved the lowest intrinsic overpotential of 554 mV to

reach an ECSA-normalized current density of 10 mA.cm^{-2} , unequivocally demonstrating the highest inherent quality of its active centers. This finding stands in contrast to the overall best catalyst, NMB400, which displayed a slightly higher intrinsic overpotential of 603 mV at the 10 mA.cm^{-2} benchmark, despite benefiting from a much higher total ECSA. Fig. 4.14 (c) provided a quantitative head-to-head comparison between the geometric and the ECSA-normalized current densities for the various catalysts at a fixed potential of 1.691V (corresponding to an overpotential of 461 mV). At this potential, the NMB400 catalyst exhibited the highest geometric current density. This result decisively validates its role as the optimal catalyst for practical applications, as this measure incorporates the beneficial effect of maximizing the sheer quantity of accessible active sites and the resulting ECSA, a factor that effectively outweighed the marginal advantage offered by the superior intrinsic efficiency (or quality) of the active sites on the NMC sample which recorded the highest ECSA-normalized current density, a finding that definitively confirms its superior intrinsic current output per individual active site. The comparative results thus showcased a distinct and strategic balance between structural engineering (quantity) and electronic tuning (quality). Specifically, the high-temperature calcination applied to NMB enhanced its pore architecture and, most crucially, successfully created the highest concentration of OER active Mn^{3+} species and an increased number of oxygen vacancies. These structural features are primarily responsible for increasing the abundance and accessibility of the active sites, which ultimately leads to the highest ECSA. In contrast, NMC, despite having a lower ECSA due to poor structural development, retained a specific local electronic configuration with a higher content of catalytically active Ni^{3+} and the greatest proportion of oxygen vacancies. This unique electronic tuning optimally adjusted the OER intermediate binding energies, which explains its high intrinsic quality causing a lower overpotential per active site.

II) Evaluation of electrochemical parameters

a) Tafel slope: The Tafel slopes were derived from the Tafel polarization plots (Fig. 4.15(a)), which correlated the LSV derived logarithmic current density with the overpotential represented as the difference between the applied potential and the theoretical OER potential of 1.23 V. The NMB400 catalyst, with its lowest Tafel slope value of $88.94 \text{ mV.dec}^{-1}$, conclusively demonstrated the fastest OER kinetics and highest intrinsic activity among all synthesized materials. This was in sharp contrast to the slower kinetics of the other variants, which showed progressively higher Tafel slope values with

NMB at 103.17 mV.dec⁻¹, NMC at 107.12 mV.dec⁻¹, NMA at 114.44 mV.dec⁻¹, and the undoped OMS-2 at 131.4 mV.dec⁻¹. This substantial difference in slope underscores the optimized surface chemistry and charge transfer efficiency in NMB400 catalyst.

The oxygen evolution reaction in alkaline media typically proceeds through an Adsorbate Evolution Mechanism (AEM) (depicted in Fig. 4.15(c)), which is a complex electrochemical process involving the transfer of four electrons through a series of four steps. The process of oxygen evolution on a metal catalyst, designated by the active site M*, is a complex multi-step sequence involving various transient intermediate species such as *O, *OH and *OOH. Mechanistic insights into the OER pathway are frequently determined by analysing the Tafel slope, as distinct slope values are indicative of different rate-determining steps. Specifically, a Tafel slope of roughly 120 mV.dec⁻¹ generally points to the initial electron transfer step as the RDS, which involves the discharge of hydroxide ions to produce the M*OH intermediate. In contrast, a slope around 60 mV dec⁻¹ often signifies that the second electron transfer, which culminates in the formation of the M*O intermediate, acts as the RDS.

Furthermore, a Tafel slope of approximately 40 mV dec⁻¹ typically suggests that the formation of the metal-peroxo intermediate, M*OOH is the rate-limiting step. However, for dynamic metal oxide catalysts, the participation of lattice oxygen also plays a significant role in OER, meaning the active sites are not strictly limited to surface metal centres. This involvement is frequently evidenced by deviations in the Tafel slope values from the conventional 120, 60, or 40 mV dec⁻¹ benchmarks, signalling a more intricate OER mechanism [46]. In this alternative pathway, known as the Lattice-Oxygen-Mediated mechanism (LOM) [47], the active lattice oxygen directly participates in the OER, thereby actively facilitating the necessary O-O bond coupling step, as also represented in Fig. 4.15(c). Within the lattice oxygen mechanism, the initial two reaction steps follow a pathway identical to that of the conventional adsorbate evolution mechanism. However, the subsequent mechanistic step involves the coupling of an M*O intermediate species with a lattice oxygen atom. This specific coupling event results in the creation of an oxygen vacancy within the crystal lattice of the material. This vacancy is then quickly regenerated by the migration of hydroxide ions originating from the surrounding electrolyte. The definitively recorded Tafel slope of 88.94 mV.dec⁻¹ for OER on the NMB400 catalyst is a strong kinetic indicator, confirming that the operative mechanism is

a sophisticated process that clearly deviates from the predictable, conventional AEM models.

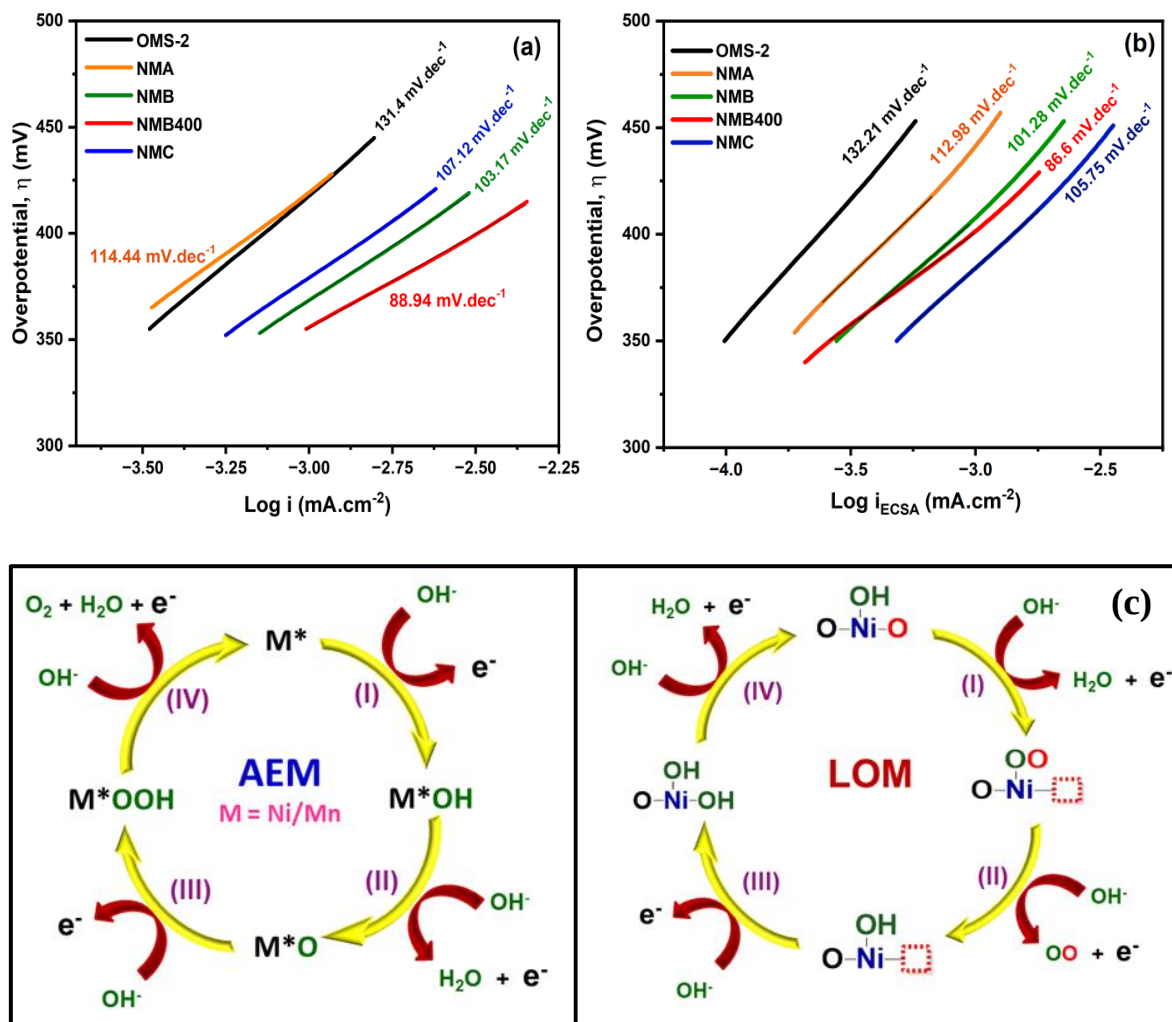


Figure 4.15: (a) Tafel polarisation curves (b) ECSA normalised Tafel polarisation curves of the samples (c) Schematic illustration of Adsorbate Evolution Mechanism (AEM) and Lattice Oxygen Mediated Mechanism (LOM) on metal oxide

Specifically, surface species like NiOOH serve as the primary active sites, initially facilitating the electrochemical activation of hydroxide ions and the subsequent electron transfer steps. Upon achieving a sufficiently high oxidation state, these Ni active sites become potent electrophilic centres capable of abstracting an electron from an adjacent nucleophilic lattice oxygen located within the MnO₂ framework. This action effectively activates the lattice oxygen for direct participation in the electrophilic peroxo O-O bond formation, which is crucial for initiating the OER. This pathway is analogous to the metal-peroxo cycle reported by H. Lee et al. [48] in their research on tungstate-modified iron-

nickel (oxy)hydroxide (W/FeNiOOH) as an OER catalyst. A similar complex OER mechanism was reported by doping Ru into Co_3O_4 lattice [49]. This non-ideal Tafel slope of $88.94 \text{ mV.dec}^{-1}$ observed on NMB400 is highly consistent with such a complex, synergistic pathway, potentially indicating that the rate-determining steps involve the activation of lattice oxygen, the influence of surface heterogeneity, or a subtle interplay between both the traditional adsorbate and the lattice oxygen pathways.

Intriguingly, the ECSA-normalized Tafel plot in Fig. 4.15(b) confirmed that the NMB400 catalyst sustained an equally minimal intrinsic Tafel slope of 86.6 mV.dec^{-1} , while the NMC sample registered a higher value of $105.75 \text{ mV.dec}^{-1}$. Although, the lower overpotentials in ECSA normalized LSV curves of NMC indicated least energy requirement for initial activation by binding OH^* intermediate, however, it encountered a kinetic impediment during subsequent reaction steps. Conversely, the NMB400 material facilitated the fastest rate determining step and possessed superior kinetic efficiency specifically at the practically relevant, high current densities. Due to such advantages, NMB400 is designated as the optimal catalyst as it successfully integrates the fastest intrinsic kinetics with the maximum quantity of accessible active sites. This synergistic combination guarantees its best-in-class performance across all relevant operational current regimes, which is ultimately validated by its achievement of the highest geometric current density.

b) Turnover frequency (TOF): A crucial parameter for accurately assessing a catalyst's OER efficacy is its TOF, a quantitative metric that defines the absolute rate of reaction per mole of active sites (s^{-1}). At a consistent overpotential of 461 mV, the NMB400 catalyst achieved the highest TOF of 0.0052 s^{-1} as shown in Fig. 4.16(a). This figure provides definitive confirmation of its superior catalytic kinetics and validates its standing as the most fundamentally active electrocatalyst within the entire series of synthesized materials.

c) Electrochemical impedance: The EIS analysis, presented as Nyquist plots in Fig. 4.16 (b), recorded at a constant potential of 1.677V versus the RHE was fitted using the complex equivalent circuit $R(C(R(Q(R(C(RW))))))$. The NMB400 catalyst unequivocally demonstrated superior electrochemical properties, exhibiting the lowest solution resistance (R_s) of 1.737Ω at the electrode-electrolyte interface and the lowest charge transfer resistance (R_{ct}) of 25.39Ω among all tested catalysts. In comparison, NMA, NMB, NMC, and the base OMS-2 sample showed considerably higher R_{ct} values of 45.95Ω , 35.58Ω ,

45.28 Ω , and 46.88 Ω , respectively. Furthermore, the Nyquist plot of NMB400 displayed a notably shorter linear segment in the low-frequency region. This observation is due to faster ionic diffusion to the electrode surface, a characteristic, actively facilitating more efficient oxygen evolution kinetics.

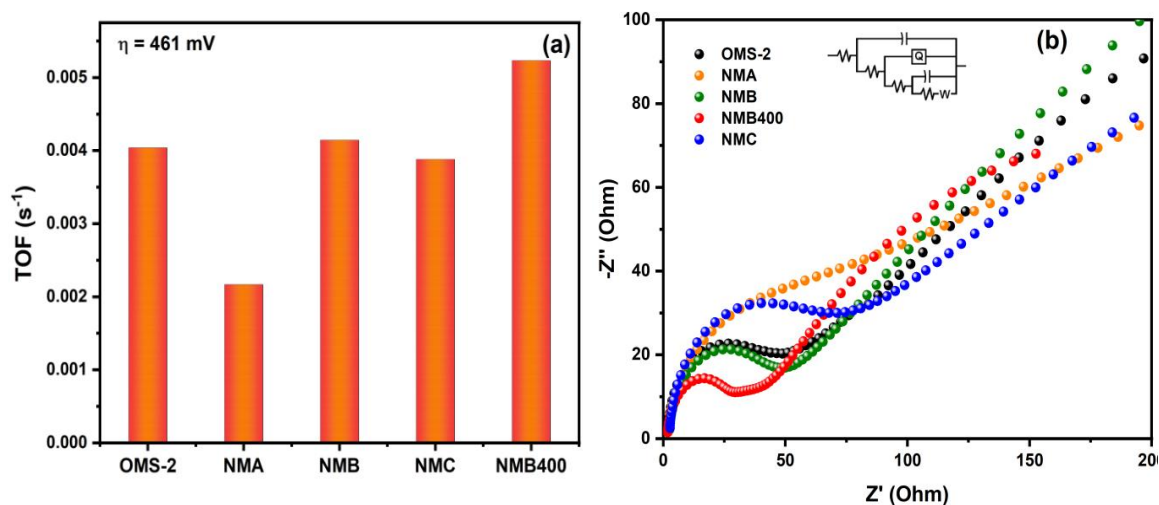


Figure 4.16: (a) Bar graph of TOF of OER on various samples (b) Nyquist plots of NMA, NMB, NMB400, NMC and OMS-2

III) Chronoamperometric stability analysis

The long term OER stability of the NMB400 catalyst was evaluated using a chronoamperometry test conducted over 6 hours in 1 M NaOH solution at a fixed potential of 1.627V, represented in Fig. 4.17(a). This extended test revealed an initial gradual reduction in activity that eventually stabilized, resulting in a long-term 50% retention of the original OER activity for NMB400. This observed stability decay and subsequent stabilization are attributed to surface reconstruction processes occurring on the catalyst. Notably, the activity of catalyst could be substantially improved immediately upon introducing a fresh 1 M NaOH electrolyte solution, which clearly indicates that the sustained performance is sensitive to reactant concentration (as evidenced in Fig. 4.17(b)). To accurately understand the specific cause of the activity reduction observed after the 6 hours period, ex-situ characterization of the samples was subsequently performed following the completion of the OER stability studies.

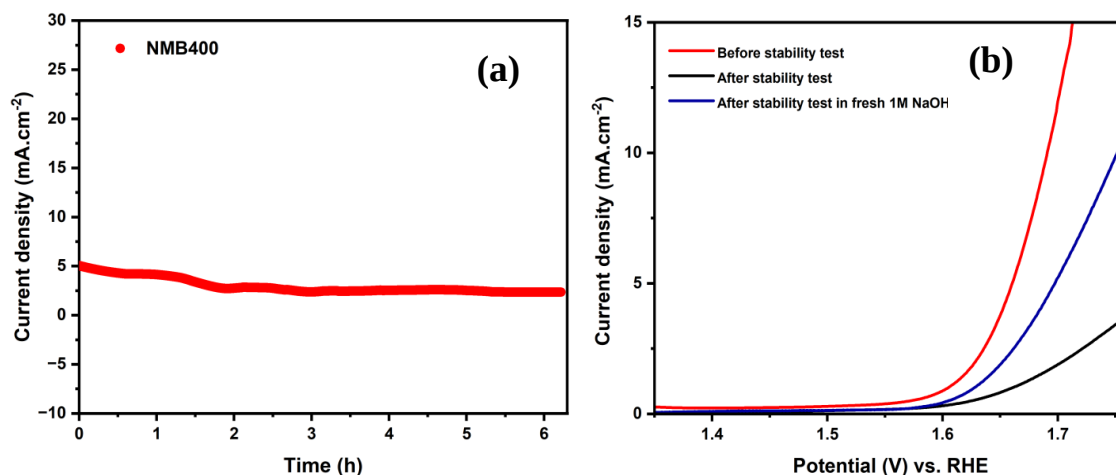


Figure 4.17: (a) Chronoamperometric i-t curve of NMB400 at 1.627V vs. RHE recorded for a duration of over 6 hrs. (b) LSV curves of NMB400 before and after stability test in 1M NaOH

4.3.4 Post-OER Structural and Compositional characterization

Under sustained OER conditions, the NMB400 catalyst exhibited outstanding durability and stability, a performance underpinned by a stable structural core that supports a dynamic reconstruction confined strictly to the surface. As illustrated in pre and post OER stability run X-ray diffractograms in Fig. 4.18(a) and FTIR spectra in Fig. 4.18(b), which verified the bulk structural integrity of the material after sustained OER. Specifically, the XRD patterns revealed that the primary α -MnO₂ phase persisted throughout the testing period, while FTIR confirmed that Mn-O lattice vibrations (400 – 800 cm⁻¹) were preserved, a stability attributed to the thermodynamically robust Mn⁴⁺ core. However, analysis of the post-OER XRD patterns revealed a decrease in peak intensity with peak broadening, pointing to a gradual amorphization and disordering of crystallites confined to the surface. Visual corroboration provided by SEM micrographs of this material in Fig. 4.19(a)-(c) depicted these surface modifications; although the NMB400 nanorods maintained their overall OMS-2 structure, they developed a thin amorphous coating and displayed slight particle aggregation following extended OER exposure. This newly developed surface layer is identified as an electrochemically activated, amorphous film enriched with Ni in the form of nickel oxyhydroxide.

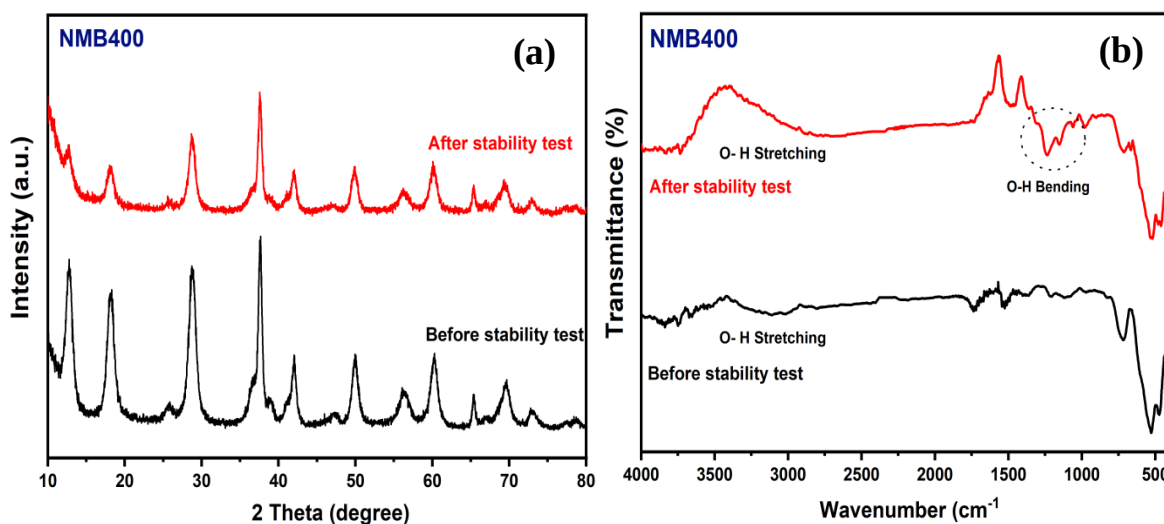


Figure 4.18: Post OER (a) XRD pattern (b) FTIR spectra of NMB400 catalyst

FTIR analysis chemically validated the emergence of this active layer via a significant broadening of the O-H band ($3000\text{--}3600\text{ cm}^{-1}$) which offered a conclusive proof of a highly hydrated surface rich in hydroxyl groups. Furthermore, intensified bands within the $1000\text{--}1150\text{ cm}^{-1}$ range, attributed to O-H bending modes reinforced the presence of this surface alteration that stabilized the active Ni/Mn oxyhydroxide layer. Notably, the XRD data did not display characteristic Bragg diffraction peaks for NiOOH. Absence of this peak is consistent with the amorphous nature of the film, which lacked the long-range atomic order required for coherent X-ray scattering.

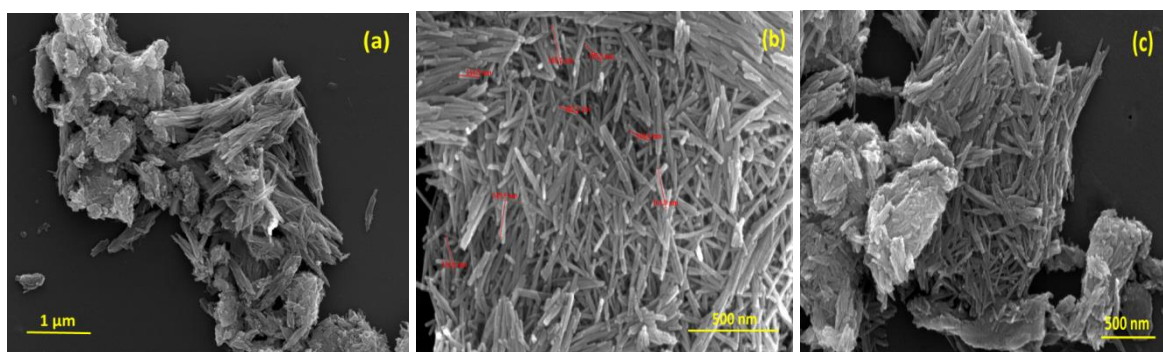


Figure 4.19: (a)-(c) SEM images of varying magnification of NMB400 post OER stability test

The activation mechanism, driven by nickel enrichment, was precisely quantified (Table 4.4) through XPS analysis of the electrochemically treated surface as shown in Fig. 4.20(a)-(d). It is realised from the XPS data that the application of a continuous anodic potential successfully drives the active Ni component toward the surface through migration evidenced by a significant rise in the surface Ni/Mn ratio from 0.1347 to 0.2052. This

surface restructuring correlates directly with an increase in the concentration of highly active chemisorbed oxygen (O_{ads}) from 15.12 to 16.32, a critical intermediate for O-O bond formation via the adsorbate evolution mechanism (AEM). Furthermore, the Ni^{2+}/Ni^{3+} redox accessibility is enhanced with the ratio increasing from 1.493 to 2.142 attributed to vacuum relaxation during XPS measurement causing the reduction of Ni from higher oxidation states to Ni^{2+} . The resulting Ni-enriched NiOOH/MnOOH film functions as the primary turnover centre, wherein, Ni^{3+} /highly oxidised Ni^{4+} redox couple drives the reaction (confirmed by the shift in the Ni^{2+}/Ni^{3+} ratio), while Mn^{3+} provides synergistic stability and activity. Consequently, the entire OER process is facilitated by a highly efficient dual AEM-LOM pathway, with the lattice oxygen mechanism explicitly validated by XPS data showing an increase in oxygen vacancies, O_{vac} from 23.53% to 24.71%. Within this mixed surface film, Mn^{3+} sites electronically tune the adjacent Ni sites; this modulation optimizes the binding energy of OER intermediates (O^* , OOH^*) on Ni, effectively reducing the overpotential required for the rate-determining step, while the Mn^{4+} component provides a rigid structural scaffold, with unaltered average oxidation state of Mn.

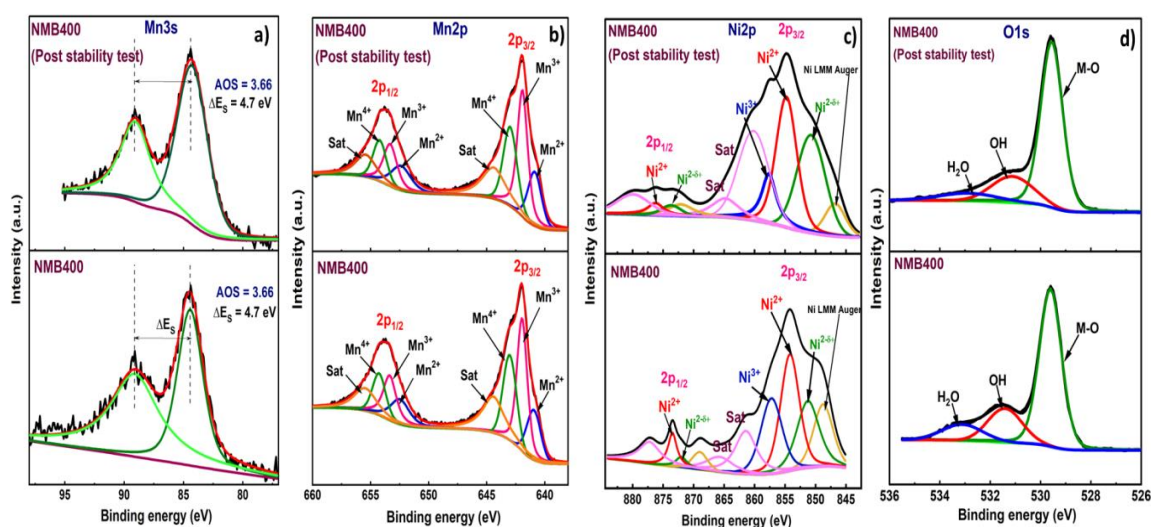


Figure 4.20: Core scan XPS spectra of (a) Mn3s (b) Mn2p (c) Ni2p (d) O1s of NMB400 before and after OER stability test

Table 4.4: Surface composition and chemical state analysis of NMB400 from XPS measurements

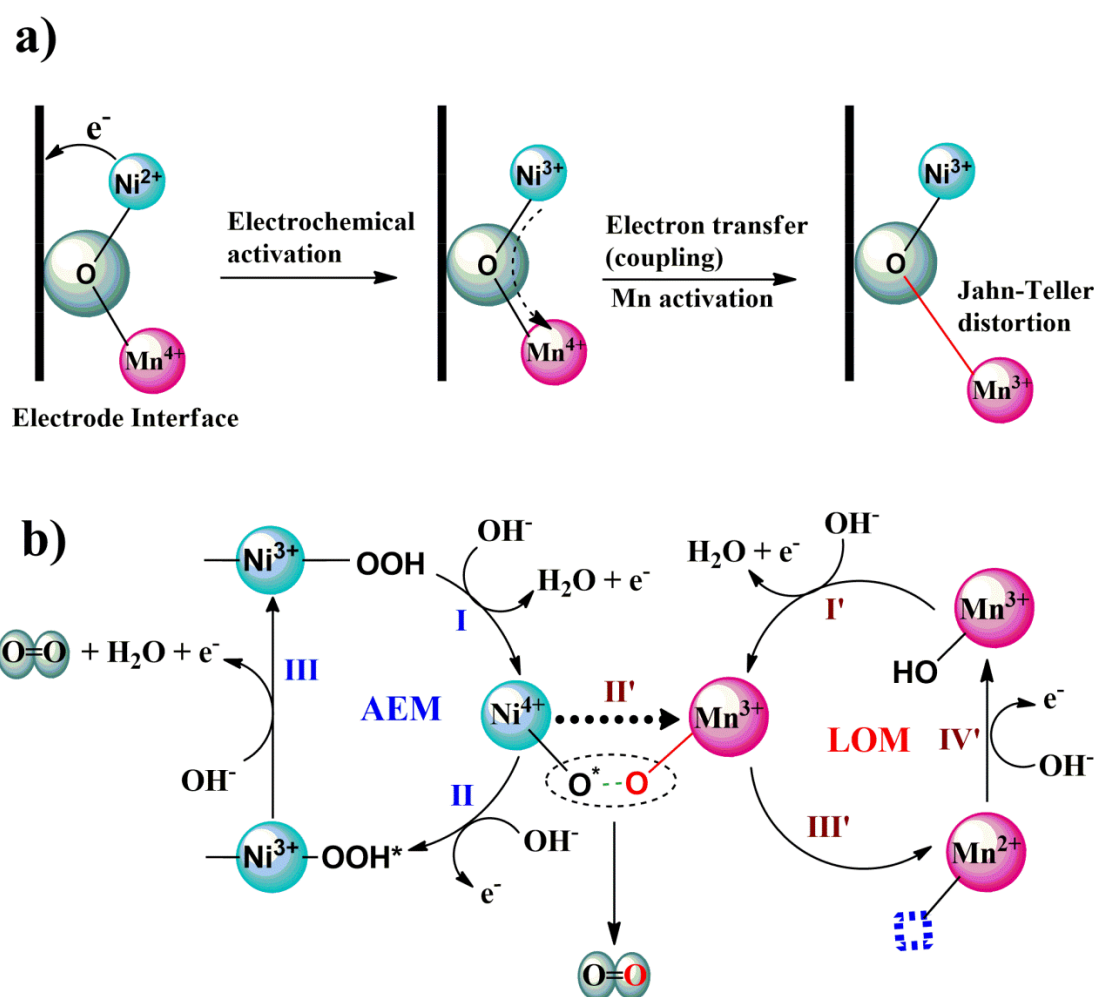
Sample	K/Mn	Ni/Mn	$\frac{Mn^{3+}}{Mn^{4+} + Mn^{3+} + Mn^{2+}}$	Mn (AOS)	$\frac{Ni^{2+}}{Ni^{3+}}$	O _{ads}	O _{vac}	O _{lat}
			(%)					
NMB400	0.0311	0.1347	36.80	3.66	1.493	15.12	23.53	61.35
NMB400 Post stability test	0.0901	0.2052	36.35	3.66	2.142	16.32	24.71	58.98

4.3.5 Mechanistic discussion

Synergistic Nickel-Driven Lattice Oxygen Mechanism Facilitated by Mn³⁺ Stabilization

The superior OER performance observed in the NMB400 catalyst is attributed to a sophisticated dual-pathway mechanism that effectively circumvents the scaling limitations associated with the adsorbate evolution mechanism through synergistic electronic and structural cooperation between adjacent metal sites. The high-turnover AEM is sustained by the high-potential Ni³⁺/Ni⁴⁺ redox couple, which facilitates efficient oxygen evolution from electrolyte derived OH⁻ groups. Simultaneously, the lattice oxygen mechanism which is responsible for the observed low overpotential capabilities is fundamentally activated by the Ni-promoted stabilization of the Mn³⁺ state. Mechanistically, the electrochemical oxidation of Ni²⁺/Ni³⁺ induces an electron transfer across the oxygen bridge to Mn⁴⁺, thereby continuously regenerating highly active surface Mn³⁺ species; this transformation is quantitatively corroborated by the increase in Mn³⁺ proportion as observed in the XPS data. This unstable, high-spin (d⁴) Mn³⁺ state possesses a single e_g orbital occupancy, which induces a dynamic Jahn-Teller distortion within the surrounding [MnO₆] octahedra [50]. As illustrated in Scheme. 4.1(a), this distortion manifests structurally as an elongation of the Mn-O bonds. This induced structural lability is critical, as it facilitates the active

participation of lattice oxygen, O_{lat} in the rate-determining O-O bond formation step of the OER [51], as well as in the oxidative removal of carbonaceous intermediates from Ni sites during the MOR. Consequently, this mechanism provides the kinetic advantage responsible for the superior performance metrics in the catalyst, including the lowest Tafel slope and high turnover frequency (TOF). Furthermore, the Mn component ensures long-term stability through a self-regulating "lattice healing" process. As depicted in Scheme 4.1(b), electrolyte OH^- ions rapidly occupy the resulting oxygen vacancies (V_o), effectively acting as a re-oxidation event that restores the thermodynamically stable Mn^{4+} state and preserves the bulk structural integrity of the catalyst.



Scheme 4.1: (a) Ni^{3+} triggered Mn activation facilitating superior OER kinetics (b) Synergistic OER mechanism on Ni-Mn oxyhydroxide exhibiting dual AEM-LOM pathways

While the OMS-2 framework exhibits a robust structural stability, the initial short-term decay observed in the oxygen evolution rate can be ascribed to a reversible kinetic

limitation induced by the continuous high anodic potential. This driving force converts the active species into an excessively dense, kinetically slow and thermodynamically stable amorphous Ni^{4+} film due to the over-oxidation of Ni sites. This phenomenon results in minor active site shielding and causes the aggregation of nanorods (as visually confirmed by SEM), which restricts mass transport and shields the underlying active Ni sites from the electrolyte, thereby lowering the OER turnover frequency to levels comparable to other Mn- and Ni-based catalysts [25].

As the high-valence $\text{Ni}^{3+}/\text{Ni}^{4+}$ species relax in vacuum during XPS analysis leading to its reduction to Ni^{2+} , producing a dominant Ni^{2+} signal, the analysis confirms that the OER process enriched the surface with a Ni redox-active oxyhydroxide structure, effectively enhancing OER kinetics via the AEM, when fresh electrolyte is introduced [52]. The identification of this unstable Ni^{4+} film on the nanorod surface serves as a confirmation that the deactivation is strictly a surface kinetic issue, and not a structural failure, as the bulk stability was confirmed across other analytical techniques. Therefore, the gradual drop in activity over long-term operation is considered a reversible surface kinetic limitation. The catalyst stabilizes at 50% of its initial activity throughout the test, characterizing NMB400 as a highly resilient material capable of full restoration via simple *in-situ* reactivation. Moreover, NMB400 outperforms other monofunctional Ni-doped transition metal oxide catalysts, which typically retain less than 50% of their activity after only one hour at significantly lower potentials [21]. In contrast to noble metal oxides, which undergo rapid dissolution and irreversible phase changes under anodic stress (e.g., the over-oxidation of RuO_2), the NMB400 system successfully preserves its bulk structural integrity.

4.3.6 Structural and morphological analysis of ex-situ NiOMS-2 nanocomposite

I. Structural Analysis by X-ray Diffraction

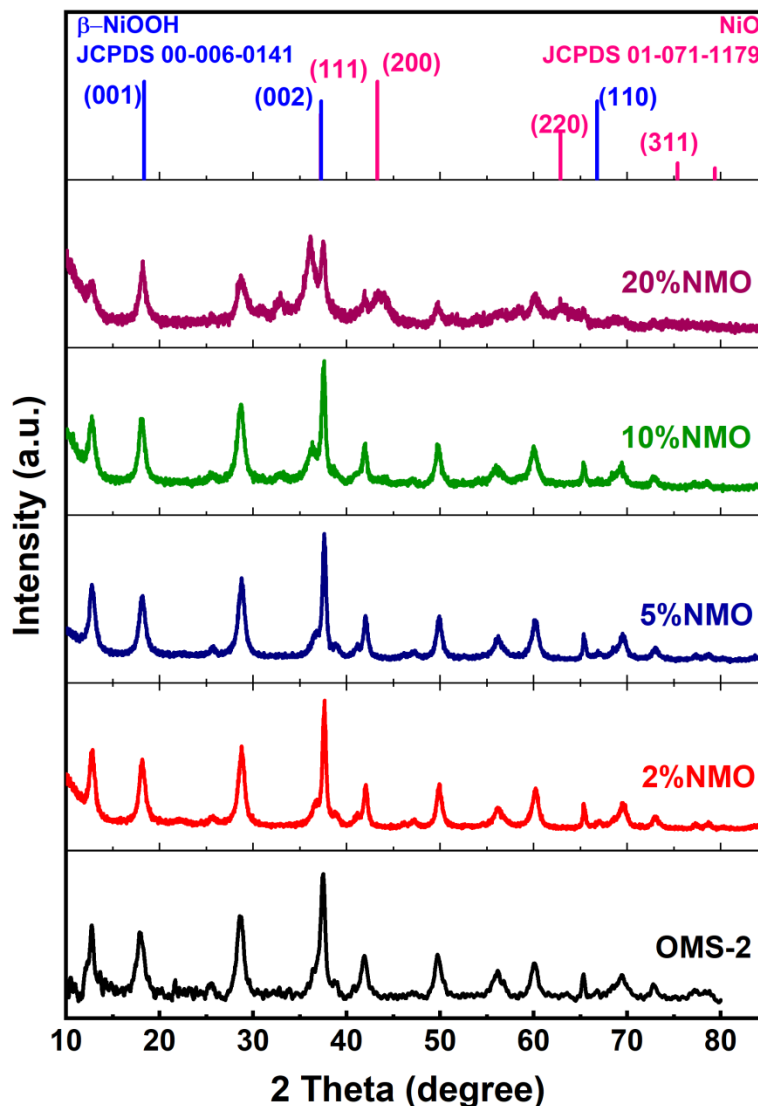


Figure 4.21: XRD patterns of OMS-2, 2%NMO, 5%NMO, 10%NMO and 20%NMO

The XRD patterns for pristine OMS-2 and all ex-situ nickel-doped samples with varying metal loadings are displayed in Fig. 4.21. The diffractogram of the pristine OMS-2 sample exhibits well-resolved, sharp diffraction peaks indexed to the tetragonal cryptomelane phase of α - MnO_2 (JCPDS card no. 00-044-0141). The major characteristic reflections observed at 2 theta values of 12.80, 18.10, 28.79, 37.52, 41.94, 49.86, 56.31, 60.12, 65.28, and 69.58, are indexed to the (110), (200), (310), (211), (301), (411), (600), (521), (002), and (541) crystal planes, respectively. The high intensity and narrow width of these peaks indicate that the pristine material possesses a high degree of crystallinity with a well-

ordered 2×2 tunnel structure with a particle size of 10.01 nm obtained from Scherrer analysis.

Upon the introduction of nickel species into the manganese oxide framework, the structural integrity of the host lattice is maintained at lower dopant concentrations upto 5%, showing no emergence of new diffraction peaks due to impurities. This absence of secondary phases suggests that at these loading levels, nickel ions are successfully incorporated into the interstitial sites of MnO_2 lattice forming a homogeneous solid solution. However, a gradual broadening of the diffraction peaks is observed as the nickel content increases from 5% to 20%, implying a reduction in crystallite size and an increase in lattice strain due to mismatch of ionic radius between the dopant Ni^{2+} and the host manganese ions. The particle size of 2%, 5%, 10% and 20%NMO from Scherrer analysis were determined to be 9.46 nm, 9.96 nm, 8.53 nm and 5.67 nm respectively. A significant structural transformation is evident in the sample with the highest nickel loading of 20% in 20%NMO revealing a substantial decrease in peak intensity and severe peak broadening, due to its transition into a more amorphous or poorly crystalline material. The characteristic cryptomelane peaks diminish in intensity with emergence of new peaks arising from the precipitation of a mixed secondary β -NiOOH and nickel oxide phase (confirmed from β -NiOOH JCPDS 00-006-0141 and NiO JCPDS 01-071-1179 card) representing the solubility limit of nickel within the OMS-2 framework. Consequently, while the OMS-2 structure is robust at lower doping levels, high concentrations of nickel lead to lattice disorder and phase segregation.

II. FTIR spectra

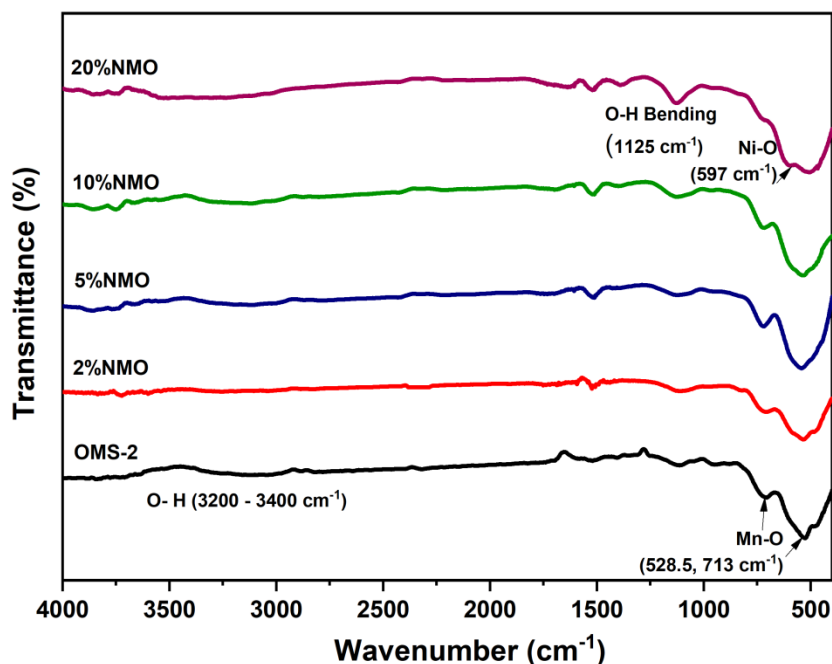


Figure 4.22: FTIR spectra of OMS-2, 2%NMO, 5%NMO, 10%NMO and 20%NMO

The FTIR spectra of OMS-2 and its ex-situ Ni doped forms is shown in Fig. 4.22, wherein, the spectrum of the pristine OMS-2 serves as the baseline, displaying characteristic vibrational bands associated with the cryptomelane structure. The broad absorption band between 3200–3400 cm⁻¹ is attributed to the stretching vibrations of hydroxyl groups (O-H) and physisorbed water molecules located within the 2 × 2 tunnels or on the surface of the material. Additionally, a weaker band around 1125 cm⁻¹ corresponds to the O-H bending vibrations, confirming the presence of structural water essential for stabilizing the tunnel framework. The pristine OMS-2 displayed four characteristic sharp bands representing high crystallinity and well-ordered octahedral arrangement of the OMS-2 lattice, at approximately 713 cm⁻¹, 528.5 cm⁻¹ and 484 cm⁻¹ corresponding to Mn-O stretching vibrations within the octahedral [MnO₆] framework of α -MnO₂. Specifically, the band at 528.5 cm⁻¹ is typically ascribed to the Mn-O stretching mode relative to the translation of octahedral chains, while the band at 713 cm⁻¹ is associated with the asymmetric stretching vibrations of the Mn-O-Mn bridges.

Upon 2% nickel doping, the spectral features largely retained the characteristic shape and position of the Mn-O vibrational bands seen in the pristine sample implying that the local coordination environment of the manganese oxide framework remains intact, with nickel

ions successfully incorporating into the lattice without disrupting the long-range order. However, with increasing loading, a significant broadening causing merging of bands and a reduction in their intensities indicated increased lattice disorder and a reduction in the symmetry of the $[\text{MnO}_6]$ octahedra, likely caused by the lattice strain induced by the substitution of Mn ions with Ni ions. Most notably, in the 20% NMO sample, a new vibrational feature emerges at 597 cm^{-1} representing Ni-O stretching vibration, providing spectroscopic evidence for the presence of a segregated nickel oxide phase due to exceeding solubility limit of host framework, aligning with XRD results. The amorphous nature of NMO at increased Ni concentration is also supported by increased intensity of OH bending vibrations, referring to their higher concentration at higher dopant levels.

III. Thermal analysis

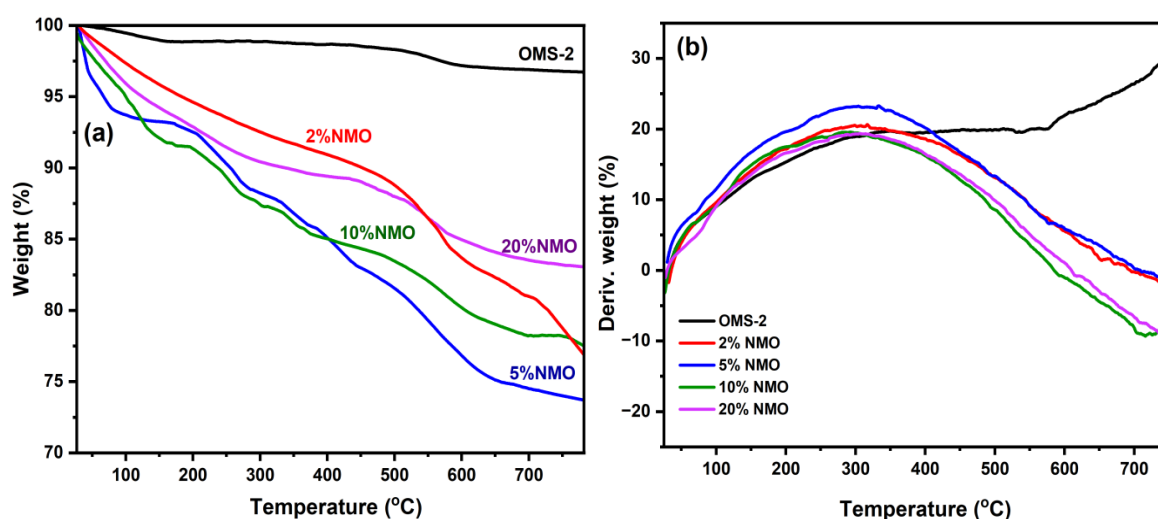


Figure 4.23: (a) Thermogram (b) DTA profile of OMS-2 and ex-situ Ni doped forms

The thermograms in Fig. 4.23(a), demonstrates the thermal stability of the materials. All samples showed an initial weight loss below 150°C , which is typically attributed to the removal of physisorbed (surface) and chemisorbed residual water molecules. The major weight loss of 7.91% was observed with 10%NMO indicating higher quantity of adsorbed oxygenated groups. The pure OMS-2 exhibits the highest thermal stability, showing minimal weight loss (only 3.29% up to 800°C), suggesting its structural integrity is largely maintained across this temperature range. In contrast, all the ex-situ Ni doped OMS-2 samples displayed significantly greater weight loss, especially in the temperature range of $150 - 450^{\circ}\text{C}$ accounting for the loss of lattice oxygen, and within 450 to 600°C for phase

transformation of host α -MnO₂ structure to Mn₂O₃ due to increased vacancy defects upon Ni loading. A further increase in temperature to 800°C led to a likely subsequent phase transformation or decomposition to stable lower oxidation states of Mn and Ni. A comparatively lowest thermal stability was observed upon Ni incorporation upto 5% loading, resulting in a highest overall weight loss of 26.4% and a comparatively higher exotherm in differential thermogram in Fig. 4.23(b). Further increase in Ni loading led to a successively increased thermal stability with an overall weight loss of only 17% in 20%NMO. The weight loss at different temperature stages in all samples is displayed in Table 4.5.

In differential thermograms in Fig. 4.24(b), pure OMS-2 shows a relatively flat baseline until about 575°C, where a small positive deviation with a sharp rise is observed due to phase change accompanying change in oxidation state, at very high temperatures. In contrast, the nickel doped samples exhibited a broad exotherm accompanying its gradual decomposition.

Table 4.5: Thermal decomposition stages and corresponding weight loss in various samples

	Weight loss				Total weight loss (%)
Temperature	150°C (%)	(150-450°C) (%)	(450-600°C) (%)	(600-800°C) (%)	
OMS-2	1.04	0.42	1.37	0.46	3.29
2%NMO	4.16	5.79	6.37	7.42	23.74
5%NMO	6.75	10.27	6.15	3.23	26.40
10%NMO	7.91	7.75	4.15	2.96	22.77
20%NMO	5.78	5.19	4.07	1.96	17.00

IV. Surface morphology and textural analysis

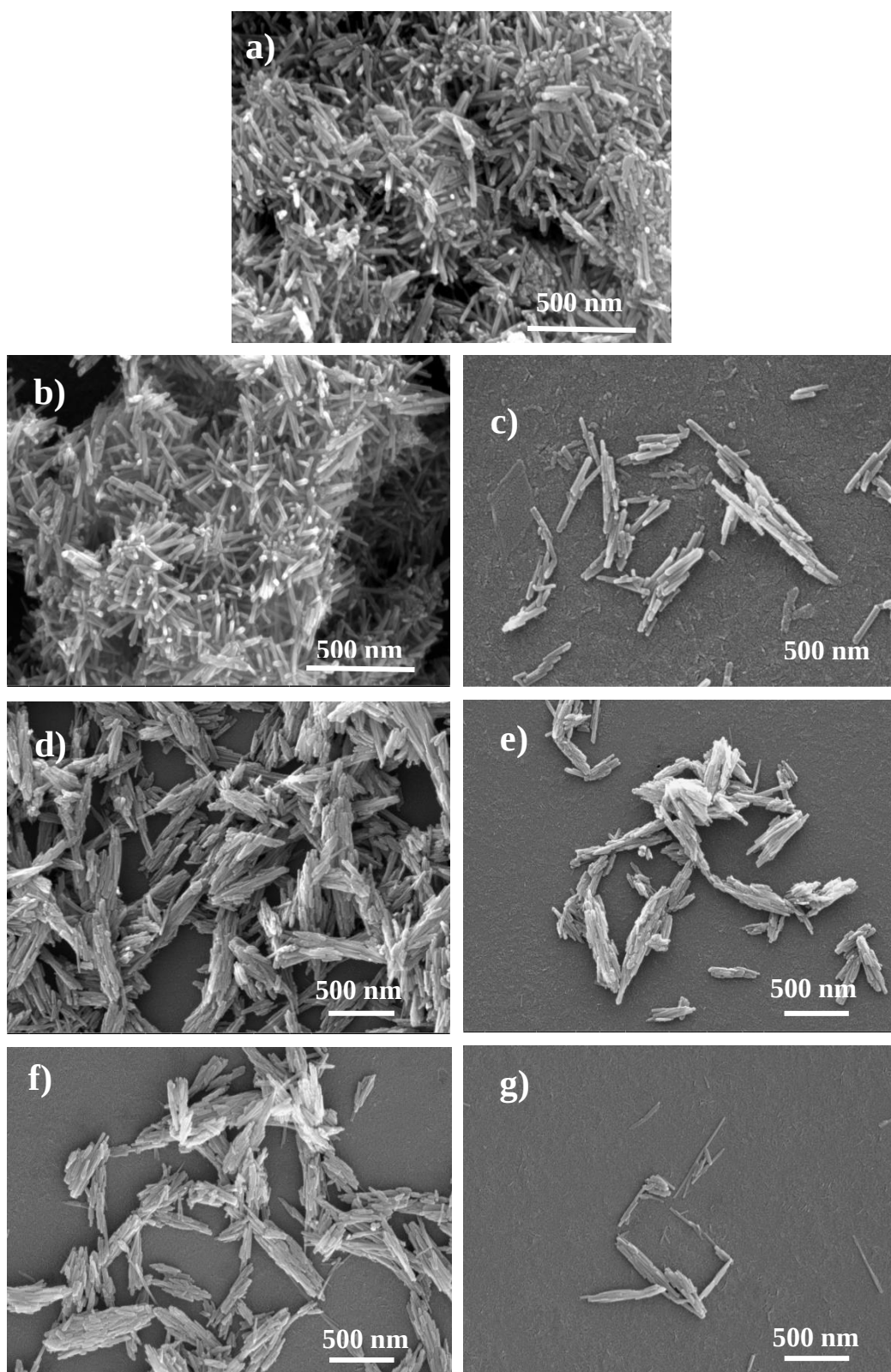


Figure 4.24: SEM images of (a) OMS-2 (b)-(c) 2%NMO (d)-(e) 5%NMO (f)-(g) 20%NMO

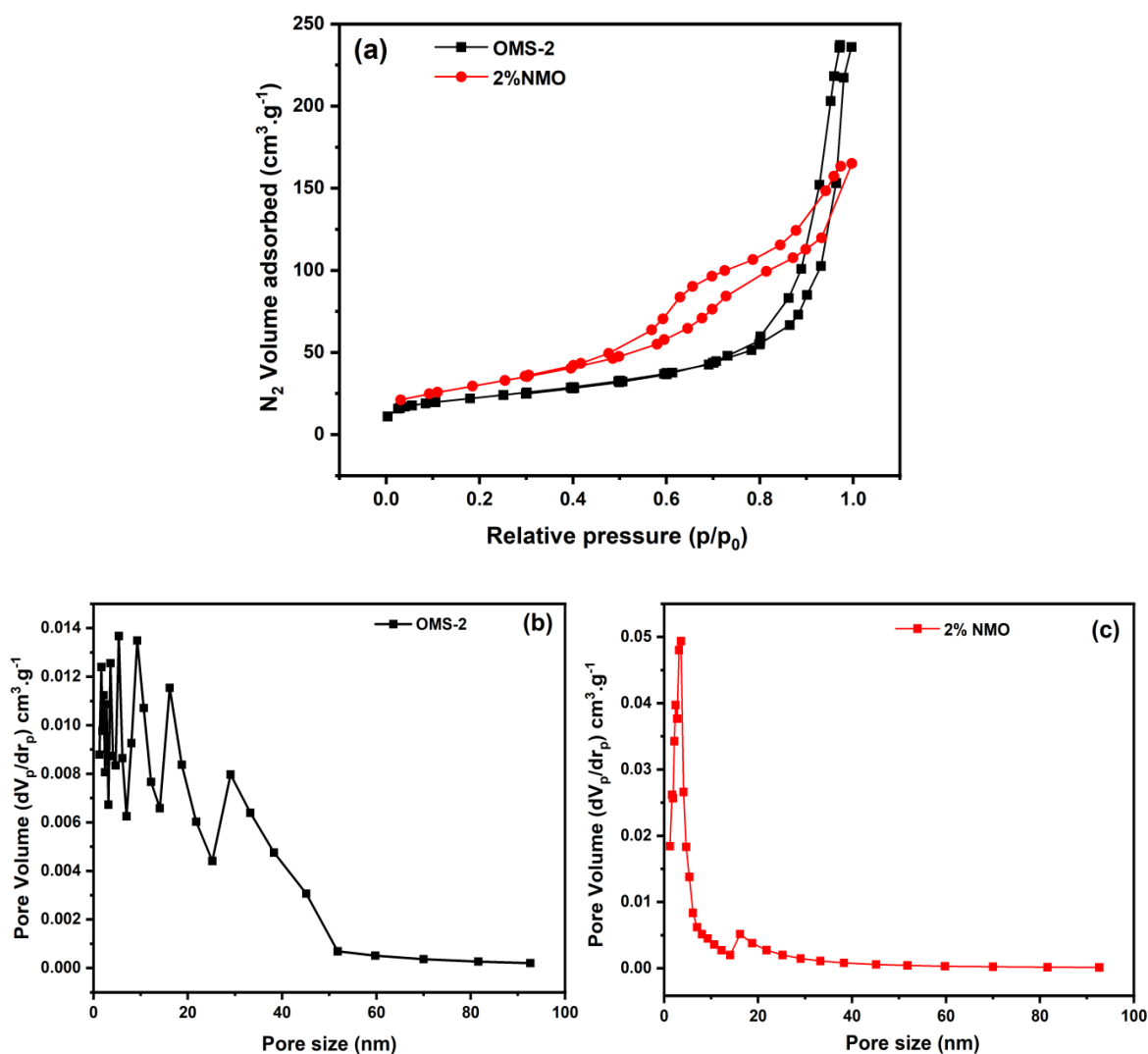


Figure 4.25: (a) N_2 adsorption–desorption isotherms of OMS-2 and 2%NMO (b) Pore size distribution curve of OMS-2 (c) 2%NMO

The SEM images in Fig. 4.24 (a)-(f) clearly illustrated the impact of Ni dopant incorporation on the structure of the OMS-2 host. The pure OMS-2 material exhibits characteristic one-dimensional nanorod morphology with relatively smooth facets and well-defined boundaries. The length of the nanorods lie within 100 – 200 nm range but possess a noticeable diameter (~ 30 nm), resulting in a moderate aspect ratio (length/width) of 8.10. The nanorods are moderately dispersed with no dense aggregates formation. This morphology was well maintained with 2% ex-situ Ni loading with minimal aggregation and an aspect ratio of 9.08. However, a further increase in Ni concentration led to transition of nanorods to thinner needle like nanofibres with dense aggregation as observed in 5 and 20%NMO. This reduction in particle diameter suggests that Ni dopant acts as a growth inhibitor for the OMS-2 lattice, restricting radial crystal growth and consequently

increasing the aspect ratio to 14.73 and 32.86, respectively in the resulting nanostructures. The individual nanorods/nanofibres are entangled, forming a highly porous network structure. This dense, felt-like arrangement suggests interlocking of a larger number of smaller particles.

The nitrogen adsorption-desorption isotherms in Fig. 4.25(a) showed that both OMS-2 and 2%NMO exhibited a Type IV isotherm with an H4 hysteresis loop, confirming their mesoporous structure with pores arising from the aggregation of rod-like particles (slit-shaped pores). The 2%NMO sample has a significantly higher BET surface area of $106.2 \text{ m}^2.\text{g}^{-1}$, compared to the pure OMS-2 which has $79.629 \text{ m}^2.\text{g}^{-1}$. This increase in surface area, despite the aggregation of nanorods is attributed to the smaller diameter and higher aspect ratio of the 2%NMO nanorods, which collectively expose more active material surface. Despite the higher surface area, the 2%NMO sample showed a lower total pore volume of $0.2477 \text{ cm}^3.\text{g}^{-1}$ compared to the pure OMS-2 with $0.3541 \text{ cm}^3.\text{g}^{-1}$. This outcome is consistent with the denser aggregation and tighter packing of the refined nanorods. Moreover, the pore size distribution, determined using the Barrett-Joyner-Halenda (BJH) method, revealed a broad, heterogeneous distribution of pores spanning the mesoporous range and a peak pore radius of 5.35 nm in OMS-2 sample in Fig. 4.25(b), while the NMB400 material in Fig.4.25(c) exhibited a sharper, more uniform distribution with a considerably narrower peak pore radius of 3.59 nm indicating the presence of higher concentration of finer, narrower mesopores. The 2%NMO material achieved a higher specific surface area by creating a network of highly accessible small pores, which maximizes the exposure of the active catalytic sites for higher catalytic activity.

V. Surface and Bulk Compositional Analysis

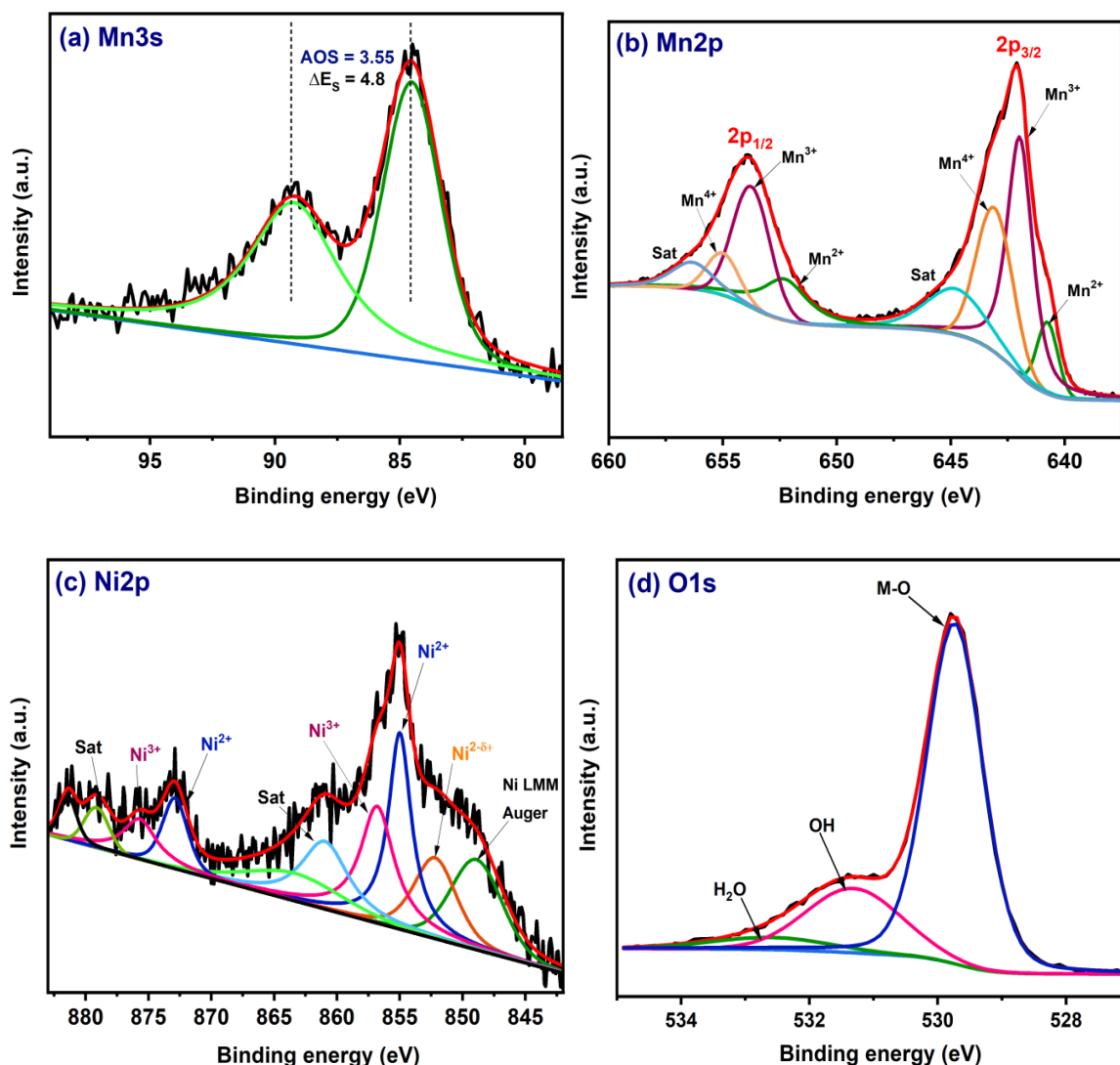


Figure 4.26: Core level XPS scan of (a) Mn3s (b) Mn2p (c) Ni2p (d) O1s in 2%NMO

The core level XPS scan of Mn3s in 2%NMO in Fig. 4.26(a) was utilised to obtain the average oxidation state of Mn in 2% NMO determined using AOS equation as discussed previously in section 4.3.1(IV) and was found to be 3.55 similar to pristine OMS-2. The core level Mn2p spectra in Fig. 4.26(b) was deconvoluted into two primary peaks at similar binding energy values as OMS-2 in Fig. 4.5(b), corresponding to 642.1 eV for Mn2p_{3/2} and 653.9 eV for Mn2p_{1/2} with a spin orbit splitting energy of 11.8 eV, confirming the non-stoichiometry of Mn in host structure. Further deconvolution of Mn2p_{3/2} and Mn2p_{1/2} peaks into 3 peaks each, confirmed the presence of Mn in +2, +3 and +4 oxidation states. The Mn²⁺ species were identified from peaks obtained at 640.8 and 652.3 eV, Mn³⁺ at 642 and 653.8 eV, Mn⁴⁺ at 643.2 and 655.1 eV along with 2 satellite peaks at 644.9 and

656.4 eV. The absence of any shift in peak position ruled out the possibility of Ni substitution in OMS-2 framework via replacement of Mn. The ratio of $\text{Mn}^{3+}/\text{Mn}^{4+}$ was found to be relatively higher than OMS-2, revealing formation of more catalytically active Mn^{3+} state upon Ni loading as shown in Table 4.6. The incorporation of the Ni dopant into the $[\text{MnO}_6]$ framework was confirmed to occur in the interstitial sites which was confirmed from constant K/Mn value of OMS-2 and 2%NMO obtained via ICP-MS analysis. While upon increasing the concentration of Ni, K/Mn ratio reduced from 0.078 to 0.074, which revealed reduction in number of K^+ ions in tunnel via its substitution by Ni ions at high dopant concentrations as represented in Table 4.6.

The core level Ni2p spectra in Fig. 4.26(c) displayed two main peaks at 855.1 eV for $\text{Ni}2\text{p}_{3/2}$ and 873 eV for $\text{Ni}2\text{p}_{1/2}$, representing the predominance of Ni^{2+} state. These peaks were further deconvoluted into peak corresponding to $\text{Ni}^{2-\delta+}$ at 852.3 eV for its interaction with $[\text{MnO}_6]$ octahedral environment, Ni^{2+} at 855 and 872.9 eV, catalytically active Ni^{3+} at 856.8 and 875.8 eV accompanied with shake up satellite peaks at higher binding energies. The ratio of $\text{Ni}^{2+}/\text{Ni}^{3+}$ in 2%NMO was found to be 1.185. The O1s core scan spectra, as displayed in Fig. 4.26(d), was successfully deconvoluted into three distinct peaks corresponding to lattice oxygen at 529.8 eV, oxygen vacancy at 531.3 eV and adsorbed water at 532.7 eV, with their relative proportion being 65.32%, 24.61% and 10.07%, respectively from Table 4.6. It can be noted that the inclusion of Ni dopant led to an increase in oxygen vacancy defects rendering higher catalytic activity to the final material.

Table 4.6: Surface composition and chemical state analysis from ICP-MS and XPS measurements

Sample	K/Mn		Ni/Mn		$\frac{Mn^{3+}}{Mn^{4+}+Mn^{3+}+Mn^{2+}}$ (%)	Mn (AOS)	Ni^{2+}/Ni^{3+}	O _{ads}	O _{vac}	O _{lat}
	ICP-MS	XPS	ICP-MS	XPS						
OMS-2	0.078	0.033	--	--	35.55	3.55	--	10.69	21.29	68.02
2%NMO	0.078	0.032	0.0155	0.0999	40.70	3.55	1.185	10.07	24.61	65.32
10%NMO	0.074	--	0.1352	--						

4.3.7 Electrocatalytic assessment of Ex-situ NixOMS-2 nanorods : Methanol Oxidation Reaction

I) Effect of Ni loading on catalytic activity

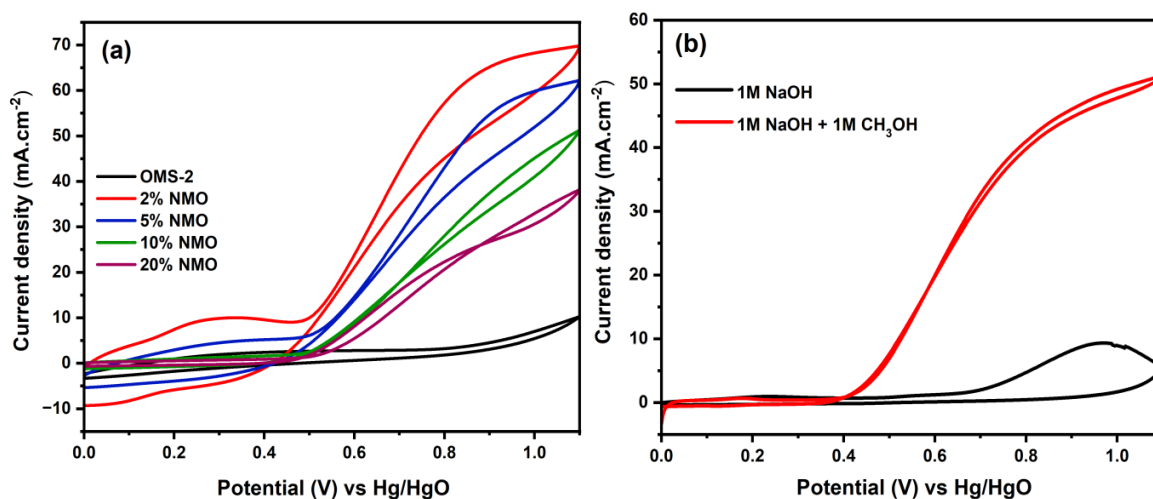


Figure 4.27: (a) CV of OMS-2 and ex-situ Ni loaded OMS-2 variants for methanol oxidation recorded at 50 mV.s⁻¹ scan rate spanning a potential range of 0 to 1.1V vs. Hg/HgO in a mixture of 1M methanol and 1M NaOH (b) Comparative CV of 2%NMO recorded in the presence and in the absence of methanol in 1M NaOH at 2 mV.s⁻¹ scan rate.

The data presented in the cyclic voltammograms in Fig. 4.27(a) confirmed the potent electrocatalytic properties of the Ni loaded OMS-2 materials for the methanol oxidation reactions, while also demonstrating its high selectivity by suppressing the undesirable oxygen evolution reaction. From Fig. 4.27(a), a lowest MOR activity at high onset potential was observed on OMS-2 due to its intrinsic limitations of lower electrical conductivity and active sites. The introduction of Ni drastically enhanced the current density, confirming Ni species as the primary active sites for methanol oxidation, likely undergoing the facile redox transition from Ni²⁺ to form active NiOOH, serving as the active state in alkaline media. Furthermore, the introduction of Ni in OMS-2 also improved the number of active sites by enhancing the oxygen vacancies and active Mn³⁺ facilitating efficient oxidative removal of carbonaceous intermediates from catalyst active sites. Among the various Ni loaded forms, 2% Ni loading resulted in a highest anodic peak current density of 64.08 mA.cm⁻² at 0.88V signifying 2% Ni as the optimum loading

concentration for generating the maximum number of exposed active sites. As the Ni loading increased from 2% to 20%, the MOR current density progressively decreased due to aggregation of nanorods causing masking of active sites, ultimately reducing the effective electrochemical active surface area.

Further a direct comparison of the performance of 2%NMO catalyst in the absence (OER) and in the presence (MOR) of methanol is shown in CV recorded at 2 mV.s^{-1} scan rate in Fig. 4.27(b), establishing its potential use in fuel cells. In pure 1M NaOH electrolyte, 2%NMO exhibited a low current response at high potentials, primarily representing the oxygen evolution reaction which is an undesirable parasitic reaction in a fuel cell anode. Upon the addition of 1M methanol, the current density at all potentials increases dramatically. The sharp rise in current at a lowest onset potential of 0.372V reaching a high current density of 49.16 mA.cm^{-2} indicated the highly favored methanol oxidation reaction over oxygen evolution. The catalyst surface selectively and preferentially consumes methanol over water/hydroxide ions at the active Ni sites. This high selectivity is a key performance indicator for the 2%NMO catalyst, ensuring that the majority of the current generated contributes to the desirable fuel oxidation pathway, which is essential for maximizing the efficiency and power density of a DMFC.

II) Effect of scan rates

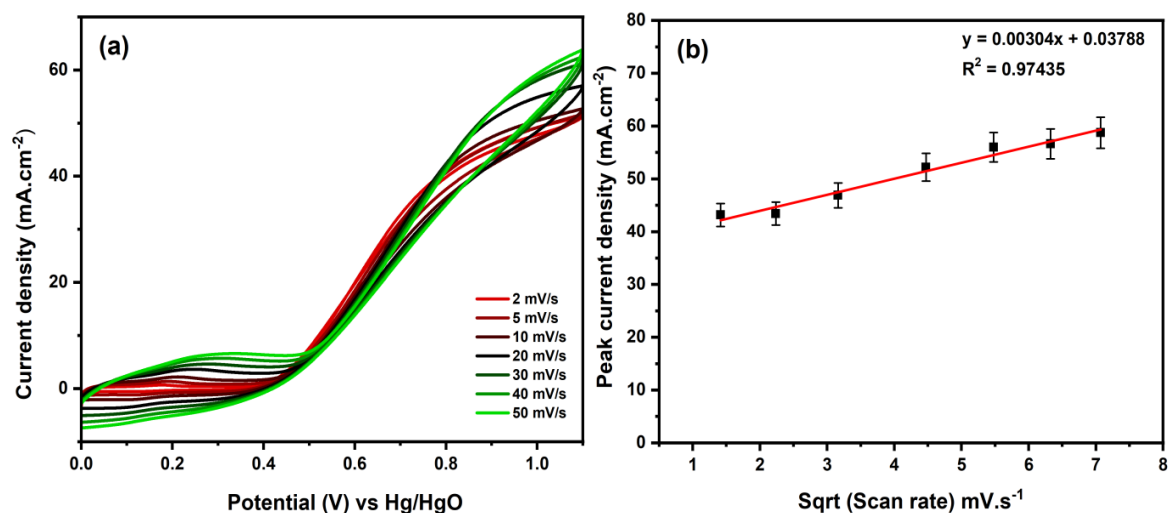


Figure 4.28: (a) Effect of scan rates on CV of 2%NMO for methanol oxidation (b) Current density vs. square root of scan rate plot of 2%NMO

A comprehensive electrochemical study was also conducted by recording CVs across a scan rate range of 2 to 50 mV.s^{-1} , as represented in Fig. 4.28(a) to understand the influence of the scan rates on current density of the reaction. The peak current densities for methanol oxidation increased with increasing scan rates. Similarly, the anodic peak potential exhibited a positive shift. Further plotting the peak current densities against the square root of corresponding scan rates, gave a linear relationship in Fig. 4.28(b). This relationship was accurately modelled by the equation $y = 0.00304x + 0.03788$. This linearity is the crucial evidence that confirmed the predominant diffusion controlled methanol oxidation kinetics on the 2%NMO catalyst surface with a correlation coefficient of 0.9743.

III) Evaluation of electrochemical parameters

a) Tafel polarisation studies

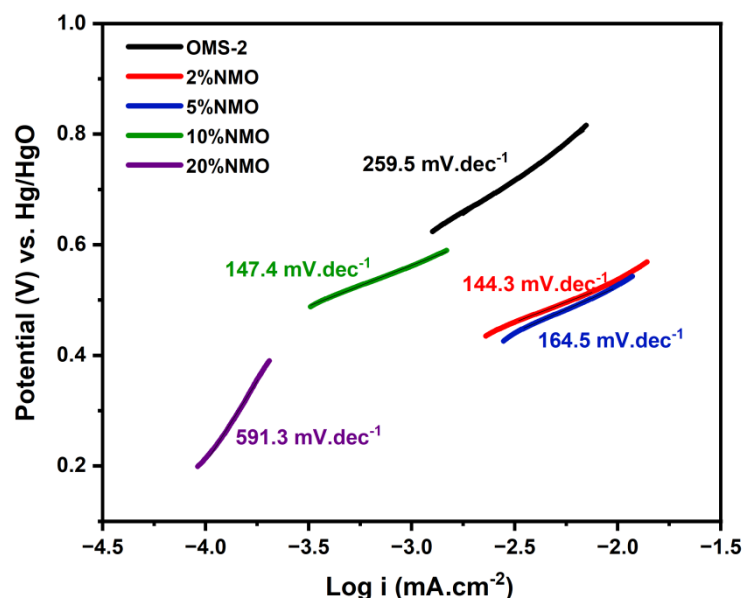


Figure 4.29: Tafel polarisation curves of OMS-2 and ex-situ Ni loaded OMS-2 catalysts

The Tafel polarisation curves in Fig. 4.29 provided crucial insights on kinetics of MOR on OMS-2 and its Ni loaded forms. The pristine OMS-2 exhibited a high Tafel slope of 259.5 mV.dec^{-1} , suggesting very sluggish reaction kinetics and confirming its intrinsic limitations due to poor electrical conductivity and a slow charge transfer process. The introduction of Ni drastically improves the kinetics, with the optimal 2%NMO catalyst displaying a significantly lower Tafel slope of 144.3 mV.dec^{-1} . This substantial reduction signifies a much faster charge transfer and a change in the RDS, demonstrating the

catalytic effect of the Ni species. With further increase in Ni loading to 5%NMO and 10%NMO, the Tafel slopes remain relatively low ($164.5 \text{ mV.dec}^{-1}$ and $147.4 \text{ mV.dec}^{-1}$, respectively), indicating that the Ni sites are still governing the reaction rate. However, a significant kinetic limitation is incurred at the highest 20% loading in 20%NMO, where the Tafel slope dramatically increases to $591.3 \text{ mV.dec}^{-1}$. This kinetic regression is consistent with the severe aggregation observed in the morphological studies and the drastically reduced ECSA for the 20%NMO sample, where excessive aggregation masks the active sites and reintroduces mass transport and charge transfer limitations as observed in Nyquist plots exhibiting highest charge transfer resistance, effectively suppressing the intrinsic kinetics achieved at the optimal 2% Ni loading.

b) Electrochemical active surface area:

As discussed in the experimental section, the ECSA was determined from CdI measurement, from the cyclic voltammograms plotted in non faradaic region (0.03 to 0.13V) for each sample as represented in Fig. 4.31(a) – (e) and the slope of derived linear plot of Δj vs. scan rate (Fig. 4.31(f)). The analysis demonstrated that the 2%NMO catalyst recorded the highest ECSA value of 140.75 cm^2 . The 5%NMO, 10%NMO, 20%NMO and the undoped OMS-2 samples yielded ECSA of 76.25, 28.5, 20.25 and 122.5 cm^2 , respectively. The optimal structure of 2%NMO with higher BET surface area, provides the greatest number of exposed active Ni sites which serve as the primary promoters of MOR via the facile $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$ transition and synergistic Mn sites with higher oxygen vacancies necessary for stripping intermediates ultimately yielding highest current density and low Tafel slope. Conversely, higher Ni loadings above 2% cause excessive nanorod aggregation leading to a progressive and sharp reduction in ECSA to 20.25 cm^2 with 20% Ni loading, directly masking the active sites and consequently suppressing the overall MOR performance.

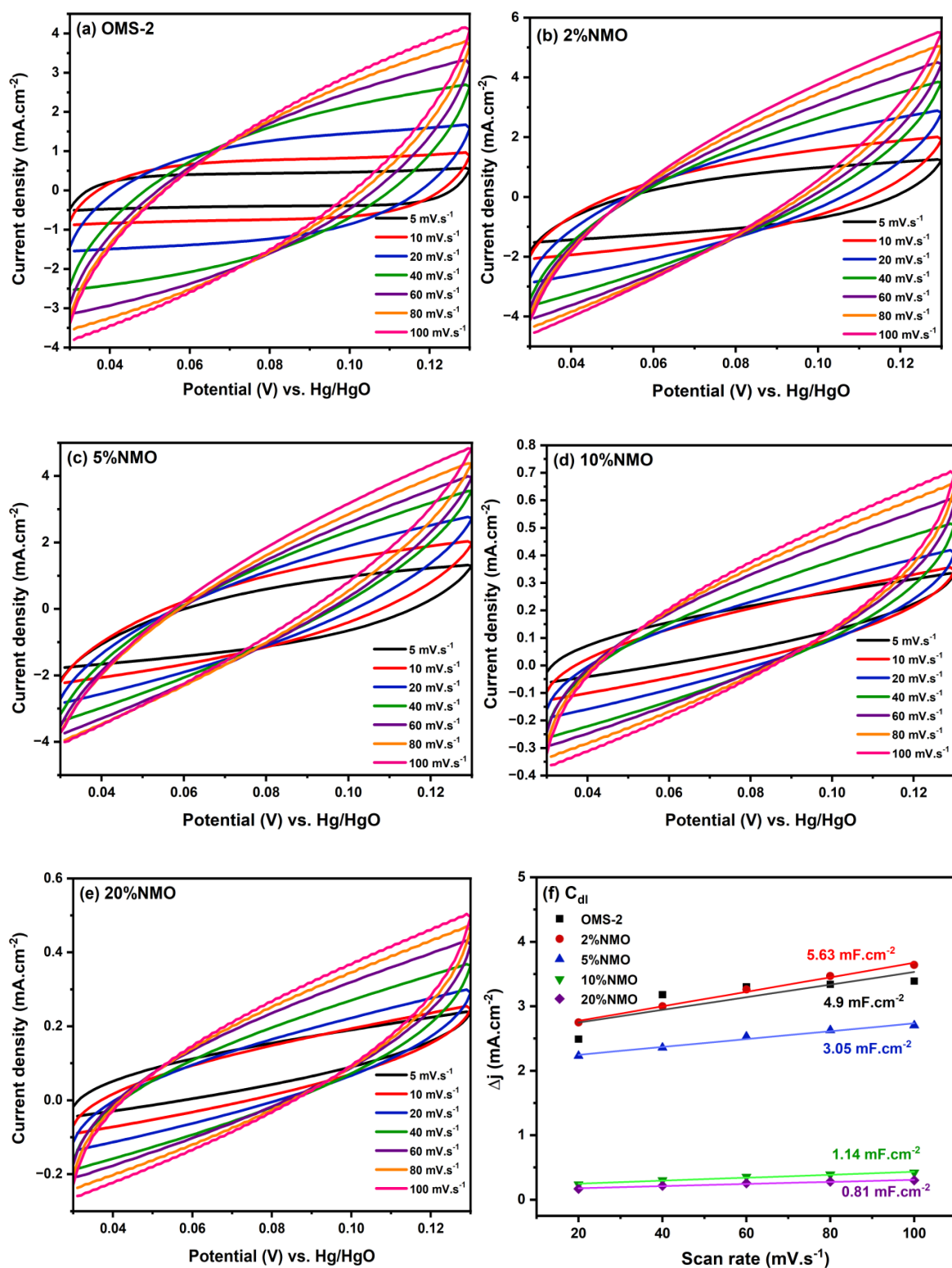


Figure 4.30: Cyclic voltammograms of (a) OMS-2 (b) 2%NMO (c) 5%NMO (d) 10%NMO (e) 20%NMO in non-faradaic region spanning between 0.03 to 0.13V vs. Hg/HgO in 1M NaOH (f) Δj vs. scan rate plot for C_{dl} measurement

c) Electrochemical impedance spectra

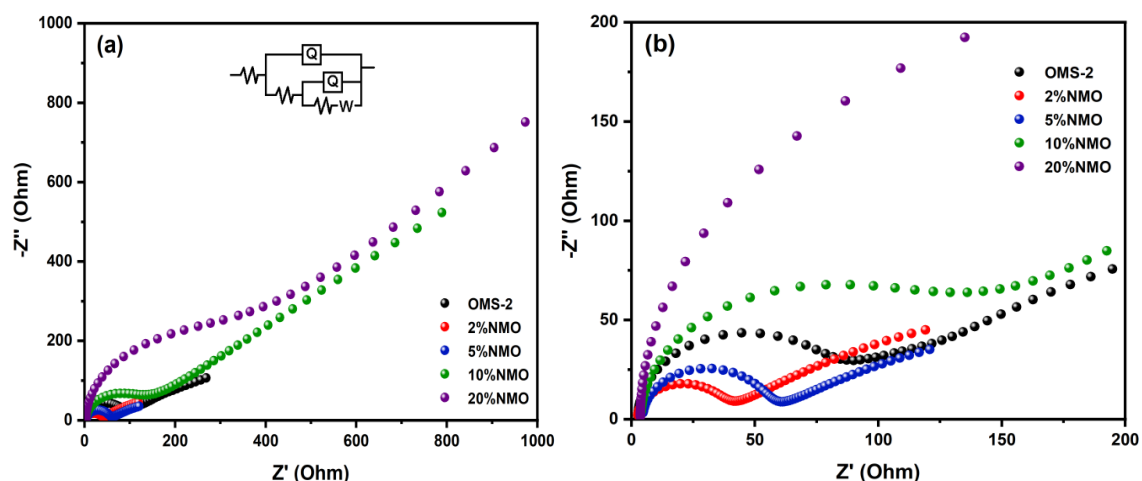


Figure 4.31: (a) Nyquist plots of OMS-2 and ex-situ Ni loaded OMS-2 forms (b) Magnified view of Nyquist plots

The charge transfer kinetics of the catalysts were systematically evaluated by assessing the Nyquist plots obtained from EIS measurements of each sample and fitted to an equivalent circuit $R(Q(R(Q(RW))))$ using ZSimpWin 3.21 software, as shown in Fig. 4.31(a). These plots, which are composed of a semicircle in the high-frequency range and a linear tail in the low-frequency range, were recorded at a fixed potential of 0.45V vs. Hg/HgO. The pristine OMS-2 catalyst exhibited the largest semicircle at high frequencies. Its large diameter signifies the highest charge transfer resistance (R_{ct}) of 85.09 Ω (Fig. 4.31(b)) and consequently, the sluggish kinetics, aligning with its lowest MOR activity and high Tafel slope. Upon the deliberate incorporation of Ni dopants, 2%NMO displayed the most favorable characteristics, consistent with its highest ECSA (140.75 cm²). Specifically, the 2%NMO sample showed the lowest charge transfer resistance of 33.07 Ω , which was visually evident from its smallest semicircle diameter, a strong indication of significantly faster charge transfer kinetics for the methanol oxidation reaction. This kinetic enhancement supports the BET finding of 2%NMO having a higher BET surface area and an ideal porous structure. Furthermore, the Nyquist plot of 2%NMO and 5%NMO featured a relatively shorter linear region at the lower frequency end compared to the highly aggregated 20%NMO. This shorter linear segment corresponds to a lower Warburg impedance, suggesting faster diffusion of ions or methanol molecules to the high surface area active sites of the optimal electrodes. The detrimental effect of high loading is clear, as the 10%NMO and 20%NMO sample exhibited the largest R_{ct} of 119.6 Ω and 348 Ω ,

respectively, higher than R_{ct} of pristine OMS-2 and steepest Warburg tail, demonstrating severe charge transfer and mass transport limitations due to nanofibre aggregation.

IV) Chronoamperometric stability analysis

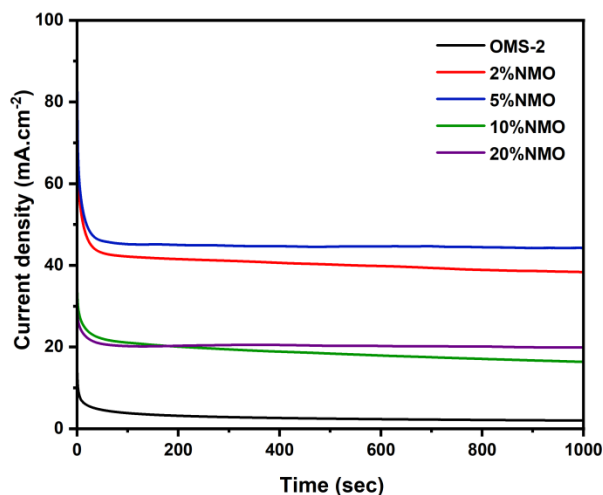


Figure 4.32: Chronoamperometric stability test performed at 0.98V vs. Hg/HgO

The long-term operational stability and poisoning tolerance of the catalysts were assessed using chronoamperometric stability run at a fixed potential of 0.98V vs. Hg/HgO as shown in Fig. 4.32 for a period of 1000 sec. in a mixture of 1M methanol and 1M NaOH electrolyte. The initial steep decay in current density observed for all samples is attributed to the charging of the electrical double layer and the initial consumption of available surface-adsorbed methanol, which quickly transitions to a steady-state current density governed by diffusion kinetics and the formation of carbonaceous poisoning intermediates on the active sites. The 2%NMO and 5%NMO demonstrated superior stability, maintaining the highest steady-state current densities of approximately 38.36 mA.cm⁻² and 44.28 mA.cm⁻², respectively, throughout the entire 1000 sec. duration. This robust performance confirms their excellent poisoning tolerance, which is likely facilitated by the OMS-2 support enhancing the oxidative elimination of poisoning intermediates through the synergistic action of Mn³⁺ active species, thereby freeing up the Ni²⁺ sites for sustained MOR. Conversely, the undoped OMS-2 showed the fastest degradation, settling at the lowest current density (2 mA.cm⁻²), reflecting its intrinsic poor kinetics and high susceptibility to poisoning. Furthermore, the 10%NMO and 20%NMO catalysts, characterized by their highly aggregated nanorod morphology, demonstrated significantly

suppressed long-term stability, settling at lower steady state current densities of 16.36 mA.cm⁻² and 19.93 mA.cm⁻², respectively. This failure mode confirms that despite the presence of Ni active sites, the kinetic hindrance imposed by the structural disorder and the drastic reduction in their effective ECSA severely compromises both their initial catalytic activity and their long-term operational resilience against poisoning intermediates.

Table 4.7: Electrocatalytic parameters of OMS-2 and ex-situ Ni loaded OMS-2 samples

Sample	Onset potential (V)	Anodic peak current density (mA.cm ⁻²) at 50 mV.s ⁻¹	Anodic peak potential (V)	Tafel slope (mV.dec ⁻¹)	ECSA (cm ²)	R _{ct} (Ω)
OMS-2	0.640	10.24	1.1	259.5	122.5	85.09
2%NMO	0.372	64.08	0.880	144.3	140.75	33.07
5%NMO	0.390	56.64	0.937	164.5	76.25	48.4
10%NMO	0.446	43.55	0.978	147.4	28.5	119.6
20%NMO	0.448	25.90	0.878	591.3	20.25	348

Table 4.8: Comparative physicochemical and electrocatalytic profile of ex and in-situ Ni_xOMS-2 nanostructures

Sample	Particle size(nm)	Mn AOS	K/Mn	Ni/Mn	Mn ³⁺ /Total Mn	Ni ²⁺ /Ni ³⁺	O _{vac}	BET surface area (m ² .g ⁻¹)	Pore size (nm)	Pore volume (cm ³ .g ⁻¹)
OMS-2	10.01	3.55	0.0331	--	35.55		21.29	79.629	5.35	0.3541
In-situ (NMB400)	8.01	3.66	0.0311	0.0128	36.80	1.493	23.53	66.631	2.14	0.2715
Ex-situ (2%NMO)	9.46	3.55	0.032	0.0155	40.70	1.185	24.61	106.2	3.59	0.2477

Sample	Onset potential (V)	Peak current density (mA.cm ⁻²) at 2mV.s ⁻¹	Tafel slope (mV.dec ⁻¹)	R _{ct} (Ω)	Overpotential (mV) @ 10 mA.cm ⁻²	Tafel slope (mV.dec ⁻¹)	R _{ct} (Ω)	ECSA (cm ²)
OMS-2	0.640	10.24	259.5	85.09	>570	131.4	46.88	122.5
In-situ (NMB400)	0.464	29.61	151.3	38.39	461	88.94	25.39	235
Ex-situ (2%NMO)	0.372	43.83	144.3	33.07	--	--	--	140.75

The comparative physicochemical and electrocatalytic profiles of Ex and In-situ Ni_xOMS-2 nanostructures in Table 4.8 displayed a clear structure-property interrelation between targeted Ni doping strategies and resultant multifunctional catalytic performance in electrochemical energy conversions, specifically the methanol oxidation reaction and oxygen evolution reaction.

The synthesis method critically governs the properties and catalytic activity of the material. The in-situ method yielded bifunctional materials with a refined nanostructure (smaller particle and pore sizes) and high electrochemical surface area, optimizing mass transport kinetics, while the ex-situ method excelled at electronic modification, resulting in the high BET surface area and an increased concentration of Mn³⁺ active sites and oxygen vacancies. The in-situ synthesis with thermal optimisation led to bifunctional activity with optimal intrinsic kinetics to catalyse methanol fuel oxidation for application in DMFC as a noble metal free anode catalyst, along with catalysing sluggish water oxidation for generating hydrogen fuel. Moreover, the ex-situ synthesis offered an excellent selectivity to catalyse methanol oxidation at a much reduced onset potential by 92 mV generating 1.5 times higher current density than in-situ form. Ultimately, this comprehensive analysis established a structure-property relationship, demonstrating the enhanced performance stemming from the synergistic effect of improved surface area, morphology, concentration and type of active sites along with tuned electronic states (Mn³⁺/Mn⁴⁺), which provide a critical design principle for developing next-generation MnO₂ based electrocatalysts.

4.4 Conclusion

1. The in-situ synthesis method via scalable reflux-based precipitation successfully achieved lattice incorporation of Ni into the OMS-2 framework, evidenced by a shift in XRD peaks and the formation of an intimate Ni-O-Mn structure detectable by XPS. The ex-situ synthesis method via wet impregnation primarily resulted in Ni occupying interstitial sites or substituting K^+ ions within the OMS-2 tunnels at higher loadings, confirmed by ICP-MS analysis.
2. The in-situ doping approach yielded a bifunctional catalyst (NMB400) that exhibited superior activity for both the Methanol Oxidation Reaction (MOR) and the Oxygen Evolution Reaction (OER). The ex-situ doped samples demonstrated negligible performance in catalysing the OER while exhibiting excellent selectivity primarily to the methanol oxidation reaction.
3. Post synthesis thermal engineering was critical for the in-situ materials, with calcination at 400°C (NMB400) significantly enhancing the performance by optimizing the Ni^{3+} and Mn^{3+} active site concentration.
4. The optimal in-situ catalyst, NMB400 showed superior intrinsic reaction kinetics for MOR and OER, achieving the lowest Tafel slope among all tested catalysts due to its highest electrochemical active surface area (ECSA) than ex-situ catalyst. The optimized ex-situ catalyst, 2%NMO, possessed the highest electrochemical active surface area among the impregnation series, emphasizing the advantage of the surface deposition approach for maximizing exposed active sites.
5. The ex-situ 2%NMO exhibited the lowest charge transfer resistance among the impregnation series than in-situ catalyst forms indicating highly facile charge transfer kinetics for MOR at optimal surface loading. High Ni loading in the ex-situ catalysts led to a severe reduction in ECSA and an excessive increase in charge transfer resistance due to irreversible particle aggregation, confirming a detrimental structural-kinetic effect.
6. The superior OER activity of the in-situ catalyst, NMB400 is attributed to the synergistic action of Ni^{3+} induced Mn^{3+} activation, which induced Jahn-Teller distortion and facilitated the participation of highly reactive lattice oxygen in the rate-determining step favoring a combined adsorbate evolution and lattice oxygen mediated mechanism.

7. The in-situ synthesis largely prevented the formation of separate nickel oxide impurity phases within the optimal doping range, successfully preserving the cryptomelane structure. While in ex-situ forms, the mixed phases were apparent at high Ni concentrations.
8. Both the optimal in-situ (NMB400) and ex-situ 2%NMO and 5%NMO catalysts demonstrated superior long-term operational stability against carbonaceous poisoning in MOR compared to the pristine OMS-2. While long term oxygen evolution on NMB400 led to surface reconstruction with intact bulk structure, stabilizing its OER activity to 50% after 6 hours of operation.
9. The optimal ex-situ catalyst demonstrated a more favorable and lowest MOR onset potential compared to the in-situ counterpart by 92 mV and 1.5 times higher current density for methanol oxidation.
10. In summary, in-situ synthesis followed by thermal optimization is mandatory for bifunctional activity and optimal intrinsic kinetics, whereas the ex-situ method provides a high-performing alternative with high selectivity and current output for methanol oxidation via maximal ECSA enhancement at low loadings.

4.5 References

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CHAPTER V

GENERAL CONCLUSIONS AND FUTURE SCOPE

Chapter 5

General conclusions and future scope

5.1 General conclusions

The research presented in this thesis demonstrates the rational design of manganese oxide and graphene-based nanostructures, achieving the following key innovations:

1. **Multifunctional Role of Heteroatom-Modulated Graphene:** The primary innovation lies in the engineering of a multifunctional N,S-codoped reduced Graphene Oxide (N,S-RGO) platform that bridges energy storage and conversion. By utilizing an optimized reflux doping strategy, the carbon lattice was reconfigured to simultaneously provide high surface wettability and pseudocapacitive transitions for supercapacitors and act as a superior, CO-tolerant support for Platinum nanoparticles in the Methanol Oxidation Reaction (MOR), significantly outperforming commercial Pt/C catalysts having 6.7 times higher Pt loading.
2. **Synergistic Hybridization for Energy Storage:** The successful integration of Cerium-doped Manganese Oxide with N,S-codoped Reduced Graphene Oxide represents a significant advancement in supercapacitor technology. The innovation lies in the synergistic effect where the heteroatom-doped graphene provides a high-surface-area conductive network, while the Ce-doped manganese oxide contributes high pseudocapacitance, resulting in superior energy density and long-term cyclic stability.
3. **Structural Engineering of OMS-2 via Metal Substitution:** A major breakthrough of this work is the development of Nickel-substituted Octahedral Molecular Sieves (NiOMS-2). By strategically replacing manganese ions within the 2×2 tunnel structure of cryptomelane, and by incorporating nickel ions within interstices, the electronic environment was tuned to enhance charge transfer and selectivity. This structural modification successfully lowered the overpotential for key electrochemical reactions.

4. **Bifunctional Electrocatalysis and High Selectivity for Green Energy:** The thesis demonstrates that partial substitution of framework Mn by Ni atoms in NiOMS-2 nanostructures renders remarkable bifunctionality effective not only for the methanol oxidation reaction, which is critical for Direct Methanol Fuel Cells (DMFCs), but also for the Oxygen Evolution Reaction (OER), essential for water splitting. This reduces the need for multiple expensive catalysts in integrated energy systems. While interstitial substitution of Ni atoms in OMS-2 renders enhanced selectivity with high current densities for MOR.
5. **Transition to Non-Noble Metal Catalysts:** A core innovation is the significant reduction in reliance on noble and costly metals like Platinum (Pt) and Ruthenium (Ru). By utilizing earth-abundant manganese and carbon-based materials, this work provides a cost-effective and scalable pathway for the fabrication of high-performance electrodes without compromising on electrochemical efficiency.

5.2 Future scope

To build upon the findings of this PhD work, the following areas are proposed for future investigation:

1. **Device-Level Fabrication (Prototype Testing):** While this work focuses on half-cell electrochemical characterization, the next logical step is the fabrication of full-cell asymmetric supercapacitors and the integration of the Ni-OMS-2 catalyst into a working Direct Methanol Fuel Cell (DMFC) stack to evaluate performance under real-world operating conditions.
2. **In-situ Characterization Studies:** Future studies should employ In-situ Raman or X-ray Absorption Spectroscopy (XAS) during electrochemical cycling. This would provide deeper insights into the structural changes and oxidation state transitions of Manganese and Nickel during the OER and MOR processes, allowing for "operando" tracking of the active sites.
3. **Exploration of Ternary Doping:** Building on the success of N,S-codoping, the introduction of a third heteroatom (such as Boron or Phosphorus) into the graphene

lattice could further modify the electron density and potentially enhance the anchoring of manganese oxide nanoparticles, leading to even higher performance.

4. **Scaling and Environmental Impact (LCA):** Future research should focus on a Life Cycle Assessment (LCA) to measure the environmental impact of making these materials (using the Reflux and Marcano methods). The goal is to find "greener," eco-friendly ways to produce these electrodes on a large industrial scale without harming the environment.

Appendix : List of Chemicals and Reagents

Chemical Name	Chemical Formula	Purity	Supplier
Graphite	C	AR (99.9995 %)	Thermo Scientific
Sulphuric acid	H ₂ SO ₄	AR (98%)	Thomas Baker
Orthophosphoric acid	H ₃ PO ₄	AR (85%)	Thomas Baker
Potassium Permanganate	KMnO ₄	AR (≥ 99%)	Thomas Baker
Manganese Sulphate Monohydrate	MnSO ₄ .H ₂ O	Extrapure AR (99%)	SRL Pvt. Ltd.
Hydrogen peroxide	H ₂ O ₂	AR (30%)	Thomas Baker
Hydrochloric acid	HCl	35%	Thomas Baker
Thiourea	CH ₄ N ₂ S	AR (99%)	Alfa Aesar
Urea	(NH ₂) ₂ CO	AR (≥ 99.3%)	Alfa Aesar
Hexachloroplatinic acid Hexahydrate	H ₂ PtCl ₆ .6H ₂ O	99.9%	Sisco Research Laboratories (SRL)
Sodium Borohydride	NaBH ₄	AR (99.99%)	Thomas Baker
Nickel acetate tetrahydrate	(Ni(OCOCH ₃) ₂ .4H ₂ O)	AR (≥ 99%)	Thermo Scientific
Nitric acid	HNO ₃	69.0% – 70.0%	Thomas Baker
Cerium sulfate tetrahydrate	Ce(SO ₄) ₂ .4H ₂ O	AR (≥ 98%)	Merck Millipore
Sodium hydroxide	NaOH	97%	SRL Pvt. Ltd.
Potassium hydroxide	KOH	85%	Thomas Baker
Methanol	CH ₃ OH	AR (99.5%)	Thomas Baker
Nafion TM 117	C ₇ HF ₁₃ O ₅ S.C ₂ F ₄) _x	5 wt. %	Sigma-Aldrich

I. Research Publications

1. A.K. Naik, P. V Samant, Thiourea modulated supercapacitive behavior of reduced graphene oxide, *Diam. Relat. Mater.* 145 (2024) 111122. <https://doi.org/10.1016/j.diamond.2024.111122>.
2. A.K. Naik, P. V. Samant, Rationally designed NixOMS-2 nanostructures for enhanced bifunctional methanol oxidation and oxygen evolution electrocatalysis, *J. Power Sources* 665 (2026) 239057. <https://doi.org/10.1016/j.jpowsour.2025.239057>.

II. Awards / Paper Presentations at International /National Conferences / Seminars / Workshops attended

1. Best Oral Presentation Award (2nd Place)

“Synthesis Controlled Electrocatalytic Activity of Ni-Substituted OMS-2 Nanorods for Sustainable Energy Applications”

“**Chem Scholar’s Connect 2026**” One Day Symposium for Chemistry Ph.D. students, School of Chemical Sciences, Goa University in association with CDFAA held on 6th April, 2026.

2. Best Poster Presentation Award (2nd Place)

“High-Performance Bifunctional Electrocatalysis on Ni substituted OMS-2 (Ni_xOMS-2) Nanorods for Sustainable Energy Applications”

International Conference on “Sustainable Energy and Environment (ICSEE-2025)”, Department of Chemical Engineering, BITS Pilani, K. K. Birla Goa Campus from 8th – 10th March, 2025.

3. Best poster presentation award (4th place)

“Effect of Nitrogen and Sulphur on Supercapacitive Behaviour of Reduced Graphene Oxide”

National Conference on “Advances in Material Science” Department of Chemistry, Government College of Arts, Science and Commerce, Khandola – Goa in association with DHE, Goa on 9th and 10th February 2024.

4. “Activating MnO₂ Redox Centers through Ce-Doping and NS-RGO Synergy for Ultra Stable Hybrid Supercapacitor Electrodes”

International Conference on Green Hydrogen and Energy Technology (ICGHT-2026) Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur, Tamilnadu from 8-10th January 2026.

5. “Electrochemically activated Nickel doped Octahedral Molecular Sieves (NiOMS-2) catalyst for Methanol Oxidation and Oxygen Evolution Reaction”

International Conference on “Green Energy : Powering a Sustainable Future” Department of Chemistry & Cluster Research Centre, Government College of Arts, Science and Commerce, Khandola – Goa, in association with Ibaraki University, Japan on 24th and 25th September 2024.

6. “Reduced Graphene Oxide supported NiOMS-2 as a Platinum free electrocatalyst for Methanol electrooxidation”

International Conference on “Green Chemistry and Intellectual Property for United Nations Sustainable Development Goals”, Department of Chemistry, DM’s College and Research Centre, Assagao, Bardez – Goa in association with DHE, Goa on 22nd and 23rd March 2024.

7. "Reduced Graphene Oxide supported Pt/OMS-2 as an electrocatalyst for Direct Methanol Fuel Cell"

“International Conference on Women in Electrochemistry (ICWEC-2023)”, The Electrochemical Society of India, IISc Bengaluru on 7th and 8th April, 2023.

8. “Nitrogen and Sulphur doped Graphene Oxide Support for electrocatalysis of Methanol Oxidation reaction” at the **International Conference on “Electrochemistry in Industry, Health and Environment (EIHE-2020)”**, Indian Society for Electroanalytical Chemistry, BARC, Mumbai, from 21st to 25th January, 2020.

9. Two week online workshop on **“Electrochemical data analysis”** SIAS research centre, Kerala, India in association with Metrohm India from 7th to 18th October, 2024.
10. **“Research Grant Writing Workshop”** Goa State Higher Education Council, GSRF & DHE on 9th September 2023.
11. **International e-symposium on Materials Development and Scale-up for Membrane Separation, Sensing, Energy and Biological Applications (MDS-MSEB)** (Virtual mode), Department of Chemical Engineering, SRM Institute of Science and Technology, Kattankulathur on 24th and 25th January, 2023.
12. Workshop on **“X-ray Crystallography”**, School of Chemical Sciences and School of Physical & Applied Sciences, Goa University, Goa from 21st to 23rd July, 2022.
13. **Industry-Academia International Symposium (Virtual) on “Fuels for Environmental Sustainability”**, Department of Chemistry, Government College of Arts, Science and Commerce, Khandola – Goa on 8th and 9th October, 2021.
14. Virtual Conference on **“Materials for Energy Harvesting and Catalysis”** TIFR, Mumbai and IISER, Kolkata from 1st to 3rd May 2020.

