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**CARBON-BASED NANOMATERIAL
HYBRIDS FOR ENERGY STORAGE
APPLICATIONS**

ANJALI JAYAKUMAR

**SCHOOL OF CHEMICAL AND BIOMEDICAL
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**SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING (SCBE)**

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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This thesis contains material from 4 paper(s) published in the following peer-reviewed journal(s) where I was the first and/or corresponding author.

Chapter 3 is published as **Jayakumar, A.**; Yoon, Y.J.; Wang, R.; Lee, J.M., Novel graphene/polyaniline/MnO_x 3D-hydrogels obtained by controlled morphology of MnO_x in the graphene/polyaniline matrix for high performance binder-free supercapacitor electrodes, **RSC Advances** **2015**, 5 (114), 94388-94396, DOI:10.1039/C5RA16884H

The contributions of the authors are as follows:

1. Assoc.Prof Lee Jong Min and Assoc.Prof Yong Jin Yoon provided the initial project direction and later edited the manuscript drafts.
2. I conducted all the experiments and characterisations and wrote the manuscript.
3. Dr.Wang Ronghua helped in the project planning, execution, helped in conducting characterisations and in preparation and editing of the manuscript.

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2. Dr. Rajini Antony conceived and initiated the project idea and helped prepare and edit the manuscript. She also helped with all the discussions to draw inferences from the results obtained. She also conducted the SAED data analysis.

3. I conducted all the experiments and characterisations and wrote the manuscript.

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2. Dr. Zhao Jun helped in synthesising all the electrode materials using carbonisation techniques and helped in editing the manuscript.

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4. Dr. Rajini Antony conducted the OER studies and helped write and edit the manuscript. She also helped with all the discussions to draw inferences from the results obtained.

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Table of contents

Statement of Originality.....	i
Supervisor Declaration Statement.....	iii
Authorship Attribution Statement.....	v
Acknowledgements.....	ix
Table of contents.....	xi
Abstract.....	1
Chapter 1 Background and Specific Aims	3
1.1 Background	3
1.2 Specific Aims	8
1.3 Dissertation Overview	10
Chapter 2 Literature Review	13
2.1 Supercapacitors as Energy storage devices	13
2.2 Hybrid materials from EDLCs and pseudocapacitors.....	18
2.3 Graphene hybrid hydrogels- An emerging EDLC material	19
2.3.1 Graphene hydrogels – Some major synthesis routes	21
2.4 Biomass-derived carbon hybrids – A cheap substitute for graphene ..	31
2.5 Transition metal oxides, Conducting polymers for supercapacitors ...	37
2.5.1 Manganese oxides and Polyaniline for supercapacitors	37
2.5.2 Nickel-cobalt oxides/nanoparticles for supercapacitors	40
2.6 Zeolite imidazole framework-derived transition metal nanoparticles/oxides for supercapacitors	42
Chapter 3 Novel Graphene/PANI/ MnO _x 3D-hydrogels for high performance binder-free supercapacitor electrodes	45
3.1 Materials and methods	47
3.1.1 Chemicals.....	47
3.1.2 G.O synthesis and G.O: PANI Synthesis.....	47
3.1.3 MnO ₂ Synthesis	47
3.1.4 PGM and PGM-HCl Ternary composite hydrogel synthesis	48

3.1.5	Electrochemical Measurements	49
3.1.6	Materials Characterisation	50
3.2	Results and discussions	51
3.2.1	XRD Studies	51
3.2.2	Morphological studies.....	53
3.2.3	FTIR spectral analysis.....	55
3.2.4	XPS Spectral Analysis	57
3.2.5	Electrochemical Performance Analysis	58
3.3	Conclusions	65
Chapter 4 MOF-derived hollow cage $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ and their synergy with graphene for outstanding supercapacitors.....		67
4.1	Materials and methods	69
4.1.1	Chemicals.....	69
4.1.2	Synthesis of Nickel cobalt mixed oxide $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ from ZIF	69
4.1.3	Synthesis of pure Co_3O_4 crystals from ZIF-67	70
4.1.4	Synthesis of Nickel cobalt mixed oxide/graphene 3D-hydrogel (GNi:Co 1:1).....	70
4.1.5	Electrochemical measurements.....	71
4.1.6	Materials characterisation	73
4.2	Results and discussions	73
4.2.1	XRD studies	74
4.2.2	Raman spectroscopy	75
4.2.3	Morphological characterisations	77
4.2.4	The XPS studies	80
4.2.5	Electrochemical characterisation	81
4.2.6	Asymmetric supercapacitor (ASC)	87
4.3	Conclusion.....	91
Chapter 5 Coconut leaf sheath-derived, N-doped carbon network for high performance supercapacitors		95
5.1	Materials and methods	97
5.1.1	Chemicals and raw materials:	97
5.1.2	Synthesis of graphitized nitrogen doped carbon 0.5M-700N-800C: 97	

5.1.3	Synthesis of graphitized nitrogen doped carbon, other ratios:.....	98
5.1.4	Synthesis of Pure graphene hydrogel (Pure G).....	99
5.1.5	Electrochemical measurements.....	100
5.1.6	Materials characterisations.....	101
5.2	Results and discussions	102
5.2.1	XRD measurements	102
5.2.2	Raman spectroscopic measurements.....	104
5.2.3	Morphological studies.....	106
5.2.4	The XPS spectral analysis.....	109
5.2.5	Electrochemical measurements.....	110
5.3	Conclusions	115
Chapter 6 MOF-derived Ni, Co metal nanoparticles in a N-doped biomass-derived carbon matrix for high performance supercapacitors and OER catalysis		119
6.1	Materials and methods	121
6.1.1	Chemicals.....	121
6.1.2	Synthesis of nitrogen doped carbon from coconut leaf sheath ..	121
6.1.3	Synthesis of Ni, Co nanoparticles decorated on biomass-derived N-doped carbon	121
6.1.4	Electrochemical measurements.....	123
6.1.5	OER catalysis.....	125
6.1.6	Materials characterisation	127
6.2	Results and discussions	127
6.2.1	XRD measurements	127
6.2.2	Raman spectroscopic measurements.....	128
6.2.3	Morphological characterisations	130
6.2.4	XPS measurements	132
6.2.5	Electrochemical characterisation	134
6.2.6	Asymmetric supercapacitor (ASC)	139
6.2.7	OER studies	142
6.3	Conclusion.....	144
Chapter 7 Conclusions and future work		147

7.1	Conclusions	147
7.2	Comparisons of all the supercapacitors assembled: Economic analysis and recommendations.....	150
7.3	Future work and perspectives.....	152
APPENDIX-I Supplementary information		157
APPENDIX- II List of publications.....		171
APPENDIX III Table of Figures		173
APPENDIX IV Abbreviations		179
APPENDIX V References		181

Abstract

Supercapacitors are emerging as highly promising electrochemical energy storage devices, which can be sources of clean and sustainable energy. Off late, a lot of studies are ongoing in the field of carbon-based hydrogels for use in electrodes for supercapacitors. A lot of hybrid materials employing carbon frameworks and pseudo-capacitive materials are finding a lot of importance in the current scientific environment, as they synergistically improve the electrochemical performance of the supercapacitor electrode. It is also highly imperative to carefully choose the components of the hybrid, since the final properties and performance of the material will highly depend on the individual properties of the components. In the light of these important parameters, my study focuses on the synthesis of hybrid materials with carbon-based materials for a base.

In the initial phase of my work, soft materials like three-dimensional graphene hydrogel hybrid systems were used. Polyaniline and manganese oxides nanoparticles were embedded in a graphene hydrogel matrix and their performance was studied for supercapacitor applications. Zeolite imidazole framework-derived (ZIF-67) nickel cobalt mixed oxides were then embedded in graphene hydrogels and were found to perform better than the Manganese oxide/polyaniline/graphene hydrogel. A biomass-derived carbon/Ni Co metal nanoparticle system was designed to mimic this graphene/Ni Co mixed oxide system, with a new and non-conventional use of a coconut tree fibre, coconut leaf sheath; a cheap substitute for graphene. My study shows the possibility of using

a well-studied, optimised and functionalised biomass-derived carbon as a cheap substitute for graphene and the detailed comparison studies have shown that the energy-power density matrix for a biomass derived carbon framework embedded with ZIF-derived Ni-Co nanoparticles is comparable with a graphene/ZIF-derived Ni Co mixed oxide system. This highlights the untapped potential in our abundantly available renewable resources like biomass.

Chapter 1 Background and Specific Aims

1.1 Background

Climate change and the depleting fossil fuels require society to move towards sustainable and renewable resources. As a result, we are observing an increase in renewable energy production from sun and wind, as well as the development of electric vehicles or hybrid electric vehicles with low CO₂ emissions. Renewable energy sources like solar and wind energy cannot be tapped consistently because of their unpredictable variations, making energy storage systems to play a larger part in our lives.^{1, 2} At the forefront of these are electrical energy storage systems, such as batteries and electrochemical capacitors (ECs).³⁻⁶ However, we need to improve their performance substantially to meet the higher energy necessities of future energy systems like portable electronics, hybrid electric vehicles and large industrial equipment, by developing new materials and advancing our understanding of the electrochemical interfaces at the nanoscale.

Supercapacitors, also called ultracapacitors or electrochemical capacitors, have attracted a great deal of attention from both industry and academia due to their high power density, superior rate capability, rapid charging/discharging rate, long cycle life (5000-10000 cycles), simple principles, fast charge transfer reactions (few seconds) and low maintenance cost.^{7 5, 8-10} Since General Electric for the first time demonstrated and patented in 1957, supercapacitors have attracted significant attention from both scientists and engineers.¹¹ The possibilities of

obtaining high power ($>10 \text{ kW Kg}^{-1}$) makes them ‘super’ capacitors and their ability to dispense this high-power at a very short span makes them quite attractive in a lot of applications requiring a burst of power; like the emergency doors for Airbus, memory-backup systems, consumer electronics, moving and power electronic systems/components in industries etc.^{1, 6, 7} They can be found bridging the gap between normal electrolytic capacitors and batteries, where they store more charges than a capacitor and have better power densities than batteries.⁷ Their high power densities could also be made use of in hybrid electric vehicles as temporary energy storage systems, in combination with batteries and fuel cells (which can provide high energy densities) and could help in emergency braking systems, starters, generators etc.^{5, 12-15}

Figure 1.1 Specific power against specific energy for different energy storage systems (Ragone plot). Times shown (the time constants of the devices) are obtained by dividing the energy density by the power, reproduced with permission from ⁷, Copyright 2013, Wiley.

Several types of ECs can be distinguished, depending on the charge storage mechanism as well as the active materials used (**Table 1.1**). Electrochemical double layer capacitors or EDLCs, the most common devices at present, use carbon-based active materials with high surface area.¹³ A second group of ECs, known as pseudo- capacitors or redox supercapacitors, use fast and reversible surface or near-surface reactions for charge storage.¹⁶ Transition metal oxides as well as electrically conducting polymers are examples of pseudo-capacitive active materials.^{8, 14} Hybrid capacitors, combining a capacitive or pseudo-capacitive electrode with a battery electrode, are the latest kind of EC, which benefit from both the capacitor and the battery properties.

Electrochemical capacitors currently fill the gap between batteries and conventional solid state and electrolytic capacitors (**Figure. 1.1**). They store hundreds or thousands of times more charge (tens to hundreds of farads per gram) than the latter, because of a much larger surface area ($1,000\text{--}2,000\text{ m}^2\text{g}^{-1}$) available for charge storage in EDLC. However, they have a lower energy density than batteries, and this limits the optimal discharge time to less than a minute, whereas many applications clearly need more.

Since the early days of EC development (in the late 1950s), there has not been a good strategy for increasing the energy density; only incremental performance improvements were achieved from the 1960s to 1990s. The impressive increase in performance that has been demonstrated in the past couple of years is due to the discovery of new electrode materials and improved understanding of ion behaviour in small pores, as well as the design of new hybrid systems combining

faradic and capacitive electrodes. This makes the study of new electrode materials crucial in the improvement of the energy density of supercapacitors for large scale applications, especially for green electric vehicles, portable energy devices etc.¹⁷

Table 1.1 Types of Supercapacitors and their main features and differences

Supercapacitors	
EDLCs- Electrochemical Double Layer Capacitors	Pseudocapacitors
Charge storage via a direct, physical, electrostatic way (Formation of a Helmholtz double-layer at the electrode-electrolyte interface)	Charge storage via an indirect, chemical, Faradic process- Fast redox reactions at or near the surface
EDLCs deliver energy quickly due to the physical nature of charge storage mechanism	Energy delivery slower than EDLCs due to the chemical nature of energy storage; i.e. redox reactions
Capacitance limited, due to the electrode confinement	Capacitance much more compared to EDLCs due to the chemical nature of redox reactions happening both at or near the surface
Examples- Carbon-based materials like Graphene, CNT, Activated carbon etc.	Examples: Transition metal oxides like MnO ₂ , conducting polymers like Polyaniline etc. (which contain redox centres)

Table 1.2 Examples of some supercapacitor materials and their characteristic properties

Ref. and year	Main material constituents	a) Three/Two electrode setup b) Capacitance	Energy density vs Power density	Cycle life- % capacitance retention	Other main features
1. ¹⁸ , 1999	PEDOT: PSS	a) Two-electrode aqueous symmetric device, b) NA	~ 6Wh Kg ⁻¹ at 3 kW Kg ⁻¹	NA	Completely based on conducting polymer
2. ¹⁹ , 2012	L-glutathione reduced-Graphene	a) Two-electrode solid state asymmetric device, GH/MnO ₂ -NF b) 41.7 Fg ⁻¹ at 1 Ag ⁻¹	14.9 Wh Kg ⁻¹ at 10 kW Kg ⁻¹	83.4 % (current density NA) after 5000 cycles	Eco-friendly reagent for hydrogel synthesis
3. ²⁰ , 2013	Hydroquinone functionalized graphene	a) Two-electrode solid state symmetric device, b) 412 Fg ⁻¹ at 1 Ag ⁻¹	NA	87% (at 10 Ag ⁻¹) after 10000 cycles	High mechanical flexibility, low discharge course
4. ²¹ , 2013	N-doped graphene using organic amine or ammonia	a) Two-electrode aqueous symmetric device, b) 113.8 Fg ⁻¹ at 185 Ag ⁻¹	205 kW/Kg at 185 A/g (Energy density NA)	95% (at 100 Ag ⁻¹), after 4000 cycles	Extremely high rate capability with 109.4 Fg ⁻¹ at 250 Ag ⁻¹
5. ²² , 2013	Fe ₃ O ₄ NPS-Watermelon-derived carbon	a) Three-electrode system, b) 369.2 Fg ⁻¹ at 5 mV s ⁻¹	NA	96 % (at 1 Ag ⁻¹) after 1000 cycles	Majorly based on biomass, green synthesis
6. ⁹ , 2013	Cotton-derived carbon (KOH activated)	a) Three-electrode system, b) 283 Fg ⁻¹ at 1 Ag ⁻¹	NA	97% (at 4 Ag ⁻¹) after 20000 cycles	High rate capability with 79% capacitance retention at 100 Ag ⁻¹
7. ²³ , 2016	NiOOH-Graphene	a) Two-electrode aqueous asymmetric device H-NiOOH/GS//H-GS, b) 165 Fg ⁻¹ at 5 mVs ⁻¹	66.8 Wh Kg ⁻¹ at 800 W Kg ⁻¹	85.3% (at 4 Ag ⁻¹) after 8000 cycles	Solvothermal synthesis, optimisation study

8. ²⁴ , 2016	N, B co-doped carbon from agarose hydrogel	a) Two-electrode aqueous symmetric device, b) 214 Fg ⁻¹ at 0.2 Ag ⁻¹	NA	89 % (5 Ag ⁻¹) after 3000 cycles	Green synthesis, Biomass-based starting material
9. ¹⁰ , 2018	Phytic acid-doped-Polyaniline, graphene	a) Two-electrode solid state symmetric device, b) 112 Fg ⁻¹ at 0.08 Ag ⁻¹	8.8 mWh cm ⁻³ at 30.77 mW cm ⁻³	86% (at 1.26 Ag ⁻¹) after 17000 cycles	All-solid state, stretchable device

Table 1.2 contains details about various materials used for supercapacitor applications. Of all the materials listed in the table above, biomass-derived materials are the cheapest, since they use bio-wastes/low cost natural products like cotton, watermelon, agarose etc. and would be a very good substitute for more expensive carbonaceous counterparts like Graphene. Conducting polymers like Polyaniline, PEDOT etc. are also cheap options though they have low electrochemical stabilities due to degradation over long cycles.²⁵⁻²⁷ A lot of low cost, earth-abundant transition metal oxides/hydroxides like Manganese oxides, Nickel oxides, Vanadium oxides etc. are used as pseudocapacitor materials in hybrid materials and are replacing costly yet high-performing materials like RuO₂.^{7, 16} It is important to make hybrid materials which are rationally designed, with a good leverage on cost-effectiveness, possibilities for using it for large-scale applications; without compromising on electrochemical performance.

1.2 Specific Aims

Because of the humungous potential in the field of developing supercapacitor electrode materials for green and sustainable energy storage, the study and development of such materials is of immense importance. The scientific

community has developed quite a few materials in this regard, but the results are far from satisfactory for use in large scale applications. The path is full of challenges and hurdles and hence more research is quite imperative to lift the performances of the current age supercapacitors to meet the energy needs of an energy-starved mankind. Keeping in mind the challenges and the extreme potential of supercapacitors, this thesis aims at studying new strategies to largely develop carbon-based nanomaterial hybrids for supercapacitor applications.

The specific objectives of this dissertation are:

1. Firstly, to identify a suitable combination of pseudocapacitor material and graphene, build a three-dimensional network using a hydrothermal procedure and to run an optimisation study to understand the dependence of electrochemical performance to parameters like morphology, phase of the materials etc (A Graphene/Polyaniline/ MnO_x ternary composite is built).
2. To devise a strategy and build uniform three-dimensional core-shell structures of binary mixed oxides, systematically derived from a metal organic framework (Graphene/ $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$). The optimised sample is incorporated in a graphene hydrogel matrix. An asymmetric supercapacitor is assembled using the optimised sample as the positive electrode and a pure graphene hydrogel as a negative electrode.
3. The performances of the Graphene/Polyaniline/ MnO_x and Graphene/ $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ networks are compared. The better of the two systems is chosen and a strategy to mimic this system with a biomass-derived carbon network as a substitute for graphene is adopted.

4. Development of an alternative biomass-derived carbon-based material as a cheap substitute for graphene. For this, an unconventional and new material called coconut leaf sheath (a coconut fibre) is chosen based on various factors like availability, a high lignin to cellulose ratio, shelf life, light weightiness, cost effectiveness etc for making biomass-derived carbon through carbonization. The material is thoroughly studied, nitrogen doped, functionalised and optimised by modifying parameters like the annealing time, temperature, the amount of nitrogen functionalization precursors and graphitisation degree.
5. The optimised biomass-derived nitrogen doped carbon network is later used as a support for the growth of metal organic framework derived- Cobalt Nickel metal nanoparticles and a coral shape framework obtained is studied for use in supercapacitors. An asymmetric supercapacitor is assembled using the above-mentioned material as a positive electrode and pure optimised biomass-derived carbon as a negative electrode. The graphene-based system and the biomass-derived carbon -based systems are compared and conclusions are drawn.

1.3 Dissertation Overview

Chapter 1 of this thesis highlights the importance and the current need for developing materials for supercapacitor applications. The background and specific aims are given in detail. *Chapter 2* deals with the state-of-the-art literature in this field, all the current research highlights pertaining to this area

and how/why we zeroed in on the materials that we worked on. The fundamentals of supercapacitors, their different types, various electrode materials used, synthesis strategies and their performances are critically discussed in detail. *Chapter 3* deals with the synthesis of a new Graphene/Polyaniline/MnO_x ternary composite, its characterisation and detailed optimisation and electrochemical performance study. *Chapter 4* details about a new strategy to develop core-shell Cobalt, Nickel mixed oxides from a metal organic framework. These structures are synthesised under various reaction conditions and optimised to give maximum electrochemical performance. A detailed optimisation study, the incorporation of the optimised sample in to a graphene hydrogel framework and the subsequent assembly of an asymmetric supercapacitor is explained. The synergistic performance, origin and type of capacitance of the mixed oxide incorporated graphene hydrogel network are studied in detail using empirical equations. It is concluded from *Chapter 3* and *Chapter 4* that Graphene/Ni, Co oxides perform better than Graphene/Manganese oxide/polyaniline hybrids and hence Ni, Co-based material is chosen for the subsequent studies. *Chapter 5* deals with the synthesis, optimisation and electrochemical study of coconut leaf sheath-derived carbon for use as a negative electrode material for supercapacitors. This is done as an effort to find a biomass-derived carbon material, as a substitute for graphene. *Chapter 6* contains the study on incorporating metal organic framework-derived nickel cobalt metal nanoparticles on the optimised biomass derived carbon framework developed in *Chapter 5*. An asymmetric supercapacitor assembly is also made and studied. *Chapter 7* contains discussions

on the previous chapters, the comparisons and conclusions drawn from them. It provides an insight in to the future on supercapacitors, need for clean synthesis strategies, and the parallel study of these carbon-based hybrid materials for applications in various other sectors like the energy, health and environmental arena.

Chapter 2 Literature Review

2.1 Supercapacitors as Energy storage devices

With the increasing demand of energy sources, it is a huge challenge to develop newer and greener energy storage systems to utilize the renewable sources of energy. It is crucial to fuel the growing needs of mankind and to fight the growing environmental bottlenecks created by conventional sources of energy like coal and petroleum. Supercapacitors are emerging as highly promising electrochemical energy storage devices, which can be sources of clean and sustainable energy.^{28 7} These supercapacitors with their attractive high energy density, high power density, and high life cycles are emerging as promising candidates for portable electronic devices, bio medical applications and electric vehicles.²⁹ Super capacitor materials mainly come in two types based on their electrode design and working principle. The EDLCs (Electric Double Layer Capacitors) mainly use carbon and carbon derivative electrodes and capacitance arises from the formation of a double layer of accumulated charges¹², whereas in Pseudo Capacitors, capacitance arises from quick reversible redox reactions at the material interface.³⁰ Graphene³¹, a major EDLC, has attracted and remains to be of extreme interest to the scientific community, as its properties of high conductivity, large theoretical surface area, excellent mechanical flexibility, and chemical stability are un-paralleled in comparison to many other carbonaceous materials which are available.^{10 32 13} Though graphene has a high theoretical

specific capacitance of around $500\text{--}550\text{ F g}^{-1}$, the unfavourable restacking of the graphene sheets owing to the strong π - π interaction reduces its surface area leading to low overall capacitive performance with low specific capacitances of $80\text{--}118\text{ F g}^{-1}$.²⁰ This has also called for research for other carbon-based materials like biomass-derived carbon, functionalised graphene, carbon nanotubes etc.^{9, 33-}

39

An EDLC stores its charge electrostatically. Hence there is no transfer of charge between the electrolyte and electrode. The earliest model of the electrical double layer was made by Helmholtz.³⁰ He treated the double layer as similar to a conventional capacitor, which are two layers of opposite charges that form at the interface of the electrode and electrolyte, separated by a distance at the atomic scale. For an EDLC the electrolyte is either an aqueous or non-aqueous liquid, or a solid material like a conducting polymer. The charged ions are ordered in an array at the electrode surface according to Helmholtz. The model was modified by Gouy and Chapman who looked at the continuous distribution of cations and anions in the electrolyte. The distribution is determined by thermal motion and this layer is called the diffusion layer. The Gouy–Chapman model of the double layer overestimated the capacitance of the electrochemical double layer capacitor, due to the assumption of point charges at the electrode surface. Later Stern was treating this problem by suggesting the combination of the Helmholtz and Gouy–Chapman models, giving an internal Stern layer (which is a Helmholtz layer) and an outer diffuse layer (**Figure 2.1**).

Figure 2.1 A half-cell is shown to the left with electrolyte and electrode, in the middle a magnification of the electrode showing mesopores where the ions in the electrolyte (orange) can move freely. To the right the ions forming the double layer is shown, reproduced with permission from ³⁰, Copyright 2014, Elsevier

Supercapacitors using pseudo-capacitance instead of storing the energy electrostatically suggests energy storage by a different mechanism which is of Faradaic origin. In this case we have charge transfer across the double layer at the electrode surface (**Figure 2.2**). Three different types of pseudo-capacitances in electrochemical capacitors have been used. The first is surface adsorption of ions from the electrolyte and the second is redox reactions that involve ions from the electrolyte. These two processes are mostly dependent on a surface mechanism and thus rely on the surface area as one factor for a large capacitance; the other being the permittivity of the material. The third type is doping and undoping of electrically conducting polymers in the electrode. Conducting polymers are less surface dependent and through its bulk. EDLCs and pseudo-capacitors have different advantages which depend on their ways of storing

energy. Pseudo-capacitors have a higher energy density, but lower power-densities than EDLCs.

Pseudocapacitive materials which are widely used are transition metal oxides and conducting polymers of which manganese oxide and polyaniline have attracted wide attention owing to its low cost, environment friendliness and easy methods of preparation from existing abundant raw materials.⁴⁰⁻⁴² Transition metal oxides like manganese oxides, nickel oxides, cobalt oxides, ruthenium oxides, iron oxides, vanadium oxides etc. have extremely large theoretical capacities and they can significantly add to the specific capacitance of the electrode material.⁴³⁻⁴⁷ They exist in multiple oxidation states of Mn^{2+} , Mn^{3+} , Mn^{4+} , Ni^{2+} , Ni^{3+} , Co^{2+} , Co^{3+} etc, and also exist in different phases due to redox reactions.³⁶ MnO_x , can be collectively represented as manganese in multiple phases and oxidation states. However, their low conductivity and stability makes it very difficult to integrate them in composite materials.⁴⁰ Conducting polymers like polypyrrole, polyaniline etc. on the other hand have a good conductivity and also a high specific capacitance, but it suffers from poor cyclic stability issues due to structural degradation caused by shrinking and swelling during the charge discharge process.^{42, 48}

Figure 2.2 Mechanism of charge transfer in a) EDLC, explaining the electrostatic charge storage mechanism without any charge transfer b) pseudocapacitors, explaining the faradaic charge-transfer of the pseudocapacitance, reproduced with permission from ⁴⁹, Copyright 2013, Electrochemical Society

The performances of supercapacitors are influenced and determined by a lot of factors like: 1) a high specific capacitance; 2) a substantially high power density; 3) a relatively high energy density; 4) an excellent cyclability; 5) fast charge/discharge rates; 6) low self-discharging; 7) safe operating conditions, and 8) cost effectiveness.^{1, 12, 15, 32, 50} It is well-known that several factors significantly affect the performances of a supercapacitor such as pore structure of electroactive materials (specific surface area (SSA) and pore size distribution (PSD)), intrinsic properties of the electrolyte, microstructure/ morphology and electrical conductivity of electroactive materials, and the interface between electrode and electrolyte (**Figure 2.3**).^{12, 15, 51} In addition to the above factors, there are some other influencing factors, such as operating voltage, reasonable matching of negative/positive electrode, and asymmetric design, that strongly affect the energy density for supercapacitors.²³

Figure 2.3 Schematic sketch of different approaches to advance the energy density of a supercapacitor, reproduced with permission from ⁷, Copyright 2013, Wiley.

2.2 Hybrid materials from EDLCs and pseudocapacitors

To address the limitations when individually using EDLCs and pseudocapacitors, a lot of hybrid materials employing low cost carbon materials and pseudocapacitive materials are finding a lot of importance in the current scientific environment as they are believed to synergistically improve the electrochemical performance of the electrode compared to electrodes made from the individual components.^{21, 52 53} It is also highly imperative to carefully choose the components of the hybrid since the final properties and performance of the material will highly depend on the individual properties of the components.⁵⁴ A good engineered approach to model the hybrid material will give due consideration to the morphology, optimized ratio of the individual components to maximize synergy in terms of electrochemical performance, durability, and cost effective strategies for employing it in wide practical applications.⁵⁵ In the

present thesis, the first half of the work deals with graphene based hybrid hydrogels, while the second part deals with biomass-derived carbon based hybrid materials. Metal organic framework-derived metal oxides/nanoparticle materials have also been significantly used as the pseudocapacitive components in the hybrid. For pseudocapacitors, transition metal oxides like RuO_2 were commonly used, but owing to their high cost and lesser availability, more earth-abundant and cheaper transition metal oxides/nanoparticles like Manganese oxides, Nickel oxides, Cobalt oxides etc. and conducting polymers are used.^{8, 7} For EDLCs, biomass-derived carbons are gaining a lot of interest because of their extremely low cost and environmental-friendly nature and are much cheaper than other carbon-based products like graphene, Carbon Nanotubes (CNT) etc.^{39, 56}

2.3 Graphene hybrid hydrogels- An emerging EDLC material

Graphene is a sheet of sp^2 -bonded carbon which is one-atom thick and this two-dimensional allotropic form of carbon is the thinnest known material known so far and can be rightly called the mother of all other graphitic forms.^{53, 57} For instance, rolling a single graphene sheet would give CNTs while they can also be stacked to give 3D graphite and a spherical fullerene can be assembled on wrapping after adding more pentagons to graphene.^{32, 57} Graphene is a zero-bandgap semiconductor with unique electronic properties; its charge carriers are described by a Dirac-like equation, unlike the normal Schrodinger equation for charge carriers.⁵³ With the highest electron mobility ($15000 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$ or $10^6 \text{ } \Omega \text{ cm}$), an ultrahigh mobility of temperature-independent charge carriers

($200000 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$) and a Fermi velocity comparable to the speed of light (10^6 m s^{-1}), graphene clearly stands apart from other carbon allotropes like diamond, fullerene, CNT etc.⁵³ Not only are its electronic properties special; graphene also has outstanding optical, electrochemical, optical and mechanical properties. With a theoretical surface area of close to $2630 \text{ m}^2/\text{g}$, a high mechanical strength proved by a 1.0 TPa Young's modulus for its single-layer, it also has a 97.7% optical transmittance, a high thermal conductivity of $5000 \text{ W m}^{-1} \text{ K}^{-1}$ and an extremely high electrical conductivity of 2000 S cm^{-1} .^{13, 31 32, 53} All these properties make graphene an exciting material for the scientific community and has been used in various areas like electrocatalysis, energy storage, energy conversion and other optical and mechanical applications.^{13, 31}

Graphene hydrogels are three dimensional structures formed from their corresponding two-dimensional forms like graphene and graphene oxide.^{31, 32} These structures are better compared to its 2D counterpart at preventing the agglomeration of the stacked layers of graphene sheets, (which is the major challenge in fully exploiting the properties in 2D graphene).^{58, 59 58, 59} These gels have more superior properties than their 2D forms, arising from their hierarchical structure, which significantly improves their electrical and mechanical properties and gives better porosities.^{31, 32, 60} They are better than the conventional 1D carbon nanotubes and other carbon forms, in terms of cost, ease of synthesis etc. A major part of the thesis concentrates on hybrid materials with graphene hydrogels as a base, for incorporating various pseudocapacitive materials. The three-dimensional structure is maintained and driven by various forces, some of

them predominantly being π - π stacking and interactions, van der Waals force, hydrogen bonding etc.

2.3.1 Graphene hydrogels – Some major synthesis routes

The synthesis of graphene hydrogels can be classified mainly into hydrothermal and solvothermal reactions, gel formation via cross-linking polymers and template-based synthesis. Some major synthesis routes are discussed below.

2.3.1.1 Hydrothermal and solvothermal reactions

The reduction of graphene oxide (G.O) solution via the hydrothermal or solvothermal reduction reaction is the most common and most straight-forward method for the preparation of three-dimensional graphene hydrogels or aerogels (**Figure 2.4**).³¹ Hydrothermal and solvothermal reactions involve a self-assembly process, usually from their corresponding graphene or graphene oxide building blocks. G.O is initially prepared via the hummers method or modified hummers method, which involves the chemical oxidation and exfoliation of graphite flakes in an acidic environment.^{31, 32} This solution is subjected to a hydrothermal reduction reaction in Teflon lined autoclaves at temperatures ranging from 100-200 °C. In some cases, the use of reducing agents like urea, melamine, hydroquinone, ascorbic acid etc have been used, which helps to reducing the reaction temperatures to below 100 °C.²⁰ In this section, we discuss various methods to prepare graphene hydrogels and the various ways by which their strength, elasticity and functionality can be fine-tuned to serve various applications.

Figure 2.4 Schematic showing the self-assembly of 3D-graphene hydrogels from graphene oxide solution via a one-step hydrothermal reduction reaction

For instance, Chen et al. synthesised nitrogen-doped graphene hydrogels using ethylenediamine as the nitrogen precursor and reducing agent (**Figure 2.5**).²¹ The ethylene diamine used here, apart from being used as the nitrogen dopant, plays a crucial role in assisting with the ordered self-assembly of the graphene sheets in the three-dimensional structure of the hydrogel. Here, the organic amine was mixed in to the graphene oxide solution of concentration 2 mg mL^{-1} and stirred magnetically for 10 min to give a homogenous mixture. This mixture was then subjected to a hydrothermal reduction reaction in a Teflon-lined autoclave at 180°C for 12 hours. The graphene sheets, with their highly conjugated networks have strong π - π interactions and hydrophobic forces, which are strong enough to form bonds leading them to stack and self-assemble into a three-dimensional porous network during the hydrothermal reduction. Wang et al. synthesised a multi-composite NiOOH/graphene hydrogel via a combined hydrothermal/solvothermal reaction (**Figure 2.6**).²³ Here, a mixture of N,N-dimethylformamide (DMF) and water was used with nickel acetate as the Ni

precursor and the ratio of DMF and H₂O were varied and the resulting hydrogels were studied in detail. The hydrogels were prepared using a similar hydrothermal reaction as explained in the previous case, with the difference that the time was reduced to 6 hours instead of 12 hours. When the solvent was pure water, Ni(OH)₂ was formed and for mixed DMF and H₂O solvents, a new phase, NiOOH was formed, as validated by the XRD spectra in **Figure 2.6d**.

Figure 2.5 a) Photographs of a typical GN-GH using GO and ethylenediamine (100 mL) as precursors after hydrothermal process at 180 °C for 12 h, (b) SEM image of the typical GN-GH microstructures, (c) magnified SEM image of the typical GN-GH microstructures, reproduced with permission from ref ²¹ , Copyright 2013, Elsevier

Figure 2.6 (a–c) SEM images of NiOOH/GS hydrogel after vacuum freeze drying, prepared via a solvothermal reaction, d) XRD spectra of various hydrogel samples prepared in different DMF:H₂O ratios e) A digital photograph of NiOOH/GS hydrogels, reproduced with permission from ref ²³, copyright 2016, from Elsevier

Figure 2.7 Morphology and formation mechanism of the cork-like graphene elastomer. (a–c) Typical top-view (a,b) and side-view (c) SEM images of graphene monolith of 5.10 mg cm⁻³. Scale bars, (a,c) 50 mm and (b) 10 mm, (d) Schematic showing the formation mechanism of the cork-like monolith by freeze casting. Photos of the corresponding samples are presented in the insets.², reproduced with permission from ref ⁶¹, Copyright 2012, Springer Nature

Qiu et al. synthesised super-elastic graphene hydrogels, inspired by the hierarchical honey-comb structure of the cells in cork.⁶¹ These biomimetic structures showed high electrical conductivity and high efficiency for energy absorption. They used ascorbic acid as a reducing agent and incorporated ice

physics via a method called freeze casting in to the graphene hydrogel synthesis to obtain this cork structure-inspired material. This was achieved by controlling the degree of reduction of the graphene oxide solution (by controlling the oxygen groups through optimising the reduction time) and by controlling the freezing conditions. Here, a pr-GO sheet containing solution was frozen, the pr-GO sheets surrounded the ice crystals and a squeezing effect aligned them along the ice growth direction (**Figure 2.7d**) and a 3D monolith was formed when the ice was sublimed. This monolith was reduced again and freeze-dried to a fully reduced and super elastic graphene aerogel. Compression tests showed the high resilience of these monoliths (density 5.1 mg cm^{-3}) with a compressive stress at 8 kPa at the plateau and at a strain of 80 % (18 kPa), 2-9 times higher than carbon foams with similar density and even twice the density.

2.3.1.2 Gel formation via cross-linking polymers and biomolecules

Hydrogels are also synthesised with the help of long chain biomolecules or cross-linking polymers like polyvinyl alcohol (PVA), Poly Vinyl Pyrrolidone (PVP), biomolecules like DNA (Deoxyribo nucleic acid) etc, which provide sufficient drive for self-assembly via rich hydrogen-bonding and other functional moiety interactions between the graphene layers and the long-chained molecules/polymers. These molecules also often help in giving the hydrogels some useful functionalities via these cross-linking bond formations, resulting in better electroactivities and they introduce themselves between the graphene layers, thereby preventing them from aggregation and making the framework

more porous for the free movement of electrolyte. This method also has the advantage of using room temperatures or significantly lower temperatures in comparison with hydrothermal reaction for synthesis.

In one such synthesis, Fu et al. uses PVA as the cross-linking polymer for the synthesis of reduced graphene oxide hydrogels embedded with a highly uniform distribution of Ni/MnO particles, whose schematic representation is shown in **Figure 2.8A** and the SEM, TEM images are shown in **Figure 2.8B**.⁶² The formation of hydrogen bonds and the assumption of these bonds being the major players in the hydrogel formation is validated by the FTIR spectra in **Figure 2.8 A), b**. There is an obvious shift from 3423 cm^{-1} (G.O) to 3406 cm^{-1} (PVA-G.O) in the hydroxyl peak. The change in this hydroxyl is usually associated with the introduction of hydrogen bonds, thus validating the successful hydrogen-bond formation between the oxygen rich graphene oxide and the hydroxyl groups abundantly available in PVA.

Figure 2.8 A) Schematic representation for the synthesis of Ni-MnO/ rGO aerogels via cross-linking polymer assisted hydrogel formation, b) FT-IR spectra

of GO, PVA, and GO PVA aerogels. c) Schematic interaction between PVA and GO. d) XRD patterns of GO, PVA, and GO–PVA aerogels. B) Morphological and structural characterizations of Ni–MnO/rGO aerogels: a, b) SEM images; c, d,) TEM images at different magnifications e) HRTEM image; f) STEM image reproduced with permission from ref ⁶², Copyright 2018, Wiley

Xu et al. used in situ formed single-stranded DNA (ssDNA) chains for a 3D assembly of G.O sheets via a noncovalent-functionalization strategy, where the DNA chains interacted with the G.O sheets via π - π interactions, where the DNA chains interacted with the G.O sheets via π - π interactions and acted as glue, sticking together the graphene sheets in a 3D hierarchical structure.⁶³ The process involved the addition of double-stranded DNA (dsDNA) in to G.O solution, which was then mixed well and heated at 90°C for 5 min. These double strands later unleash into single strands and occupy themselves between the graphene layers via π - π interactions and thus lead to the three-dimensional network assembly. Raman spectroscopy was used to confirm this assumption, wherein a red shift of 6 cm⁻¹ was found for the G band of GO/ssDNA when compared to the raman spectra of GO/dsDNA and pure GO solutions. A very similar phenomenon is observed while wrapping CNTs with DNA and this is due to a charge transfer between the DNA strands and the GO sheets which results in this red shift. A rheological test (**Figure 2.9a**) also further clarified this phenomenon, with the storage modulus, G' showing a steep increase when the temperature was raised from 40 °C to 90 °C and this is in the range of the unwinding of dsDNA to ssDNA, holding the anticipated mechanism true. However, the direct mixing

of G.O with ssDNA does not yield a homogeneous hydrogel, since the ssDNA bonds bonded rapidly with the G.O sheets and resulted in a non-uniform gelation.

Figure 2.9 (a) Thermal melting curve of dsDNA monitored by absorption spectrum and temperature-dependent curve of storage modulus (G') of SH recorded during rheological test; (b) 514 nm excited Raman spectra of GO (black), GO/ds DNA mixture before heating (red), and GO/DNA SH (blue). (c) Schematic representation for the synthesis of Ni-MnO/ rGO aerogels via cross-linking polymer assisted hydrogel formation, reproduced with permission from ref ⁶³, Copyright 2010, American Chemical Society.

2.3.1.3 Template-assisted synthesis

Li et al. synthesised Microporous Graphene Monoliths (MGMs) via a GO-hexane droplet emulsion method, where, the hexane droplets served as templates to produce a highly porous, three-dimensional matrix (**Figure 2.10**).⁶⁴ The hydrogel formation was induced by hexane droplets acting as soft template and these

droplets from size range 10- 200 μm can easily form a homogeneous suspension with G.O solution. They are subjected to a hydrothermal reduction,

Figure 2.10 a) Optical microscope image of the emulsion made from the mixture of 2 mL hexane and 4 mL 5 mg mL^{-1} GO dispersion. b, c, d) Cross-sectional SEM images of MGM-5 at different magnifications; e) Cross-sectional SEM image of G-Aerogel-5. f) Photographs of MGM-5 (left) and G-Aerogel-5 (right) g) Schematic illustration of the preparation of an MGM, reproduced with permission from ref ⁶⁴, Copyright 2013, Elsevier

where the G.O sheets wrap around the spherical droplets during the self-assembly. The hydrogels are later dialysed in water at 80 °C wherein the hexane evaporates out. In comparison, the hydrogel formed from pure G.O solution (G-Aerogel-5) at 5 mg mL^{-1} concentration was seen to have irregular pores, whereas

the hydrogels formed from this template-assisted method (MGM-5, 5 being the concentration of G.O solution) had spherical pores with wrinkled rG.O as walls, formed from the G.O sheets wrapped around the hexane droplets.

Different from soft templates, hard templates were used by Du et al., which also acted as N-doping agents.⁶⁵ Amino-functionalised silica was used as templates to prevent the ready re-stacking of graphene sheets due to their strong π - π interactions and form a reinforced N-doped graphene hydrogel. It was also clearly found that these $\text{SiO}_2\text{-NH}_2$ had very imminent effects on the surface area, porosity and the quality of carbon (having better electroactivity). Here, the functionalised silica particles were first obtained via a modified Stobers method. Tetraethylorthosilicate and (3-aminopropyl) triethoxysilane was added in to a well sonicated 0.01 g/mL of silica solution (in ethanol). This mixture was then stirred for 24 h under an inert nitrogen atmosphere at 50 °C and the resulting $\text{SiO}_2\text{-NH}_2$ particles were separated via centrifugation at 15000 rpm for 20 min and washed repeatedly with ethanol. Hummers method was used for the preparation of graphene oxide. The $\text{SiO}_2\text{-NH}_2$ in different concentrations were used (1.5 mg mL^{-1} , 3 mg mL^{-1} , 9 mg mL^{-1} , 15 mg mL^{-1}) and added to 3 mg mL^{-1} of graphene oxide solution. The mixture was sonicated to form a uniform dispersion and then subjected to a hydrothermal reaction in a Teflon-lined autoclave at 180 °C for 12 h. the obtained hydrogel was washed several times and then freeze dried to form an aerogel. The aerogel was pyrolyzed in a double temperature zone tube-furnace for 15 min and then the temperature was raised to 900 °C slowly at a rate of 5 °C /min and maintained for 1 h, followed by cooling.

The resulting carbonised N-doped graphene aerogel was then etched with hydrofluoric acid to remove out the silica particles and then washed with water, also creating uniformly distributed pores in the product in the process.

Of all the synthesis methods discussed above, we choose the hydrothermal reactions for the graphene hybrid hydrogel synthesis, the most simple and reproducible method for our studies. It is cost effective and efficient and can be done with the help of very few chemicals.

2.4 Biomass-derived carbon hybrids – A cheap substitute for graphene

Biomass energy is believed to be a major solution to our energy crisis, which is looming in to the near future. The increasing population and the industrialisation that has flowed into all nooks and corners of our planet, is causing an alarming depletion of our non-conventional sources of energy like petroleum, fossil fuels etc. The high demand for energy is also a major concern that needs to be addressed from more sustainable and non-polluting sources of energy like biomass, solar energy, wind energy etc. Interestingly, biomass is an abundant source of energy, primarily coming from the solar energy that reaches our planet earth in abundance.⁶⁶ Use of biomass as a starting material to produce more superior materials for various applications has always been a hot topic in the research world. We discuss a few examples here, where biomass materials incorporated with functional materials like transition metal oxides/nanoparticles etc have been used for energy applications. Wu et al. synthesised spongy

hydrogels from watermelon, made of carbon nano spheres and nanofibers (Figure 2.11).²²

Figure 2.11 a) Photographs of the carbonaceous hydrogel monoliths with different volumes and the corresponding carbonaceous aerogel block, (b, c) SEM images, (d, e) TEM images of the carbonaceous gels, reproduced with permission from ref ²², Copyright 2013, American Chemical Society

The carbonaceous gels were prepared by directly subjecting the soft watermelon pieces to hydrothermal treatment. The size of the monoliths can be adjusted by adjusting the size of the watermelon pieces **Figure 2.11(a)**. The carbohydrates polymerise during the hydrothermal reaction to form carbon nano spheres and nanofibers **Figure 2.11(b, c, d, e)** and the fibrous watermelon tissues form the solid carbonaceous block structure with many interconnected networks made of these nano spheres and nanofibers. This aerogel, derived from a chemical intensive process and incorporated with Fe_3O_4 nanoparticles, gave a specific capacitance of 333.1 Fg^{-1} in 6M KOH.²² Wang *et al.* synthesized porous graphitic

carbon nanosheets from cornstalk using $[\text{Fe}(\text{CN}_6)]^{4-}$ as graphitic catalyst precursor ⁶⁷, giving a specific capacitance of 213 Fg^{-1} at 1 Ag^{-1} while a specific capacitance of 286 Fg^{-1} was obtained from graphene like material from coconut shells, where FeCl_3 was used as a graphitic catalyst precursor. ⁶⁸ An activated charcoal electrode based on coconut shells was produced by a highly chemical intensive and a multi-step process by Jain *et al.* giving 356.2 Fg^{-1} as the specific capacitance ⁶⁹.

Figure 2.12) Schematic synthesis of $\text{Ni/NiO/NiCo}_2\text{O}_4/\text{N-CNT}$ as electrocatalysts, reproduced with permission from ref ³⁸, Copyright 2016, Royal Society of Chemistry.

Ma et al. used an ‘egg box’ structure of the alginate polymer as the central theme to design the seaweed biomass-derived carbon hydrogel composed of $\text{Ni/NiO/NiCo}_2\text{O}_4$ nanoparticles with carbon nanotubes (CNT) intertwined in the entire matrix.³⁸ This egg box structure of the polymer makes it possible for the

Ni^{2+} and Co^{2+} ions to form hydrogels with the CNT and thus ensure the uniform and homogeneous immobilisation of these particles in the hydrogel framework (**Figure 2.12**). In a typical synthesis, a mixture of Alginate seaweed/CNT is injected in to a 5 wt % solution containing Ni^{2+} and Co^{2+} ions and stirred to form cross-linked carbonaceous hydrogels. These hydrogels were later dehydrated by a freeze-drying procedure and then carbonised in a tube furnace to obtain aerogels for their final metal air battery application. Cotton was used as a carbon source by Cheng et al. to make a carbon fibre aerogel of extremely high surface area (maximum $-2436 \text{ m}^2 \text{ g}^{-1}$) through a carbonisation and chemical activation process using KOH (**Figure 2.13**).⁹

Figure 2.13 a) SEM image of CF (b) digital photo of aCF-6 before and after manual compression (c-e) SEM images of aCF-6 f) with different magnifications and electrical conductivity of CF and aCF measured by a standard four-probe method, reproduced with permission from ref ⁹ Copyright 2016, American Chemical Society.

A similar carbonisation technique described in the previous examples has been used here as well, wherein the cellulose gets converted in to the highly conducting fibrous aerogel and it can retain the mechanical flexibility and porous structure of the starting material, cotton. The cotton fibre is first carbonised to get carbon fibre (CF), which is then soaked in a 2 M KOH and various CF/KOH mass ratios are prepared. KOH reacts with carbon at high temperatures and leaves behind vacancies on the fibres, increasing the porosity. A negative supercapacitor electrode prepared from this material gave a capacitance of 283 Fg^{-1} at 1 Ag^{-1} with a cyclic stability of 97% even after 20000 cycles.

In our study, we have used a light-weight and abundantly available coconut tree leaf sheath (CLS) as the carbon source and a cheap substitute for graphene. Coconut tree or *Cocos nucifera* is cultivated in abundance in most tropical and subtropical countries across the world. Belonging to the family Arecaceae, these trees and its nuts and fibers have innumerable uses in the domestic, industrial and commercial sectors.⁷⁰ We have used the innermost and middle fibers, which are the thinnest and lightest among these parts.⁷¹ **Table 2.1** describes and compares the properties of various coconut tree fibers to natural fibers. An important thing to be noted here is the cellulose/lignin ratio. The natural fibers like banana, pineapple etc. have very high cellulose content compared to the lignin, which are more suitable for human consumption than for use as biomass. Also, a higher lignin ratio reduces the rotting possibilities by a large extent, making the coconut fibers more suitable for large scale storage and use for making biomass-derived products. Of all the coconut tree fibers, we have chosen the innermost and middle

leaf sheath fibers due to a favorable cellulose/lignin content, it's very low density, ease of pre-treatment, ease for transport to promote large scale storage and sheath-derived powder production.

To the best of our knowledge, it is the first time that CLS has been used as a starting material to produce carbon-based material for energy storage applications and hence very few papers related to these are available. Unlike coconut shells which require a lot of pre-treatment before use and fruit/vegetable-based biomass which have limitations on storage and large-scale applications, our material, CLS is readily available, as they mature and fall on their own, readily available for collection in coconut farms, which are available in abundance in Asia.^{68, 72-74} These can be stored for a very long time without any damage or degradation unlike high-cellulose carrying natural fruits fibers, are very light for mass transport and are rich in carbon, making it ideal for pyrolysis treatments. Coconut tree fibres like the leaf sheath have been extensively experimented for strength-enforcements in cementitious materials, for dye absorbing agents, high-value products on pyrolysis etc.^{70, 75-77}

Table 2.1 Comparison of properties of fibres from various parts of the coconut palm with other natural fibres , reproduced with permission from ref⁷¹, Copyright 1982 Springer

Fibres	Width or diameter (μm)	Density ($\times 10^{-3} \text{ kg m}^{-3}$)	Volume resistivity at 100 V ($\Omega \text{ cm}$)	Microfibrillar angle ($^\circ$)	% cellulose/lignin content	Tensile properties		
						Modulus [*] (GN m^{-2})	σ^* (MN m^{-2})	% Elongation ^{*†}
Rachis	350–400	610	$1.34 \times 10^5 - 3.06 \times 10^5$	33 ± 5	42.75/26.40	2.306(0.79)	74.26(23.15)	13.49(4.2)
Rachilla	200–400	650	$2.87 \times 10^5 - 1.36 \times 10^6$	37 ± 2	42.0/16.24	2.339(0.35)	61.357(18.42)	8.09(3.48)
Spathes	1.50–400	590	$5.15 \times 10^5 - 3.05 \times 10^6$	26 ± 3	42.0/23.46	3.141	75.66	6.0
Leaf sheath (inside top)	300–600	630	$5.38 \times 10^5 - 4.37 \times 10^6$	30 ± 5	41.90/23.36	2.447(0.49)	88.63(22.1)	14.22(2.84)
Leaf sheath (thick fibres)	1100–1600	1190	$3.75 \times 10^5 - 5.77 \times 10^7$	30 ± 3	41.90/25.85	4.543(1.36)	115.236(34.94)	3.97(1.04)
Leaf sheath (middle fibres)	300–1000	750	$8.37 \times 10^6 - 11.5 \times 10^7$	31 ± 4	41.90/29.05	3.585(1.6)	91.965(37.03)	6.227(2.55)
Bark of the petiole	250–550	690	$5.52 \times 10^5 - 2.63 \times 10^6$	21 ± 1	46.03/12.09	15.094(9.06)	185.52(62.44)	2.06(0.55)
Root	100–650	1150	—	38 ± 1	39.1/29.48	6.2	157	3
Coir	100–450	1150	$9 \times 10^5 - 14 \times 10^5$	$30-49$	43/45	4–6	131–175	15–40
Banana	80–250	1350	$6.5-7.0 \times 10^5$	11	65/5	7.7–20.0	529–754	1.0–3.5
Sisal	50–200	1450	$0.47-0.52 \times 10^5$	10–22	67/12	9.4–15.8	568–640	3–7
Pineapple	20–80	1440	$0.71-0.84 \times 10^5$	14–8	81/12	34.5–82.5	413–1627	0.8–1.6
Jute	—	1450	—	8.1	63	—	533	—

^{*}Figures in brackets are standard deviations.

[†]Gauge length is 0.05 m.

2.5 Transition metal oxides, Conducting polymers for supercapacitors

Transition metal oxides and conducting polymers are the most commonly used pseudocapacitors for supercapacitors. In our work, all the pseudocapacitor materials chosen to make hybrids were selected based on their earth-abundant nature, cost-effectiveness, electrochemical stabilities, and large-theoretical capacities compared to other oxides and polymers like iron oxide, ruthenium oxides, vanadium oxide, polypyrrole etc.

2.5.1 Manganese oxides and Polyaniline for supercapacitors

Manganese dioxides have a lot of superior properties compared to various transitional-metal oxides like those of Fe, Va, Ru, Zn etc present in the market. Manganese dioxide is an inorganic compound with oxidation state 4 or otherwise known as Manganese (IV) oxide.^{78 79} It is depicted by the chemical formula MnO_2 . It exists in the solid form and commonly exists as Pyrolusite, which is also the main ore of the metal Manganese. It occurs as a brownish black powder and crystallises mainly in the rutile phase (β - MnO_2), though there are many other polymorphs too which exist. Recently, hierarchical nanostructures with complex

architecture made by assembling of simple nanoscale building blocks, have become a major attraction in the scientific world and has the potential for a very fertile area for a lot of research in areas of chemistry, materials science and nanotechnology.^{36, 80-82} This arises from the fact that there is a lot of scope in their structural-property relation and also their superior nanoscale properties which vary from their bulk properties.⁸³ Their wide applications range from energy storage applications, catalysis, environmental studies, in sensors and even drug delivery.^{79, 84, 85} The common nanostructures in to which these oxides can be synthesised are nanoparticles, nanorods, nanowires, nanotubes, nanosheets, nanoflowers etc and these structures are believed to inherit a lot of superior properties which arise from the systematic building of the basic nanoscale building blocks.⁸⁶⁻⁸⁸

Manganese oxides are currently inviting a lot of research due to their environment friendly nature, low cost, non-toxic properties and wide range of applications in areas like supercapacitors, bio-sensing, cancer therapy, catalysis, adsorption techniques for removal of dyes etc.^{89 90, 91} They can also be synthesised easily with a wide array of techniques which can be chosen according to the end structure and type of applications they are put to use for.⁹²

Conducting polymers like Polyaniline (PANI), Polypyrrole (PPy), polythiophene and it's derivatives have been researched extensively for use in supercapacitors, however, several factors like their low solubility due to the lack of hydrophilic groups required them to be mixed with non-conductive binders.⁹³⁻⁹⁶ But this

caused the reduction in conductivity due to these non-conducting polymer additives and made them redundant for various applications requiring a homogeneous conductive network. Also, even though conducting polymers have high electrical conductivity and lower cost than other inorganic materials like metal oxides, they undergo significant damage due to swelling and shrinking during the charge-discharge cycles of a supercapacitor, giving them low cycle lives.^{96, 97} This makes it necessary to optimise the ratio of conducting polymer in the hybrid material. Of the various predominantly used conducting polymers, PANI has the highest theoretical capacitance of 750 Fg^{-1} , compared to PPy (620 Fg^{-1}) and polythiophene (485 Fg^{-1}).^{96, 98}

In the first phase of my thesis, Manganese oxides with graphene/PANI hydrogels were synthesised. The idea for this ternary composite was coined from the literature, due to the major following findings. Among the previously synthesized Graphene/PANI/MnO₂ composites for supercapacitor applications, a high specific capacitance of 755 F g^{-1} at 0.5 A g^{-1} has been reported for a composite made by depositing PANI and MnO₂ on Graphene films.⁹⁹ But these had the disadvantage of being used with binders in electrodes. Also, a two composite PANI/Graphene aerogel prepared by a hydrothermal reaction reported gave a specific capacitance of 520.3 F g^{-1} at 0.25 A g^{-1} ⁵⁹ whereas Graphene/MnO₂ 3D-network prepared by a reverse-micro emulsion method reported a specific capacitance of 709.8 A g^{-1} at 0.2 A g^{-1} .⁴³ Moreover, conducting polymers have been researched extensively for making hydrogels. However, several factors like their low solubility due to the lack of hydrophilic groups required them to be

mixed with non-conductive polymers to form a three-dimensional monolith.⁹³⁻⁹⁵ But this caused a reduction in conductivity due to these non-conducting polymer additives and made them redundant for various applications requiring a homogeneous conductive network and in some cases, addition of high concentrations of cross-linking units like multivalent ions Fe^{3+} etc made them impossible for use in physiological systems. Thus, a good mix of graphene and conducting polymers, along with a transition-metal oxide to provide abundant pseudocapacitance, was considered to have a good scope for binder free supercapacitor electrodes via a simple hydrothermal route. This resulted into the first part of my thesis, a well-structured 3-Dimensional ternary composite hybrid hydrogel comprising of graphene, manganese oxide (MnO_x) and polyaniline, nullifying the drawbacks of the individual components while synergizing their positive attributes.¹

2.5.2 Nickel-cobalt oxides/nanoparticles for supercapacitors

Recently, Nickel cobaltite oxides and nickel cobalt metal nanoparticles have attracted the scientific community for catering to high power supercapacitor applications.^{100, 101} Compared to other prominently used oxides like RuO_2 , the cost and performance matrix for the Ni, Co-based materials are far superior. The high theoretical capacitance of the nickel and cobalt oxides rising from their combined battery type redox reactions, their natural abundance and benign nature make them very prospective candidates for supercapacitor and lithium ion battery applications.¹⁰² Though a wide array of studies have been done to produce nickel

cobalt mixed oxides, very few have had optimization studies to tailor them for the best supercapacitor performances.^{45, 46, 103-111} Zheng et al. prepared hollow NiCo_2O_4 nanocubes using a coordinating etching and precipitation route and these gave a specific capacitance of 795.6 Fg^{-1} at a current density of 1 Ag^{-1} .¹¹² At the same time, a solution method was used by Zhang et al. to grow NiCo_2O_4 nanorods and nanosheets on carbon nanotube fibers, which gave a specific capacitance of 1026 Fg^{-1} and 1002 Fg^{-1} respectively.¹¹³ These Ni and Co oxides/hydroxides have been an intriguing topic of research and have been proved to be very promising candidates for use in supercapacitors, by virtue of their high pseudocapacitance^{45, 46, 104}. However, Ni and Co nanoparticles have been hardly studied for use in supercapacitors. One major reason is their ready oxidation in air and also under high pH conditions and their tendency for agglomeration owing to the large surface energies of metallic nanoparticles.¹¹⁴ The Ni and Co nanoparticles, when introduced in the aqueous alkaline electrolyte, undergo surface oxidation to give Ni and Co oxides and their subsequent redox reactions lead to the pseudocapacitance.^{115, 116} Recent studies by Wu *et. al* with nickel nanoparticles in a graphitic framework grown from a Ni organic framework yielded a specific capacitance of 886 Fg^{-1} at 1 Ag^{-1} in a 1 M KOH electrolyte.¹¹⁶ Liu *et. al* also made a negative electrode using nickel doped activated carbon microspheres, giving a specific capacitance of 361 Fg^{-1} in 6 M KOH in a potential window of 0 to -1 V.¹¹⁷ Biomass-derived N doped carbon was recently loaded with nickel-cobalt double layered hydroxides which yielded a specific capacitance of 1949.5 Fg^{-1} at 1 Ag^{-1} in a 6 M KOH solution.¹⁰³

Though the study on nickel cobalt mixed oxides and nickel cobalt nanoparticles have been researched, they lack in several aspects; there is hardly any detailed study on the optimization of the ratio of individual components thereby limiting the full exploitation of their structural, chemical and electrochemical performances.

The proof from literature stating that Ni, Co oxides and nanoparticles give high-performances inspired me to synthesize a highly-optimized Ni, Co mixed oxide in a graphene framework and then led me to try and draw similar performances of this high-performing electrode material using a biomass-derived carbon framework in place of graphene.

2.6 Zeolite imidazole framework-derived transition metal nanoparticles/oxides for supercapacitors

ZIFs or Zeolite Imidazole Frameworks are a class of metal organic frameworks which are an upcoming class of materials and have properties which are valuable for a systematic approach for the synthesis of their corresponding carbon incorporated metal oxides, metal nanoparticles etc.¹¹⁸⁻¹²¹ They have an enduring porosity leading to very large surface areas and well defined structures; their thermal and chemical stability are unparalleled compared to a lot of materials which are used in gas storage, sensing and catalysis.^{119, 122} The ability to fine tune the final structure and size of the ZIFs keep them at an enviable position of being used in a wide range of applications. In spite of their prominently wide use in areas like catalysis and gas storage^{118, 123, 124}, their use and study as a fine-tuning

template for producing carbon-metal oxides or carbon-metal nanoparticle composites for supercapacitor applications are still limited. Depending on the metal cations linked to the 2-methyl imidazolate anions via a sodalite zeolite-type topology, there are numerous ZIFs available.¹²⁵ The most commonly used ZIFs used for energy applications are ZIF-8 and ZIF-67, where Zn is the metal cation in ZIF-8 while cobalt cation forms the metallic link in ZIF-67.^{47, 126}

Ni, Co-based oxides and nanoparticles provide a high specific capacity and deriving them from ZIF-67 and a nickel precursor would promote a highly optimized, reproducible and systematic way of synthesizing nickel cobalt oxides and nanoparticles. Thus, ZIF-67 was used as an important starting material for all our Ni, Co-based material synthesis. Herein, a simple method has been adopted to derive $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ starting from ZIF-67 (ZIF-67 (Co(mim)₂) – a linked network of 2-methyl imidazolate anions and cobalt cations with a sodalite zeolite-type topology)^{125, 127} and the Ni:Co precursor amounts have been varied to understand their effects on interdependent parameters like morphology, phase and performance. This understanding will help in tapering the parameters with ease and effectiveness to maximize the electrochemical performance of the final product. The optimized $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ was integrated with a 3D graphene hydrogel. The same ZIF-67 was also used to produce Ni, Co nanoparticles in a biomass-derived carbon framework and the performances of the two systems are compared.

From the understanding and inference drawn from the literature review done during the selection of my PhD dissertation topic, I came to the idea that supercapacitors are promising energy storage systems. I came upon a few useful materials like graphene, manganese oxides, Ni/Co mixed-oxides/nanoparticles and conducting polymers. I also saw the importance of using sustainable materials, in this era of mounting environmental concerns. I decided to first build a hybrid system using graphene as a base. The aim was to show that a sustainable and cheap substitute from biomass could match the performance of an efficient electrode material derived from graphene. A very detailed optimization study was adopted with multiple materials and I have come up with a coconut-leaf sheath-derived carbon framework embedded with high-performing Ni, Co-nanoparticle-based functional moieties. This thesis thus throws light on the multitudes of possibilities and optimization techniques in green chemistry for energy storage materials.

Chapter 3 Novel Graphene/PANI/ MnO_x 3D-hydrogels for high performance binder-free supercapacitor electrodes

A novel three-dimensional ternary composite graphene-based hydrogel was prepared using a simple hydrothermal reaction. The ternary composite comprised of Polyaniline (PANI) and MnO_x as the pseudocapacitive materials in a well-knit graphene-based hydrogel prepared in an acidic environment using Hydrochloric acid (HCl). The synergistic effects created by the pseudocapacitance of PANI, MnO_x and the electrochemical double layer capacitance of Graphene highly improved the overall electrochemical performance of these hydrogels. These had the superior advantage of being used directly for binder free electrodes. The Graphene/Polyaniline/MnO_x hydrogel prepared in an acidic environment (HCl), PGM-HCl, offered an extremely high specific capacitance of 955 Fg⁻¹ at a current density of 1 Ag⁻¹ and a capacitance retention of 89% after 1000 cycles at 20 Ag⁻¹. The electrode prepared from this material gave an extremely high specific energy density of 61.2 Wh Kg⁻¹ even at a high-power density of 4.5 kW Kg⁻¹. A hydrogel PGM was also prepared using a purely hydrothermal reaction, for comparison. This gave a lower specific capacitance of 426 Fg⁻¹ at 1 Ag⁻¹ with a lower specific energy density of 25.31 Wh Kg⁻¹ at the same power density of 4.5 kW Kg⁻¹. This chapter also elaborates on how optimized hydrothermal reaction conditions succeed in producing hydrogels with superior electrochemical performance.

3.1 Materials and methods

3.1.1 Chemicals

All chemicals that were used were of analytical grade and were used directly without any further processing.

3.1.2 G.O synthesis and G.O: PANI Synthesis

G.O was prepared using a modified Hummers method.^{31 128} PANI was prepared by in-situ polymerization in G.O solution⁵⁹ using aniline as monomer and Ammonium-persulfate (APS) as an oxidizing agent by keeping it for a complete polymerization for 24 hrs at 2-3 °C; the G.O and PANI synthesis conditions were adopted according to the literature.^{10, 27, 129} The amount of aniline and APS added could be monitored accordingly to produce the desired ratios of PANI: G.O dispersion and the final concentration of the dispersion was maintained between 2-2.5 mg/mL. Two different PANI:GO ratios were used to understand the dependence of electrochemical performance on the relative EDLC: Pseudocapacitor ratio.

3.1.3 MnO₂ Synthesis

MnO₂ nanotubes were synthesized using a hydrothermal reaction using KMnO₄ as a precursor in acidic medium. 0.329 g of KMnO₄ was made up to 37.5 mL DI (De-Ionised) water.⁸⁰ 0.75 mL of conc. HCl (36%) was added to this and the mixture was stirred for 15 min. Then it was transferred to a Teflon lined autoclave

and kept at 150 °C for 15 hrs, conditions chosen as per literature.⁸⁰ It was then allowed to cool to room temperature. MnO₂ powder was obtained which was washed several times by DI water using centrifugation. This was then dried in an oven overnight at 60 °C and a brownish black powder was obtained.

3.1.4 PGM and PGM-HCl Ternary composite hydrogel synthesis

The G.O: PANI dispersion is mixed with desired amounts of the pre-synthesized MnO₂ powder and a small amount of HCl, (37 weight %) to obtain PGM-HCl hydrogel. Here, a mixture of 1 mL HCl and 1 mL DI water was added to 6 mL G.O:PANI (1:1) and dispersed well using sonication, followed by the addition of nearly 4 mg of MnO₂. This mixture was then sonicated again to obtain a well dispersed mixture and then is kept for the hydrothermal reaction in stainless steel autoclaves with Teflon lining at 180 °C for 12 hrs to obtain a PGM-HCl hydrogel. The temperature and time of the hydrothermal reaction was chosen according to the best optimum conditions for obtaining graphene hydrogels, as reported previously^{21, 23 41} A similar procedure was employed in the synthesis of PGM hydrogel for comparison purposes, with the difference being the absence of any HCl addition. An optimized sample hydrogel called the PGM-HCl-2 was also synthesized in a similar fashion by altering the ratio of the constituents while using the same reaction conditions (prepared with a mixture of 1 mL HCl and 1 mL DI water, 6 mL of G.O: PANI (2:1) and 5 mg of MnO₂). Multiple ratios were tried to understand the dependence of electrochemical performance on the ratio

of G.O and PANI, which would also throw light on the importance of an optimised ratio for hybrid materials consisting of EDLCs and pseudocapacitors.

3.1.5 Electrochemical Measurements

The electrochemical measurements of the Graphene/PANI/MnO_x were made in a three-electrode configuration using an ACHI660D electrochemical workstation. The ternary composite was used as the working electrode by directly sandwiching it between nickel foam substrates without the use of any binders. A Pt electrode acted as the counter electrode, Ag/AgCl as the reference electrode, and a neutral 1M Na₂SO₄ aqueous solution as the electrolyte. The potential window was maintained as 0-0.9 V. We used the Na₂SO₄ electrolyte and this voltage window, as MnO₂ is best known to work in a neutral electrolyte within this potential range.^{40, 130} Cyclic voltammetry was performed within a scan rate ranging from 10 mVs⁻¹ to 200 mVs⁻¹ and galvanostatic charge-discharge testing was done within a current density of 1 A g⁻¹ to 10 A g⁻¹. The specific capacitance was calculated from the galvanostatic charge-discharge curves using the **Equation 3.1:**

$$Cs = \frac{I \times \Delta t}{\Delta V \times m} \quad (3.1)$$

where Cs is the Specific Capacitance in F g⁻¹, I is discharge current, Δt is discharge time, ΔV is the potential window, and m is the mass of the active material.¹³¹ The Ragone plot for the electrode, which plots the E or the specific

Energy density (Wh Kg⁻¹) (**Equation 3.2**) and P, the Power density (kW Kg⁻¹) (**Equation 3.3**), was plotted from the galvanostatic charge-discharge data for different current densities using the following equations : ¹³²

$$E = \frac{1 \times Cs \times \Delta V^2}{2} \quad (3.2)$$

$$P = \frac{E}{\Delta t} \quad (3.3)$$

3.1.6 Materials Characterisation

Field emission scanning electron microscopy (JEOL-JSM-6700F microscope) and Transmission electron microscopy (TEM JEOL, 2010 at 300 kV) were used for detailed morphological studies. The chemical compositions were also studied using the Energy Dispersive X-Ray Spectroscopy (EDX), which was attached to the SEM. Fourier transform infrared spectra (FTIR) were observed in the range of 400-4000 cm⁻¹ on an FTIR Digilab FTS3100. X-ray diffraction study was done using an XRD Bruker D2 phaser diffractometer with Cu K α radiation. KRATOS AXIS DLD spectrometer was used to perform X-Ray photoelectron spectroscopy (XPS) for understanding the surface chemical composition. The hydrogels were freeze dried and powdered for use in XPS, XRD, FTIR and SEM measurements. Methylene blue adsorption method was adopted to obtain the surface areas of the

wet hydrogels. This method is widely employed to calculate the surface area of graphitic materials and accounts for an area of 2.54 m² for 1 mg of methylene blue adsorbed.¹³³ A known mass of hydrogel was put in to a standard solution of methylene blue and kept under constant stirring for nearly 24 hours to enable maximum adsorption. This mixture was later centrifuged, and the supernatant methylene blue concentration was tested by the UV- Vis spectroscopy at 665 nm. The difference of the supernatant concentration and the initial standard concentration yields the amount of methylene blue adsorbed and thus the surface area can be calculated. Also, the active material weights of the hydrogels were used to find the specific surface area of the hydrogel.

3.2 Results and discussions

3.2.1 XRD Studies

XRD studies were used to understand the crystal structure of the hydrogel samples and have clearly helped to understand and validate the presence of the three individual constituents in the ternary composite hydrogels. **Figure 3.1** shows the XRD spectra of the PGM-HCl and PGM hydrogels. The presence of the carbonaceous Graphene and polyaniline can be clearly seen by a broad peak at nearly $2\theta = 25^\circ$ in both PGM and PGM-HCl.⁵⁹ The peaks of PANI emeraldine salt (PANI Emr. Salt) are more prominent at 15.5° with crystal plane (0 1 1) and 20.2° (0 2 0) for PGM-HCl than PGM and hence the effect of chlorine can be clearly inferred.¹³⁴ The graphitic carbon has a peak around $2\theta = 44^\circ$, which is also a peak of manganese (IV) oxide and thus gives a cumulative larger broad

peak.¹³⁵ The manganese (IV) oxide added during the hydrothermal reaction of PGM and PGM-HCl hydrogels underwent a phase change which was clearly seen from the XRD spectra and validated by indexing them to the standard peaks. The initial pre-synthesized MnO_2 clearly shows the presence of α - MnO_2 as seen from the XRD data shown in the **Figure A2a** in the appendix and matched well with the standard peaks (JCPDS 44-0141).^{86, 88 136 85} The presence of this tetragonal phased α - MnO_2 is also reiterated in the XRD spectra of these hydrogels by the peaks at 44° , 50° and 56 - 57° which represent the crystal planes (3 0 1), (4 1 1), and (5 2 1), respectively.¹³⁶ The additional peaks other than these peaks of α - MnO_2 in the PGM and PGM-HCl hydrogels appearing after the hydrothermal reactions (which are between $2\theta=30^\circ$ to 40°) can be attributed to the Mn_3O_4 nanoparticles.^{137, 138} The peaks in both PGM and PGM-HCl, around 31° , 32 to 33° , 35 to 36.2° , and 38.2° correspond to the crystal planes of (2,0,0), (1 0 3), (2 1 1), and (0 0 4) of Mn_3O_4 respectively (JCPDS 24-0734).^{139, 140 141}

Figure 3.1 XRD pattern of PGM, PGM-HCl

The change to MnO_x from MnO_2 can also be explained by some reducing reactions happening in the presence of carbonaceous materials like graphene and PANI at a high temperature. This leads to Manganese in these multiple oxidation states, which are clear from the XRD results.¹⁴² The amorphous carbonaceous organic compounds of graphene and polyaniline combined with the amorphous nature of MnO_x , the peaks of the mixed oxides in the sample get diminished.¹⁴³

3.2.2 Morphological studies

Figure 3.2 a) SEM image of freeze dried PGM- HCl hydrogel, b) TEM image of PGM hydrogel c) TEM image of PGM hydrogel, d) & e) TEM image of PGM-HCl hydrogel at higher magnification

Morphology has always been a very pivotal factor in deciding the final properties of materials. Morphological studies for the complex ternary composite hydrogels were performed using SEM and TEM studies. It was observed that the initial MnO_2 powder synthesized for adding into the reaction mixture had a nanotube morphology as seen from our appendix (**Figure A1a, A1b**).

The PGM hydrogels prepared for comparison via a pure hydrothermal route in the absence of HCl, retained the initial manganese oxide morphology as can be seen from the TEM image in **Figure 3.2b**, where the nanotubes of MnO_x are embedded in the matrix of PGM hydrogel. The morphological studies using SEM in **Figure 3.2a** reveal the porous structure of PGM-HCl hydrogels. It basically shows a framework of layered and well stacked graphene sheets to form a three-dimensional porous matrix. The picture also shows a thin layer of PANI and MnO_x distributed uniformly on the graphene layers.

The TEM images are further in par with the SEM results. The TEM image in **Figure 3.2c** shows a dark region on the graphene layer, which clearly shows us that the graphene layers have PANI and MnO_x embedded on its layers. This is indicative that we have successfully incorporated the pseudocapacitive materials in the PGM-HCl hydrogel matrix. However, the MnO_x formed after the hydrothermal reaction was distributed as nanoparticles of diameter size 3-6 nm in the PGM- HCl hydrogels (**Figure 3.2d, 3.2e**) after the effect of a hydrothermal reaction in the presence of HCl. Here, HCl also acts as an etching agent and helps in altering the morphology, leading to the breaking down of nanotubes in to

smaller particles.⁸⁰ It has also been earlier reported that graphene hydrogels are more easily self-assembled during hydrothermal reactions at pH ranges of 1-5 and 10-14.¹⁴⁴

An acidic environment thus is favourable for the formation of a stable hydrogel and helps in fostering the uniform self-assembly of the composite hydrogels. Because we directly use the hydrogels for the electrochemical measurements, a methylene blue dye adsorption method was adopted to calculate the surface area of the hydrogels.²⁰ The PGM-HCl gave a specific surface area of 740.83 m² and thus clearly shows the superior surface area available due to the porous structure of the hydrogels.

3.2.3 FTIR spectral analysis

The FTIR spectrum in **Figure 3.3a, 3.3b** further reiterates the presence of the three composites. From both the graphs, the major peaks are obtained in the typical range of the three composites in the hydrogel. The HCl interactions have slightly blue shifted the benzenoid and quinoid peaks in the PGM-HCl composites to slightly higher wavenumbers possibly due to the additional Cl atom interactions with the carbon rings. This is due to the formation of PANI-Emeraldine salt in the presence of HCl. It can also be seen that both the composites show peaks of C-H vibrations and C=N vibrations at around 1039 cm⁻¹ and 1077 cm⁻¹, respectively.⁵⁹ The peaks around 820 cm⁻¹ represent the aromatic C-H out of the plane bending vibrational mode.⁹⁹

The peaks around $1635\text{--}1645\text{ cm}^{-1}$ represent the vibrations of the C=O bond.¹³⁴ The quinoid ring peaks are found to be more intense and sharper compared to the benzenoid ring peaks and this supports the fact that there is a very strong interaction between the conjugated PANI structure and the π bonded graphene structure in the hydrogel.¹³⁴ The characteristic polyaniline peaks are found to be weaker in the lower wave number range, which can be rationalized because of the restricted modes of vibrations due to the highly wrapped up polyaniline particles between the reduced graphene oxide layers. characteristic of Mn-O vibrations.¹⁴⁵ Characteristic Mn-O stretching vibrations transmittance peaks can be seen around 520 cm^{-1} and 696 cm^{-1} .^{99, 146 81}. The stretching of the C=C bond of the quinoid and benzenoid ring in PANI can be seen by the peaks around $1580\text{--}1590\text{ cm}^{-1}$ and $1485\text{--}1490\text{ cm}^{-1}$ (a broad peak) respectively in the PGM hydrogel.^{52, 99}

Figure 3.3 a) FTIR spectra of PGM, PGM-HCl at lower wavenumber, b) FTIR spectra of PGM, PGM-HCl at higher wavenumber.

3.2.4 XPS Spectral Analysis

Figure 3.4 XPS spectra of various elements in PGM-HCl, a) C 1s, b) O 1s, c) N 1s, d) Mn 2p

XPS studies performed reiterate the presence of all the constituents in the PGM-HCl hydrogel as can be seen in **Figure 3.4**. In the C 1s spectra shown in **Figure 3.4a**, the peaks at the binding energies of 284.5 eV, 285.48 eV, and 288.17 eV are typical representations of the C=C in the aromatic rings, C-OH and C=O bonds respectively.^{59 146 20}

The strong C=C and weak C=O further show that the graphene oxide has been reduced well during the hydrothermal reaction. In **Figure 3.4b**, the peaks at 531.3 eV, 532.6 eV, and 533.74 eV in the O 1s spectra clearly represent the Mn-O-Mn,

Mn-O-H, and C-O, H-O-H bonds respectively and is a typical spectrum for compounds with Mn^{2+} and Mn^{3+} .^{48 36 147} The **Figure 3.4d** shows the spin-orbital doublet prevalent in transition metals, with the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ at the binding energies of 654.5 eV and 642.5 eV respectively.^{137 142} The nitrogen in the PANI was verified by the Nitrogen 1s spectra as shown in **Figure 3.4c**. The peaks at 399.1 eV, 400.2 eV, and 401.31 eV represent the quinoid imine (-N=), benzenoid amine (-NH), and the cationic -N⁺- respectively, in PANI-Emeraldine salt present in the PGM-HCl.^{48 59} The presence of Mn, C, O are also verified by the EDX Spectroscopy and the spectra clearly indicates the presence of Carbon , Oxygen and Manganese in the PGM and PGM-HCl hydrogels as shown in **Figure A2b and A2c** respectively. The presence of Platinum is due to the sputtering done for the SEM study. The chlorine content in the PGM- HCl are the Cl atoms attached to the PANI to form the PANI Emeraldine salt.

3.2.5 Electrochemical Performance Analysis

The electrochemical performance of the PGM and PGM-HCl hydrogels were tested by pressing their small slices (nearly 2mm thickness) in between two nickel foam pieces of size nearly 1 cm x 1 cm to form binder free electrodes. The specific capacitance was calculated from the galvanostatic charge discharge measurements as shown in the **Figure 3.5a**. The charge discharge curves almost maintain the ideal triangular shape for PGM hydrogel with slightly broader arms, while it deviates a little more for the PGM-HCl hydrogel. This can be rationalized due to the presence of smaller MnO_x nanoparticles, which contribute more of

their pseudocapacitance in the PGM-HCl hydrogel matrix compared to the larger MnO_x nanotubes in PGM hydrogel. This also makes the PGM-HCl hydrogel to have superior electrochemical performance with a large specific capacitance of around 955 F g^{-1} at 1 A g^{-1} , while the PGM hydrogel accounted a specific capacitance of only 426 F g^{-1} at the same current density of 1 A g^{-1} . This is an unprecedented value to the best of our knowledge for a ternary composite graphene- based hydrogel involving polyaniline and manganese oxide. The charge –discharge curves at various current densities have been shown for the PGM, PGM-HCl and PGM-HCl-2 hydrogels in **Figure A3** in the supporting information. Practical applications often demand long life cycles and hence a good cyclic stability is an important property of any material used for electrochemical energy storage. The PGM-HCl also showed an extremely high cyclic stability with nearly 89% capacitance retention at 20 A g^{-1} even after 1000 cycles and even retains 69.1 % at the end of 5000 cycles. (**Figure 3.5c**). The specific energy density of the electrodes was also calculated for different power densities for different current densities and using the galvanostatic charge discharge data. This is seen from the Ragone plot in **Figure 3.5d**. PGM-HCl showed an extremely high energy density of $107.44 \text{ kW Kg}^{-1}$ at a power density of 450 W Kg^{-1} . The energy density remained high with a value of 61.2 kW Kg^{-1} even at a high the power density of 4500 W Kg^{-1} . This shows the potential use of these hydrogels in high energy applications. The energy densities of PGM hydrogel are plotted for comparison which clearly shows that they show a much lower energy density of 25.31 kW Kg^{-1} at 4500 W Kg^{-1} . But, even this value is

high compared to a lot of other composites of Graphene/PANI/MnO_x that have been reported so far. This is further validated by comparing our values of specific capacitance and cyclic stability to the values reported for other composites involving the same constituent materials. As shown in **Table A1** of the supporting information, our material clearly stands apart in view of its electrochemical performance in comparison to many other composite materials of Graphene/PANI/MnO_x reported so far.

The charge storage capacity of MnO_x is believed to be mostly surface adsorption of the electrolyte ions and proton integration.⁹¹ This is reversible to a great extent only on the outermost layer of the MnO₂ which is in close contact with the aqueous electrolyte.³⁶ This mechanism further applies for amorphous manganese oxides and our XRD peaks show the amorphous nature of MnO₂ in the hydrogels, as explained before. This further validates the improvement in the specific capacitance due to the better involvement of the very small MnO_x nanoparticles formed in the presence of HCl during the hydrothermal reaction for PGM-HCl. This is because of the larger area available for close contact and reaction in the Na₂SO₄ electrolyte since the charge storing capacity of MnO_x is heavily dependent on the outermost area exposed to the Na₂SO₄ electrolyte.³⁶

Optimization plays a very important role in designing composite materials. By altering the amount of the individual constituents in the composite, we can control the final electrochemical performance of the composite. This has been

proved by our sample which we synthesized as PGM-HCl-2 (prepared from 6 mL of 2:1 ratio of GO: PANI, 5 mg of MnO_2 , and 1 mL HCl in 1 mL D.I water).

Figure 3.5 further elaborates and compares the characteristic electrochemical properties of PGM-HCl-2 with respect to PGM and PGM-HCl. By adjusting the ratio of the pseudocapacitive materials and graphene, the hydrogel PGM-HCl-2 gave a specific capacitance of 676.6 F g^{-1} at 1 A g^{-1} and an extremely high capacitance retention of 98% after 1000 cycles and 82.1 % after 5000 cycles at 20 A g^{-1} . This undermines the importance of adjusting the composite ratios in altering the final performance of the sample. Here, an extremely high cyclic stability was obtained without compromising a lot on the specific capacitance. Furthermore, these materials were also tested for their electrochemical performance using Cyclic Voltammetry (CV). From **Figure 3.6**, the hydrogels showed nearly rectangular plots, though the combined ternary effect of the three constituents may have resulted in a slight deviation from the rectangular plots at higher scan rates. The sharp peaks in the CV curves at the higher voltage end, as shown in **Figure 3.6**, are the typical faradic peaks which are the characteristics of the pseudocapacitive materials PANI and MnO_x .^{54 146}

The current density is particularly high in the case of PGM-HCl and accounts for excellent capacitive behaviour and low contact resistance. In this case, the peaks of PANI are a little weaker owing to the pseudocapacitive materials' close interaction in the graphene-based hydrogel matrix where it has been heavily wrapped around during the G.O: PANI in situ polymerisation.

Figure 3.5 Electrochemical tests conducted in a 3-electrode system using 1 M Na_2SO_4 electrolyte with Pt electrode as counter electrode and Ag/AgCl as the reference electrode a) Charge discharge measurements of PGM, PGM-HCl, PGM-HCl-2 as working electrodes at 1 A g^{-1} , b) Specific Capacitance vs Current density data of PGM, PGM-HCl, PGM-HCl-2 as working electrodes, c) Capacity Retention Vs Number of cycles data for PGM, PGM-HCl and PGM-HCl-2 as working electrodes at 20 A g^{-1} , d) Ragone plot for PGM, PGM-HCl and PGM-HCl-2 as working electrodes

Overall, the PGM-HCl hydrogel clearly shows a better performance in comparison to the PGM hydrogel by comparing Charge- Discharge measurements in view of its specific capacitance (**Figure 3.5a, 3.5b**), capacitive

behaviour in the CV graphs (**Figure 3.6a, 3.6b**) and the high energy density values in the Ragone plot (**Figure 3.5d**). The CV curves of PGM-HCl and PGM at 10 mVs^{-1} are compared in **Figure 3.6c**. It can be clearly seen that the PGM-HCl describes a larger area, which is indicative of a larger specific capacitance, which is also supportive from the charge discharge measurements. At higher scan rates of 100 mVs^{-1} and 200 mVs^{-1} , the PGM-HCl hydrogel preserves better faradic peak incorporated-rectangular shapes of their CV curves compared to the PGM CV plots. This reiterates the superior electrochemical performance of PGM-HCl hydrogels.

The outstanding performance of these PGM-HCl hydrogels can be summed up to be because of some crucial interplaying factors. Importantly, this conducting hydrogel (both Graphene and Polyaniline are conducting) which has an extremely porous structure (**Figure 3.1a and 3.1b**), enables the free diffusion of electrolyte in and out of the system and can be used in electrode preparation without any binders. Binders offer hinder with the electrochemical performance due to its complex preparation and result in the lowered capacitance of the material.²⁰

Pseudocapacitive materials, especially conducting polymers like PANI, often have poor cyclic stability due to their degradation after many charge discharge cycles.⁴⁸ Here, the three- dimensional graphene matrix also acts as a protective binding matrix for the polyaniline and manganese-oxides, thus covering up for their stability issues.

Figure 3.6 Electrochemical tests conducted in a 3-electrode system using 1 M Na₂SO₄ electrolyte with Pt electrode as counter electrode and Ag/AgCl as the reference electrode a) CV curves of PGM-HCl as working electrode at various scan rates, b) CV curves of PGM as working electrode at various scan rates, c) CV curves of PGM and PGM-HCl compared at 10 mVs⁻¹

MnO_x formed after the hydrothermal reaction improves the charge storage capacity of the hydrogels compared to normal manganese oxides. This is because of the existence of both donor and acceptor sites in MnO_x, which can improve and speed up the faradic reactions significantly. HCl helps in altering the morphology of manganese oxide, this being an in-situ change, it enables the good

embedding of the MnO_x particles in the hydrogel matrix. These close interactions help in making a judicious use of the pseudocapacitive constituents by very rapid electron transfer through the conductive, porous Graphene/PANI layers of the hydrogel during the faradic reactions.

3.3 Conclusions

We have reported the synthesis of a novel three-dimensional ternary composite graphene-based hydrogel comprising of Polyaniline and manganese oxide, using a hydrothermal reaction in an acidic environment using HCl. Their superior advantage of being used in binder free electrodes for supercapacitors and their unprecedented electrochemical performance make them promising candidates for use in practical applications. The ease of optimized preparation and the low cost of raw materials used in the synthesis are the other positive attributes which can be tapped for use in large scale high energy applications. The pseudocapacitance of Polyaniline and Manganese oxides was synergized with the electrochemical double layer capacitance of the three-dimensional conducting graphene matrix. The morphology and the ratio of individual components in the composite could be varied to give high capacitance and high cyclic stability, thus covering up the low cyclic stability issues of the pseudocapacitive materials. The hydrogels prepared in two different methods were compared based on their electrochemical performance. The PGM-HCl prepared in an acidic environment using a hydrothermal reaction showed a very high specific capacitance of 955 F g^{-1} at a current density of 1 A g^{-1} . The electrode prepared using PGM-HCl

displayed a very high energy density of 61.2 Wh Kg^{-1} even at a high-power density of 4500 W Kg^{-1} . The PGM-HCl hydrogels also displayed very high cyclic stability with an 89% capacitance retention even after 1000 cycles. Thus, this study also paves way to the idea that environment, reaction conditions, and optimization of the number of constituents can greatly help in improving the overall performance of composite hydrogels and thus contributes highly to the scientific community for opening new vistas in the field of improvement of graphene-based hydrogels for high energy applications.

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Chapter 4 MOF-derived hollow cage $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ and their synergy with graphene for outstanding supercapacitors

In this chapter, highly optimized Nickel, Cobalt-mixed oxide has been derived from Zeolite imidazole frameworks (ZIF). While the pure cobalt oxide gives only 178.7 Fg^{-1} as the specific capacitance at a current density of 1 Ag^{-1} , the optimized Ni:Co 1:1 have given an extremely high and unprecedented specific capacitance of 1931 Fg^{-1} at a current density of 1 Ag^{-1} , with a capacitance retention of 69.5 % after 5000 cycles in a three electrode test. This optimized Ni:Co 1:1 mixed oxide is further used to make a composite of Nickel cobalt mixed oxide/graphene 3D-hydrogel for enhancing the electrochemical performance by virtue of a continuous and porous graphene conductive network. The electrode made from GNi:Co 1:1 successfully achieves an even higher specific capacitance of 2870.8 Fg^{-1} at 1 Ag^{-1} and also shows a significant improvement in the cyclic stability with 81 % capacitance retention after 5000 cycles. The mechanism of capacitance in the composite was also conferred in detailed and the study confirmed the predominance of a non-diffusion controlled capacitive type behavior. An asymmetric supercapacitor is also assembled using a pure graphene 3D-hydrogel as the negative electrode and the GNi:Co 1:1 as the positive electrode. With a potential window of 1.5 V and binder free electrodes, the capacitor gives a high specific energy density of 50.2 Wh Kg^{-1} at a high-power density of 750 W Kg^{-1} . The performance of the GNi:Co 1:1 is found to be better than the Graphene/ polyaniline/ MnO_x hydrogel.

4.1 Materials and methods

4.1.1 Chemicals

All chemicals were of analytical grade and were used as obtained without further treatments.

4.1.2 Synthesis of Nickel cobalt mixed oxide $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ from ZIF

In a typical reaction, Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2-methyl-imidazole was dissolved in (20 mL) of methanol in a molar ratio of 1:4. The solutions were thoroughly mixed and then left undisturbed for a time span of 24 hours at room temperature to obtain ZIF-67 crystals, as per literature.^{109, 125} These were washed repeatedly by centrifuging them in methanol followed by their drying in vacuum oven at 60 °C overnight. Nickel nitrate precursor ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was then mixed with the obtained ZIF-67 crystals and (20 mL) ethanol in the ratios 0.5:1, 1:1 and 1.5:1 and then kept in closed condition in a hot oven at 90 °C for 1 hour. Three ratios were used to understand and study the interdependence of electrochemical performance, phase, crystallinity etc. on Ni:Co ratios. They were denoted as Ni:Co 0.5:1, Ni:Co 1:1 and Ni:Co 1.5:1 respectively. The samples were then washed again repeatedly with ethanol, dried in vacuum oven at 60 °C and finally annealed in a muffle furnace at a heating rate of 4 °C per minute at 350 °C for an hour, followed by natural cooling.¹⁰⁹

4.1.3 Synthesis of pure Co_3O_4 crystals from ZIF-67

The as ZIF-67 crystals were directly annealed under the same conditions as that of the mixed oxide mentioned above, but without any addition of the nickel precursor.

4.1.4 Synthesis of Nickel cobalt mixed oxide/graphene 3D-hydrogel (GNi:Co 1:1)

G.O solution was prepared via the modified hummer's method.^{31, 32, 81} For the composite, a facile method saw the mixing of 6 mg of Ni :Co 1:1 with 2.5 mL of graphene oxide solution (5 mg/mL) and 6 mL of De-ionised (D.I) water. This mixture was stirred and then sonicated to ensure complete mixing and homogenization. The solution was then subjected to a hydrothermal reaction at 180 °C in a 25 mL autoclave for 12 hours. A three dimensional Nickel cobalt mixed oxide/graphene 3D-hydrogel (GNi:Co 1:1) was obtained and was washed with D.I water several times. A pure graphene hydrogel (Pure G) using the same reaction conditions (in the absence of any mixed oxide) was also synthesized for use as a negative electrode for assembling an asymmetric supercapacitor.

Figure 4.1 Schematic representation of the GNi:Co 1:1 synthesis technique

4.1.5 Electrochemical measurements

The electrochemical measurements were carried out in a CHI660D potentiostat using a 2 M KOH electrolyte, a platinum electrode as the counter electrode and an Ag/AgCl double junction electrode as the reference electrode. The mixed oxide electrodes Ni:Co 0.5:1, Ni:Co 1:1 and Ni:Co 1.5:1 and the pure Co_3O_4 electrodes were prepared by mixing their powders with polyvinylidene fluoride (PVDF) and acetylene black in the ratio 8:1:1 and using N-methyl-2-pyrrolidone (NMP) as a wetting and binding agent. This slurry was then spread on to a 1 cm^2 nickel foam piece and dried overnight before use at $60\text{ }^\circ\text{C}$. As for the GNi:Co 1:1 hydrogel samples, the sample was directly used without any binders by sandwiching a piece of the hydrogel between two nickel foam pieces of 1 cm^2 area and then pressing them at a pressure of 2-4 MPa to remove the excess water. Cyclic voltammetry (CV) was used to study the reversibility of the electrode for different scan rates from 1 to 20 mVs^{-1} . Chrono-potentiometric or galvanostatic

charge discharge measurements (GCD) were made to obtain the specific capacitance of the materials.

From the charge discharge measurements, specific capacitance (Fg^{-1}) is calculated from the following formulas

Half cell

$$C_s = \frac{I \times \Delta t}{\Delta V \times m} \quad (4.1)$$

For a three electrode cell or half cell: from **Equation 4.1**¹³¹, C_s is the specific capacitance of the electrode, I is the discharge current, ΔV is the voltage window applied, Δt is the discharging time and m is the mass of the active material.

Full cell

For a two electrode test for the asymmetric supercapacitor (ASC) assembly with a pure graphene negative electrode and the GNi:Co 1:1 positive electrode, the specific capacitance in Fg^{-1} of the entire cell is calculated from **Equation 4.2**,¹³¹

$$C_s = \frac{I \times \Delta t}{\Delta V \times M} \quad (4.2)$$

, where only the M differs from **Equation 4.1** with $M = m^- + m^+$ where, m^+ and m^- are the active masses of the material in the positive and negative electrode respectively.

The energy density (Wh Kg⁻¹) and power density (kW Kg⁻¹) of the ASC are also calculated by using the following **Equation 4.3** and **Equation 4.4** respectively¹⁴⁸, which are used for the Ragone plot

$$E = \frac{1 \times Cs \times \Delta V^2}{2} \quad (4.3)$$

$$P = \frac{E}{\Delta t} \quad (4.4)$$

4.1.6 Materials characterisation

The morphological studies were carried out using a Field emission scanning electron microscope (FESEM, JEOL-JSM-6700F) and a Transmission electron microscope (TEM JEOL, 300 kV). The crystalline phase of the materials was studied from X-ray diffraction measurements using an XRD-Bruker D2 phaser diffractometer with Cu K α radiation. XPS or X-ray photoelectron spectroscopy was used to study the bonding and for the surface chemical composition using a KRATOS AXIS DLD spectrometer. Raman spectra was obtained using a Renishaw inVia Raman Microscope using Ar⁺ ion laser (wavelength 514 nm). The composite hydrogels were freeze-dried before they were used for characterisations.

4.2 Results and discussions

4.2.1 XRD studies

The XRD studies have given us an insight in to the crystalline phase, while also giving ample information about the formation scheme and the probable features each mixed oxide shows by its signature phase characteristics. The ZIF-67 crystals have been formed successfully and this has been confirmed by matching it to the available literature data and can be verified from **Figure A4**.¹²⁶ As clearly portrayed in **Figure 4.2a**, a clear comparison can be drawn between the crystallinity of the mixed oxides by matching the peaks to the standard peaks of spinel Co_3O_4 (JCPDS 42-1467), NiO (JCPDS 65-6920) and NiCo_2O_4 (JCPDF 02-1074).

The mixed oxide Ni:Co 0.5:1 has peaks closer to pure spinel Co_3O_4 due to a small amount of Nickel, while the mixed oxide Ni:Co 1:1 and Ni:Co 1.5:1 have more broader peaks representing a dip in the size of the crystalline structures owing to higher nickel substitution in the lattice and formation of nickel oxide NiO in Ni:Co 1.5:1. The overall formula can be represented as $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ where a nickel atom knocks out the cobalt in the spinel structure. The NiO formation is higher in Ni:Co 1.5:1 as clearly seen from the stronger peaks at $2\theta=45^\circ, 37.5^\circ$ and 64.5° , which are lesser in intensity in Ni:Co 1:1. The peaks in Ni:Co 1:1 can be accounted to mainly a spinel NiCo_2O_4 mixed valence oxide where Nickel lodges itself in the octahedral sites whereas cobalt occupies both tetrahedral and octahedral sites.^{102, 149} The electronic conductivity of NiCo_2O_4 is known to be way more than the pure oxides of cobalt and nickel (two orders of magnitude

higher)^{102, 150} and makes it more favourable towards significant electrochemical performance compared to the Co₃O₄-rich Ni:Co 0.5:1 and NiO-rich Ni:Co 1.5:1.

Figure 4.2b represents the XRD spectra of GNi:Co 1:1 and clearly indicates the incorporation of the mixed oxide in to the amorphous network of carbonaceous graphene which has a characteristic strong broad peak centered at $2\theta=24.5^\circ$. The weaker peaks (due to the continuous amorphous carbon network in which they are embedded) of the mixed oxide Ni:Co 1:1 could be seen in the GNi:Co 1:1.

4.2.2 Raman spectroscopy

Figure 4.2 XRD spectra of a) the mixed oxides and pure Co_3O_4 , b) GNi:Co 1:1 and Ni:Co 1:1, Raman spectra of c) Ni:Co 1:1, Ni:Co 0.5:1, Ni:Co 1.5:1, d) Raman spectra of GNi:Co 1:1 and Ni:Co 1:1

It helped in re-confirming the formation mechanism and constitution of the mixed oxides from their signature characteristic modes of vibration as can be seen from **Figure 4.2 c and d**. An ideal spinel structure has five major Raman active phonon modes A_{1g} , E_g and three F_{2g} out of which four modes have been identified clearly for our mixed metal oxides.^{149, 151}

For the Ni:Co 0.5:1, the modes of vibrations occur closer to that of a spinel Co_3O_4 structure ($A_{1g}=691\text{ cm}^{-1}$, $E_g=488\text{ cm}^{-1}$ and F_{2g} at 522 cm^{-1} and 194 cm^{-1})¹⁵², which matches with our inference from XRD studies. As for Ni:Co 1:1, the peaks are sharp and well matched to a crystalline, spinel structure of NiCo_2O_4 ($A_{1g} = 671\text{ cm}^{-1}$, $E_g=477\text{ cm}^{-1}$ and $F_{2g} = 523\text{ cm}^{-1}$ and 187 cm^{-1})^{107, 149} which again matches with our XRD findings. These peaks are slightly more broader for Ni:Co 1.5:1 which can be related to the loss of long range order and crystallinity by the additional NiO which gets deposited.¹⁴⁹ As for the GNi:Co 1:1 and pure graphene hydrogel Pure G in **Figure 4.2d** and **Figure A5** respectively, the characteristic peaks of reduced graphene which constitutes the hydrogel is clearly inferred from the D and G bands which occur around 1341 cm^{-1} and 1581 cm^{-1} respectively.¹⁵³ While the D band is indicative of the vibrational mode of the k-point phonons of A_{1g} symmetry, the G band represents the E_{2g} mode of vibration representative of the Csp_2 atoms abundant in the material.¹⁵¹ Apart from these,

the graphene composite also shows peaks of the Ni:Co 1:1 at the lower wave numbers, though diminished by the amorphous network of graphene around it.

4.2.3 Morphological characterisations

Morphological characterisations have helped us in inferring the mechanism of formation of the mixed oxides and the role of structure and size in being crucial for electrochemical performance. This has also led to the qualitative analysis of finding the rationale of increased electrochemical performance due to some significant parameters arising by virtue of structure for a particular ratio of nickel and cobalt precursors. **Figure A6a** shows the SEM image of the well shaped ZIF-67 crystals, which are shaped like rhombo dodecahedrons and **Figure A6b** shows the SEM image of pure Co_3O_4 synthesised by direct annealing of the ZIF crystals. These are an aggregated clump of spherical-like particles which lack a well defined structure unlike all the mixed oxides which speak of almost a spherical structure carved out of the rhombo dodecahedron, as can be seen from **Figure 4.3 a,b,c,d**. Unlike the smooth surface of the ZIF-67 crystals in **Figure A6a**, an evident pattern can be seen in the thickness of surface protrusions that are present on the outer layer of the spherical shaped mixed oxides. When nickel gets added in to the system, there is a replacement of Cobalt from the spinel structure of Co_3O_4 and can be seen collectively to form $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ as mentioned in the XRD studies. Also, as the Nickel content goes higher like in Ni:Co 1.5:1, apart from the Nickel substitution in the Co_3O_4 structure, there is also the formation of Nickel oxide or NiO that can be seen on the outer layer.

Figure 4.3 SEM images of a) Ni:Co 0.5:1 with inset showing a magnified image of a smooth surfaced shell, b) Ni:Co 1:1 at lower magnification, c) Ni:Co 1:1 with inset showing a magnified image of the hollow spherical cage with a thin shell of dendrites-like surface protrusions, d) Ni:Co 1.5:1 with inset showing the magnified image of the structure with a thickened covering of surface protrusions, e) the porous magnified structure of freeze-dried GNi:Co 1:1, f) the magnified image of a wave like graphene layer in GNi:Co 1:1 embedded with the Ni:Co 1:1 nanoparticles.

Figure 4.3a, 4.3(b,c) and 4.3d shows the SEM image of Ni:Co 0.5:1, Ni:Co 1:1, Ni:Co 1.5:1 with an average size of 250-300 nm. While Ni:Co 0.5:1 has a clearer

surface, Ni:Co 1:1 has a thin layer of surface protrusions arising from the Nickel substitution and slight NiO formation. The Ni:Co 1:1 also has a hollow structure which is clear from the inset picture in **Figure 4.3c**. The Ni:Co 1.5:1 carries a dense covering of dendrites-like projections formed from an additional layer of Nickel oxide by virtue of a larger amount of nickel in the system. This pattern also has a pivotal role to play in the electrochemical performance which will be discussed in the later sections. The structure of GNi:Co 1:1 3D hydrogel has also been examined and pronounces a highly macroporous network of interlinked graphene layers (**Figure 4.3e**) on which nanosized, thin NiO-outerlayered Ni:Co 1:1 particles have been embedded (**Figure 4.3f and Figure 4.4b**) after the hydrothermal treatment. The TEM image of Ni:Co 1:1 further inspects in detail the structure as in **Figure 4.4a**. The dark outer lining and the hazy inner parts with slight darkened portions further give conclusive evidence of hollow cage-like structure with a corrugated inner and outer surface. Though the morphology of the individual Ni:Co 1:1 has not been retained in the composite, the nanosized particles with an optimum nickel cobalt ratio have contributed to the significant synergy of the composite's performance.

Figure 4.4 TEM images of a) Ni:Co 1:1 and b) GNi:Co 1:1

4.2.4 The XPS studies

The XPS studies reveal about the surface chemical composition and oxidation states of the Nickel, Cobalt, Carbon and oxygen in the GNi:Co 1:1 hydrogel as shown in **Figure 4.5**. The Ni 2p scan and the Co 2p scan in **Figure 4.5 b and c** have the typical twin spin orbital doublets which are typical of the mixed oxide.¹⁵⁴ The deconvoluted peaks of Ni 2p scan and the Co 2p show the presence of Ni²⁺ (854.9 eV for 2p_{3/2}, 876 eV for Ni 2p_{1/2}), Ni³⁺ (856.6 eV for 2p_{3/2}, 873.3 eV for Ni 2p_{1/2}), Co²⁺ (780.78 eV for 2p_{3/2}, 795.7 eV for 2p_{1/2}) and Co³⁺ (778.95 eV for 2p_{3/2}, 793.96 eV for 2p_{1/2}), which are preferred for active electrochemical reactions.^{150, 154}

Figure 4.5 XPS spectra of GNi:Co 1:1 with a) survey scan, b) Ni 2p scan, c) Co 2p scan, d) C 1s, e) O 1s scan

Their respective shake up satellite peaks (Sat.) can also be seen at binding energies higher than the main peaks of $2p^{3/2}$ and $2p^{1/2}$.¹⁵⁴ The presence of Ni^{3+}/Ni^{2+} and Co^{3+}/Co^{2+} also match with the existing literature of $NiCo_2O_4$ and also contribute to active redox centres for a high electrochemical performance.¹⁵⁰ The carbon present in the graphene hydrogel is confirmed by the C 1s spectra in **Figure 4.5d**. The high reduced state of carbon after the hydrothermal reaction in the hydrogel is confirmed by the presence of a very weak C=O peak and the presence of a strong C=C peak.¹⁴⁸ The O1s spectra in **Figure 4.5e** gives the typical metal oxygen bond by O(i) at around 530.4 eV and the O(ii) at 533 eV can collectively denote the oxygen in the surface adsorbed water, hydroxyl bonds and some defects states of oxygen respectively.^{112, 150}

4.2.5 Electrochemical characterisation

The electrochemical characterisation has provided insight in to the electrochemical performances of the synthesised mixed oxides and the graphene/Nickel cobalt mixed oxide hydrogels. The rationale of the pattern in the performances can be well explained by the formation schemes, their crystalline phases, morphology and size, which have been discussed in detail in the previous sections.

Figure 4.6 GCD graphs of a) Ni:Co 0.5:1, b) Ni:Co 1:1, c) Ni:Co 1.5:1, c) GNi:Co 1:1 in 2M KOH electrolyte

The GCD measurements carried out at different current densities from 1 to 10 Ag^{-1} of the pure Co_3O_4 , mixed oxides and the graphene composite have been presented in **Figure A7a** and **Figure 4.6** respectively. The symmetric charge - discharge legs show the reversible nature of the mixed oxide electrodes and the specific capacitance data has also been retrieved from these plots.³⁶ The cyclic voltammetry tests have also been conducted for all the samples at scan rates from 1 to 10 mVs^{-1} as seen in **Figure 4.7a**, **Figure 4.7b**, **Figure A7b** and **Figure A8**.

Figure 4.7 a) CV of Ni:Co 1:1, b) CV of GNi:Co 1:1, c) Specific capacitances of Co₃O₄, Ni:Co 0.5:1, Ni:Co 1:1, Ni:Co 1.5:1 and GNi:Co 1:1 calculated from GCD curves over current density.

They show clear and symmetric anodic and cathodic peaks within a potential window of 0 to 0.7 V vs Ag/AgCl, confirming the reversibility. The specific capacitance is highest for the GNi:Co 1:1 composite hydrogel, which is 2870 Fg⁻¹, followed by Ni:Co 1:1 with the capacitance value of 1931 Fg⁻¹ (**Figure 4.7c**). The ultrahigh value of specific capacitance for the graphene composite can be explained by the conductive porous network of highly reduced graphene surrounding the small nanoparticles of NiCo₂O₄, enabling a speedy network and

movement of electrolyte and ion diffusion through the system. The reversible redox reactions happening can be summed up as in **equation (4.5) and (4.6)** ¹⁰⁸:

The composite also shows a significant betterment in cycle life(**Figure 4.6d**) amounting to a capacitance retention of 81 % even after 5000 long cycles. Meanwhile, the mixed oxides retain their capacitance in the range of a maximum of up to 73.4 % for the Ni:Co 1:1 oxide to a 66 % for the Ni:Co 0.5:1. The highest capacitance amongst all of the mixed oxides is for Ni:Co 1:1 (1931 Fg⁻¹) owing to the optimum thickness and amount of the NiCo₂O₄ in the hollow structure, allowing fast redox reactions compared to the thick shells of Ni:Co 1.5:1(1626.5 Fg⁻¹) with an additional layer of NiO which leads to a lack of efficient diffusion through the thicker layers and a nickel deficient Co₃O₄ rich Ni:Co 0.5:1 (493.3 Fg⁻¹) with lesser redox centres. Thus, Ni:Co 1:1 was our optimised sample , which we have used to make a composite with graphene to get our final three dimensional GNi:Co 1:1 hydrogel and all our major characterisations are centred around the optimised mixed oxide Ni:Co 1:1 and the graphene composite.

The cyclic voltammetric studies of the GNi:Co 1:1 (**Figure 4.6b**) also provided ample information regarding the significant mechanisms contributing to the ultrahigh capacitance of the composite. According to the **Equation 7** ²³,

$$i = Cv^b \quad (7)$$

the capacitance can be qualitatively described as one with a dominance of capacitive behaviour or one with a diffusion controlled intercalation predominance.

Figure 4.8 a) $\log(v)$ vs $\log(i)$ plot to verify the linearity of current on scan rate and for calculating b values, b) obtained b -values vs potential for a cathodic scan, c) plot of $v^{0.5}$ vs $\frac{i(V)}{v^{0.5}}$ for obtaining k_1 and k_2 values at various potentials in the cathodic sweep, d) Percentage split up of capacitance in to surface capacitive effects and diffusion controlled intercalation contributions.

The analysis of voltammetric response which changes over scan rates can be done according to the above equation, where i is the current, v is the scan rate, C and b are adjustable parameters. Determination of b values is completed using a $\log(i)$

vs $\log(v)$ plot, with the slope of the plots at different potentials giving us the b value, as seen in **Figure 4.8a**. The values of b are plotted against their respective potentials from 0.1 V to 0.35 V in **Figure 4.8b**, giving us an insight to the capacitive contributions.

Ideally, values of b close to 1 ($i = Cv$, capacitive effect) indicate capacitance from non-diffusion controlled redox reactions on the surface, whereas b values close to 0.5 ($i = Cv^{0.5}$, battery-type) speak of diffusion-controlled redox intercalation in the material.^{155, 156} Here, for the cathodic scan, closer to the peak potentials of 0.2- 0.3 V, the corresponding b values are closer to 0.5 indicating a battery type behaviour.¹⁵⁵

In contrast, other peak potentials all have values close to 1, indicating that the material is predominantly contributing the capacitance from non-diffusion controlled surface redox reactions. We can again quantify the amount of battery type behaviour and capacitive behaviour at various scan rates by expressing the entire current as a sum of capacitive effect and battery type behaviour, using **Equation 4.8 and 4.9**,^{23, 37, 157}

$$i(V) = k_1 v + k_2 v^{0.5} \quad (4.8)$$

Where i is the current at a particular potential V , v is the scan rate and k_1 and k_2 can be determined from the slope and intercept of the straight line equation

$$\frac{i(V)}{v^{0.5}} = k_1 v^{0.5} + k_2 \quad (4.9)$$

After the values of k_1 and k_2 are obtained from the slope and intercept of $v^{0.5}$ vs $\frac{i(V)}{v^{0.5}}$ for the cathodic scan, the capacitance of GNi:Co 1:1 is plotted at various scan rates in **Figure 4.8d**, each showing a percentage split up of their characteristic mechanism of charge storage.

As can be seen, the capacitive effects contribute to almost 77.2 % of the total capacitance at 1 mV, whereas its percentage goes up by 92.2 % as the scan rate increases to 10 mV. This shows that the diffusion controlled intercalation contributions are greatly diminished on increasing the scan rate.¹⁵⁷ This is only logical, as the electrolyte doesnot get sufficient diffusion time at high scan rates due to decreasing time intervals and thus the overall capacitance also decreases due to the dip in the contribution from the battery type capacitive effect.

4.2.6 Asymmetric supercapacitor (ASC)

The feasibility of using our graphene composite in practical applications was also studied by assembling a simple asymmetric suupercapacitor with the binder free GNi:Co 1:1 as the positive electrode and Pure G as the negative electrode in a two-electrode test in a 2M KOH solution with a potential window of 1.5 V. The Pure G electrode is known to act as a good negative electrode in aqueous alkaline medium and was also tested for both GCD and CV measurements within a potential window of 0 to -1 V in 2M KOH as shown in **Figure 4.9 a and b**.^{23, 158} Our pure graphene hydrogel gave a high specific capacitance of 305 Fg⁻¹ at 1 Ag⁻¹ and showed a good rate capability by retaining a capacitance of 240 Fg⁻¹ even at 10 Ag⁻¹ as seen in **Figure 4.9c**. The pure graphene hydrogel thus proves to be far

more superior as a negative electrode, compared to the conventinal activated carbon . The possibility of using them directly without any binders, their high capacitance and chemical stability and durability, make it ideal for its use as a cathode. To maximise the capacitance, it is imperative that the anode and cathode, with different specific capacitances and active voltage, be charge balanced before they are assembled for an ASC.¹⁵⁸ For the same purpose, the masses of the anode and cathode were adjusted and charges were balanced according to the **Equation 4.10**,²³

$$\frac{m_{+}}{m_{-}} = \frac{C_{-} * \Delta V_{-}}{C_{+} * \Delta V_{+}} \quad (4.10)$$

Calculating using the values of the individual three-electrode tests of our positive and negative electrode, at a current density of 10 Ag⁻¹, the $m_{+} = 0.254 m_{-}$. The ASC was then assembled accordingly and tested for GCD and CV as seen in **Figure 4.10a** and **Figure 4.10b**. Both the charge discharge curves and the CV curves are symmetric which highlight their superior reversibility and significance for use in future practical applications.^{26, 79, 159} The specific capacitances were calculated from the GCD curves and gave a high value of 160.6 Fg⁻¹ at 1 Ag⁻¹. The specific capacitance is plotted with changing current density in **Figure 4.10c** and the cycle life has a promising 81.1 % capacitance retention after 5000 cycles as in **Figure 4.10d**. The Ragone plots in **Figure 4.11** detail about the energy density and power density obtained from GCD and a comparison is drawn between our material and some of the existing materials. They show us of the significant improvements in our energy and power density. Even a simple

assembly of our ASC GNi:Co 1:1// Pure G gave a specific energy density of 50.2 Wh Kg⁻¹ at a power density of 750 W Kg⁻¹ and the value of energy density remains to be 23.3 Wh Kg⁻¹ even at higher power density of 3.75 kW Kg⁻¹.

Figure 4.9 a) GCD plot, b) CV graph , c) Specific capacitance vs current density; all of pure graphene hydrogel (negative electrode) all in 2M KOH electrolyte

Figure 4.10 a) GCD graph of the ASC GNi:Co 1:1// Pure G, b) CV plot of ASC GNi:Co 1:1// Pure G, c) Specific Capacitance of ASC GNi:Co 1:1// Pure G vs current density, d) cyclic stability of ASC GNi:Co 1:1// Pure G, all in 2M KOH electrolyte

Figure 4.11 Ragone Plot of a) Our work ASC GNi:Co 1:1// Pure G, b) $\text{Co}_3\text{O}_4//3\text{D P.C}$ ¹²⁶, c) $\text{Ni}(\text{OH})_2//\text{A.C}$ ⁴⁴, d) $\text{NiO//Reduced graphene oxide}$ ¹⁵⁸, e)

Aluminium substituted Nickel hydroxide($\text{Ni}(\text{OH})_2$) // A.C ¹⁶⁰, f) Graphene-Multi-walled carbon nanotubes- MnO_2 composite // Graphene-Multi-walled carbon nanotubes ¹⁶¹

This also opens new doors for assembling more complex asymmetric capacitor systems with our material as anode and with more detailed analysis on choosing suitable cathodes to improve the overall performance. A few comparisons with existing literature bring us to superior ASCs like Aluminium substituted Nickel hydroxide($\text{Ni}(\text{OH})_2$) // Activated carbon (AC) ¹⁶⁰ with a specific energy density of 27 Wh Kg^{-1} at a power density of 1.1 kW Kg^{-1} while a NiO flake//Reduced graphene ¹⁵⁸ ASC gave a 22 Wh Kg^{-1} at a 5 kW Kg^{-1} . A complex ASC, assembled with a cobalt oxide or Co_3O_4 anode and a three dimensional porous carbon (3D P.C) cathode ¹²⁶, both coming from our same starting material ZIF-67, was also included in our comparison and gave an energy density of 15 Wh Kg^{-1} at a high power density of 8 kW Kg^{-1} . These comparisons speak of the improvements that we have brought about in the electrochemical performance and thus help in identifying our material to be one of impending significance for use in real life applications.

4.3 Conclusion

We have successfully synthesised Ni:Co mixed oxides from a metal organic framework ZIF-67 and a Nickel precursor. We have, in detail, studied the formation mechanism of MOF derived Ni:Co oxide by analysing their size, morphology, crystalline phase and chemical compositions. We also studied their

electrochemical performances in detail and chose Ni:Co 1:1 as the optimised mixed metal oxide by virtue of its outstanding specific capacitance of 1931 Fg^{-1} in comparison to the 1626 Fg^{-1} of Ni:Co 1.5:1 and 493.7 Fg^{-1} of Ni:Co 0.5:1. The optimised sample Ni:Co 1:1 was further used to make a composite with graphene in a hydrothermal reaction to get GNi:Co 1:1 as a binder free 3D-hydrogel. These hydrogels, by the synergistic effects arising from the conductive and porous graphene network around the nanosized mixed oxide, gave an ultrahigh specific capacitance of 2870.8 Fg^{-1} and a superior cycle life with 88.1 % capacitance retention after 5000 cycles, thus holding great promise as an anode material for supercapacitors in real life applications. The mechanism of capacitance in the composite was also conferred in detail and the study confirmed the predominance of a non-diffusion controlled capacitive type behaviour. The GNi:Co 1:1 was assembled into a simple ASC by pairing it with a pure graphene hydrogel for cathode and thereby giving an energy density of 50.2 Wh Kg^{-1} at a power density of 750 W Kg^{-1} . Thus, with the fine details of optimisation to the assembling of our graphene composite to an asymmetric supercapacitor, we have conclusive evidence to show the superior characteristics of our GNi:Co 1:1 developed after a detailed optimisation strategy, in terms of real life applications and durability. Thus, it is clear that the results are far superior than the ternary composite presented. The NiCo-mixed oxide/graphene hydrogel composite synthesised in chapter 4 is better compared to the Graphene/MnO_x/PANI hydrogel in chapter 3 in terms of its capacity, cycle life and rate capabilities.

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Chapter 5 Coconut leaf sheath-derived, N-doped carbon network for high performance supercapacitors

To find a cheap substitute for graphene, a highly graphitized nitrogen-doped carbon network is synthesized from biomass, obtained from coconut tree leaf sheath and successfully demonstrates its' high energy storage properties for use in supercapacitors. A simple thermal physical activation in carbon dioxide atmosphere also enabled to improve the electrochemical activity of the carbon. A detailed study is carried out to understand the dependence of electrochemical performance on parameters like the concentration of urea used for doping, the activation temperature, time of activation and an optimized sample is obtained to give a very high electrochemical performance. Our best sample, obtained by using a 0.5 M urea solution for doping, annealed at 700 °C under nitrogen (N₂) atmosphere and activated at an activation temperature of 800 °C under carbon dioxide (CO₂) atmosphere, named as (0.5M- 700N-800C), gave a very high specific capacitance of 360.9 Fg⁻¹ in 2 M KOH in the potential window of 0 to -1.1 V. This performance as a negative electrode exceeds the specific capacitance of graphene hydrogels (305 Fg⁻¹) that we prepared and is more than that of commercially available activated carbon 218.18 Fg⁻¹. Thus, it brings to light the possibility of using our material as an efficient, cheap substitute for negative electrode materials like graphene, carbon nanotubes etc. This process is facile, extremely cheap and environmental friendly, which utilizes urea, a non-hazardous nitrogen dopant.

5.1 Materials and methods

5.1.1 Chemicals and raw materials:

Urea was the only chemical used and was of analytical grade obtained from Sigma Aldrich, and was used as obtained without further treatments. The CLS was collected from coconut tree farms from one of the southern states of India, Kerala, named for its' abundance of coconut tree farms. Activated carbon was also purchased from Sigma Aldrich, which was tested for a comparison study.

5.1.2 Synthesis of graphitized nitrogen doped carbon 0.5M-700N-800C:

The CLS collected was from two different plots (Calicut and Palakkad districts) in the state of Kerala in India to ensure a good sampling; washed thoroughly in water to remove any sand/impurities and sundried for 2-3 days and stored for use. Unlike a lot of previous works where a lot of chemical pre-treatment was used, we tried a completely chemical-free approach to understand how the sheath would perform electrochemically. The inside top fibers were then cut out in to smaller rectangular pieces, dipped in 0.5 M urea solution overnight, with magnetic stirring, to enable uniform wettability of the CLS pieces. These urea-dipped CLS pieces were then annealed in a tube furnace at 700 °C under a nitrogen (N₂) atmosphere for 3 hours and activated at an activation temperature of 800 °C for 1 hour under carbon dioxide (CO₂) atmosphere, both at a heating rate of 5 °C/min, named as (0.5M- 700N-800C). The obtained material is then easily crushed using mortar pestle to get a very fine powder. The pictorial

representation of transformation of coconut leaf sheath to carbon powder is shown in **Figure 5.1** for reference. To ensure a good sampling set, we made these products from the fibers obtained from various trees from both the sampling locations and compared their composition and electrochemical performances. The composition remained almost identical after the pyrolysis, as evident from identical XRD peaks, which would be explained in the results sections later, assuring a good consistency of our testing material, even without any pre-treatments. More studies with pre-treatment of the sheath and its effects on electrochemical performance would be the next step in this line of work.

Figure 5.1 a) A 0.5M urea-dipped CLS piece, b) A 0.5M urea-dipped CLS piece after N_2 annealing and CO_2 activation, c) Powdered 0.5M-700N-800C, b- Different parts of the CLS fibre

5.1.3 Synthesis of graphitized nitrogen doped carbon, other ratios:

The CLS pieces were annealed and activated under different conditions by changing parameters like activation temperature, concentration of urea used for doping and time, to understand the relation between these parameters on the

electrochemical performance. This also ensured that we did not report one single ratio under one single set of temperatures as the best one; especially since this material is being used for the first time. **Table 5.1** represents various products that were prepared for our study.

Table 5.1 Various products produced by varying a few parameters like urea concentration for doping, activation temperature and time

Name of the product	Concentration of Urea solution in which CLS pieces were dipped	Annealing temperature, under N ₂ atmosphere for 3hours (°C)	Activation temperature (°C)	Time of activation (hour)
0.5M-700N	0.5 M	700	...	...
0.5M-700N-500C	0.5 M	700	500	3
0.5M-700N-800C	0.5 M	700	800	1
1M-700N-800C	1 M	700	800	1
2M-700N-800C	2 M	700	800	1
P-700N-800C	...	700	800	1

5.1.4 Synthesis of Pure graphene hydrogel (Pure G)

Graphene oxide solution was prepared by a modified hummers method.^{20, 31} 4 mL of graphene oxide solution (5 mg mL⁻¹) was mixed with de-ionized (D.I) water to make the final concentration 2 mg mL⁻¹ and was mixed well until it formed a uniform homogeneous solution. This solution was transferred to an autoclave for a hydrothermal reaction for 12 hours at 180 °C. A three-

dimensional hydrogel was obtained, which was washed several times with D.I water before it was used.

5.1.5 Electrochemical measurements

A CHI660D potentiostat was used to conduct all electrochemical measurements. We used a three-electrode system to study our samples with 2 M KOH electrolyte, a platinum electrode as the counter electrode and an Ag/AgCl double junction electrode as the reference electrode. All the potentials measured and mentioned hereafter are measured against this Ag/AgCl reference electrode. Working electrode preparation was done by mixing all the nitrogen doped CLS powders with polyvinylidene fluoride (PVDF) and acetylene black in the ratio 0.8: 0.1: 0.1 and made in to a slurry using a liquid binder N-methyl-2-pyrrolidone (NMP). This mixture was then deposited on a 1 square centimeter nickel foam, which was later dried overnight in an oven set at 60 °C. The pure graphene gel however was used without a binder or additives and was sandwiched between two 1 cm² Nickel foam pieces and pressed at a pressure of 2-3 MPa to remove the excess water. The active weight of the sample loaded on a 1 cm² nickel foam of 0.723 mm thickness is around 1.2-1.5 mg. This is the overall total weight of the sample, the conductive agents and binders. This overall weight has been used to calculate the specific capacities of the samples.

Galvanostatic Charge discharge (GCD) measurements were performed at different current densities from 1 to 10 Ag⁻¹ while cyclic voltammetry (CV) was done for different scan rates from 1 to 100 mVs⁻¹.

Specific capacitance (Fg^{-1}) is calculated from the following formulas from the GCD measurements,

$$C_{sp} = \frac{I \times \Delta t}{\Delta V \times m} \quad (5.1)$$

For a three electrode cell or half cell: from **Equation 5.1**¹³¹, C_{sp} is the specific capacitance of the electrode, I is the discharge current, Δt is the discharging time, ΔV is the voltage window, and m is the mass of the active material.

5.1.6 Materials characterisations

A Field emission scanning electron microscope (FESEM, JEOL-JSM-6700F) and HRTEM-JEOL were used for morphological studies. The crystallinity of the materials was studied from X-ray diffraction measurements using an XRD-Bruker D2 phaser diffractometer with Cu $K\alpha$ radiation. XPS or X-ray photoelectron spectroscopy was used to study the bonding and for the surface chemical composition using a KRATOS AXIS DLD spectrometer. Renishaw inVia Raman Microscope using an Ar⁺ ion laser ($\lambda = 514 \text{ nm}$) was used for raman spectroscopic studies. The pure graphene hydrogel was freeze-dried before it were used for characterisations. The nitrogen adsorption and desorption isotherms were measured and analysed to find the specific surface area and porosity by a Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) method using N₂ gas in a Tristar II 3020 instrument.

5.2 Results and discussions

5.2.1 XRD measurements

Figure 5.2a gives the XRD patterns of all samples. All the ratios have a few amorphous peaks and crystalline peaks, all of which have been indexed to either the carbon present in the samples or compounds of silica present in the sample.

A broad peak around $2\theta = 20$ to 30° represents the amorphous carbon formed predominantly by activated carbon present in all the samples, corresponding to the (0 0 2) plane.^{74, 162, 163} This peak arises from the random orientation and stacking of aromatic sheets present. A very sharp peak at $2\theta = 27^\circ$ indexed to (0 0 2) plane and a lesser intense peak at around $2\theta = 42-43^\circ$ indexed to (1 0 1) plane, correspond to the crystalline graphite present in the samples, JCPDS 75-1621.^{164, 165} The peak at $2\theta = 43^\circ$ also signifies the hexagonal graphite lattice present in the samples.⁷⁴ This confirms the presence of both amorphous carbon, resulting from the annealing and activation of the sheath and a significant amount of graphitic carbon in all the samples.

However, a visible trend can be seen in the crystallinity across the samples. This can be explained by examining the intensity of the graphitic peaks at $2\theta = 27^\circ$. The highest intensity of this peak is for 0.5M-700N-800C, signifying the highest amount of crystallinity and pure graphite content in the sample, apart from the presence of activated carbon. The next in intensity is 0.5M-700N-500C, closely followed by P-700N-800C. The samples 1M-700N-800C and 2M-700N-800C

have the lowest intensity peaks at peaks at $2\theta = 27^\circ$. 0.5M-700N also has weak peaks as it was not activated at all. This trend can be possibly due to an interplay of factors like activation temperature and the usage of the nitrogen precursor, urea.

A higher activation temperature and an optimum urea concentration shows a higher graphitic peak intensity, whereas a higher urea concentration used for doping has resulted in a reduced graphite peak intensity. This tells us that urea has helped in the formation of more activated amorphous carbon content over the crystalline graphitic content. This could be explained by the creation of more surface functionalities and distortions in the lattice due to the creation of various oxygen, nitrogen and carbon bonds when urea is introduced. This would result in losing a long-range order, thus deforming a crystalline lattice structure, resulting in the lower peak intensity of graphite. This is explained further in our raman spectral studies. The other peaks at $2\theta = 21.8^\circ$, 22° , 28° , 38° belong to the mineral compounds present in our natural fiber, namely silicon oxide (SiO_2 , JCPDS 39-1425) and peaks at $2\theta = 35.5^\circ$ comes from silicon carbide (SiC , JCPDS 29-1129).^{166, 167} The XRD and Raman analysis of our pure graphene hydrogel which we used has been done in our previous work.⁴⁷

Figure 5.2 a) XRD pattern of all samples, b) Raman shift of all samples

5.2.2 Raman spectroscopic measurements

Raman measurements provide a deeper understanding of the structure; how doping and temperature affects the crystallinity and the microstructure of the samples. XRD and Raman analysis are complimentary, if not equal, in giving an idea about the crystal structure and defects in the carbonaceous materials. Thus, it is important to analyze both XRD and Raman results independently, yet, by drawing inferences from both, before forming a conclusion about the samples.

Normally, a carbonaceous material has two major Raman-active modes of vibration- a high frequency E_{2g} mode around $\sim 1580 \text{ cm}^{-1}$ (G band), representing the bond- stretching of sp^2 pairs in both rings and chains and a low frequency A_{1g} mode around $\sim 1350 \text{ cm}^{-1}$ (D band) representing the breathing modes of sp^2 atoms in rings and is activated by the presence of some defects in the structure of the carbon materials.¹⁶⁸ A second order peak called 2D peak, at around $\sim 2700 \text{ cm}^{-1}$ arises due to the presence of zone boundary phonons, whose sensitive peak

broadens or even vanishes with various conditions like temperature¹⁶⁹ The ratio of the low and high frequency band intensities, commonly called the I_d/I_g ratio, gives an insight in to the level of defects or disorder in the system, allowing us to understand the various factors contributing to the defects, like heat treatment temperatures for activation, annealing and even heterogeneous doping.¹⁶⁸

Figure 5.2b gives the raman shift of all samples and **Table A2** gives their calculated I_d/I_g ratios. It was observed that the important parameters playing a deciding role in the level of crystallinity and the defects in the samples are temperature and the doping levels. The least I_d/I_g ratio of 0.71 and a sharper 2D peak among all the samples, belongs to the sample, 0.5M-700N, which was not activated at all, but only annealed at 700°C. This was closely followed by the sample which has the least of the activation temperatures of 500 °C, 0.5-700N-500C, with I_d/I_g ratio of 0.79. This sample was doped with a 0.5 M urea solution. Closely behind, P-700N-800C has an I_d/I_g ratio of 0.81, which had a higher activation temperature of 800 °C, though this was un-doped.

Here, the more the untreated the samples are (temperature or doping treatment), the higher their I_g peaks and lesser their I_d/I_g ratios. This shows that the I_g peak for our carbonaceous material is sensitive to higher temperatures and doping. The more we treat them to get them in their highly activated form, their I_d/I_g ratio increases owing to I_g peaks of decreasing intensity. This is in par with the literature that the I_d/I_g ratios increase for different forms of carbon, ranging from

pure graphite to glassy carbon to carbon black, the highest for carbon black.^{170,}

171

Also, it is known that hetero atom doping introduces a covalent bond like C-N, C-Si, C-O, C-F etc leading to the introduction of a D band owing to introduction of new surface functionalities and disorder and disruption in the ordered lattice.¹⁶⁸ Thus, it is rational to explain that using a higher concentration of urea for doping would lead to more chances of surface functionalities by formation of more C-O, C-N bonds leading to more intense D bands. This matches with our observations of I_d/I_g values of 0.83, 0.88, 0.89 for 0.5M-700N-800C, 1M-700N-800C, 2M-700N-800C respectively. Moreover, all samples with an activation temperature of 800 °C have more intense D band intensities compared to 0.5M-700N-500C. Also, the 2D band intensities are almost similar for all samples subjected to the same temperature treatments.

5.2.3 Morphological studies

Morphological features were revealed by SEM; BET studies provided details about the surface area and porous nature of the samples. **Figure 5. 3** has the SEM images of all our samples, including an untreated pure sheath (**Figure 5.3a**) and an HRTEM image of 0.5M-700N-800C. It is evident from the figure that the fibrous and rugged structure of an untreated sheath is lost

Figure 5.3 SEM images of a) Pure sheath, b) P-700N-800C, c) 0.5M-700N, d) 0.5M-700N-500C, e) 0.5M-700N-800C, f) 1M-700N-800C, g) 2M-700N-800C, h) HRTEM image of 0.5M-700N-800C

and the surface becomes smooth for all the treated samples. However, there is lack of a common structure and the sheath is mostly present as fine broken pieces with smooth surfaces, with the presence of both micro pores and mesopores as

studied by our BET analysis, as shown in **Figure A9**. **Figure A9b** shows the presence of micropores (< 2 nm), mostly prominent for 0.5M-700N-800C and 0.5M-700N-500C, also explained by a high nitrogen uptake at low pressures, as is clear from the isotherm in **Figure A9a** and this is characteristic of a mix of Type 2 and Type 3 behavior with hysteresis, in accordance with IUPAC recommendations.^{72, 172} The samples also have mesopores (2-50 nm) shown by the pore distribution curves and also by the predominant hysteresis loops in the isotherms.^{9, 72, 173} **Table A3** gives the BET surface areas of the samples. While the samples treated at lower temperature and un-activated samples have lower surface areas and show a predominant Type I behavior, the urea treated and high temperature treated samples have surface areas closer to 420-440 m^2g^{-1} with a mix of Type II and Type III isotherms.⁷² Our best sample 0.5M-700N-800C has a BET surface area of 419 m^2g^{-1} and it has a multi-modal distribution with a high population of peaks in the pore size of 1.5 nm, 2 nm and 3.5 nm. As shown in **Figure 5.3h** below, a high magnification TEM image shows the diffraction patterns in our 0.5M-700N-800C sample. We calculated the d spacing from the image using Image-j software and it was found to be 0.347 nm. This is in almost in par with our XRD findings, where d spacing for a [0 0 2] plane is 0.336 nm for graphite (JCPDS-75-1621).¹⁷⁴ This reiterates that we have a highly graphitised sample.

5.2.4 The XPS spectral analysis

XPS studies were performed for our best sample 0.5M-700N-800C; the corresponding spectra were de-convoluted to obtain information about various surface bonds of C 1s, N 1s and O 1s as shown in **Figure 5.4**. The presence of carbon, oxygen and nitrogen was confirmed from the survey scan, which gave photoelectron lines at binding energies of around 280-290 eV, 395-405 eV and 530-537 eV, respectively.^{175, 176} The C 1s spectra was further de-convoluted to obtain three major peaks corresponding to the sp^2 C=C peak at 284.49 eV, C-OH peak at 286.6 eV and C=O peak at 290.1 eV.¹⁷⁶ The O 1s spectra gave peaks at 531.7 eV which correspond to groups C=O (quinone type) and a peak at 532.7 eV coming from the C-OH (phenol)/C-O-C (ether) groups.^{51, 176} There is a high percentage of C=C showing the high amount of graphitic carbon and a low percentage of oxygen bonded carbon (mostly coming from the urea used for doping), present as surface functionalities (as explained in our raman and XRD analysis) and some which is naturally present in the fiber as well. The N 1s spectra stands proof for substantial nitrogen doping in the carbon matrix with 4 well-fitted peaks; pyridinic nitrogen peak at 398.7 eV, C-NH₂ peak at 400.6 eV, quaternary N-Q peak at 401 eV and a pyridine nitrogen-oxide peak at 402.8 eV.^{51, 103} Among the peaks, there is a high amount of pyridine nitrogen and quaternary nitrogen. The pyridine nitrogen can be accounted to the nitrogen substitution in the abundant sp^2 bonded carbon matrix and the quaternary nitrogen arises from

the relative positive charge a nitrogen acquires in the presence of oxygen containing surface functionalities like C-O-C, C-OH etc.¹⁷⁷

Figure 5.4: XPS spectra of 0.5M-700N-800C with a) Survey scan, b) C1s spectra, c) O 1s spectra, d) N 1s spectra

5.2.5 Electrochemical measurements

Electrochemical studies were done, and the results were analyzed to understand the superior nature of our samples. **Figure 5.5** shows the CV curves (**Figure 5.5a**) at 10 mVs⁻¹ and the GCD curves at 1 Ag⁻¹ are shown in (**Figure 5. 5b.**) The CV and GCD curves at various scan rates and current densities for commercial AC and Pure G and all our other samples are also included in **Figure A10, Figure**

A11, Figure A12 and Figure A13 respectively. Specific capacitances for all samples have been calculated at various current densities and are plotted in **Figure 5.5c. Table 5.2** lists out the specific capacitances of all samples, including commercial activated carbon and pure graphene gel which we synthesized, for comparison. It can be clearly seen that, among all these samples tested, 0.5M-700N-800C gives the highest capacitance of 360.9 Fg^{-1} . It is interesting and impressive to show that it is even higher than that of a superior graphene hydrogel which we synthesized, which gave a capacitance of 305 Fg^{-1} . The effect of optimum nitrogen doping, presence of oxygen by treating it with urea and the presence of surface functionalities has helped in increasing the ion mobility, a better electron transport and conductivity of the carbon matrix, thus explaining the superior electrochemical performance of 0.5M-700N-800C.^{20, 148, 178} Nitrogen doping also increases wettability and are known to improve the overall electroactive surface area of the carbon rich porous matrices.¹⁷⁹ Nitrogen doping ensures better electronic conductivity due to the carbon π -system and the conjugation of nitrogen lone pair electron and also ensures a better electrochemical performance due to a synergistic effect of nitrogen chained groups with oxygenated groups.¹⁸⁰ These treated carbons have the advantage of forming electric double layers quickly, due to the presence of charged surface functionalities and ordered carbon layers the electron-donor capability of these nitrogen groups increases and hastens electron-transfer reactions.¹⁸⁰ Pyridinic and pyrrolic structures improve the ionic diffusion in the carbon framework, thereby increasing the specific capacitance of the carbon electrode. Thus, a

conductive framework with these nitrogen functionalities and surface defects from doping and high temperature treatment makes it easy for the mobility of ions and helps increase the pseudocapacitance contribution arising from redox reactions occurring at the surface functional group sites.

Also, a higher activation temperature has favored a better performance, which is clear from the fact that 0.5M-700N-500C has a lower performance in comparison with 0.5M-700N-800C. However, a high nitrogen or oxygen content and surface functionalities from them may not always be advantageous beyond an optimum amount. This can be seen from the decreasing performance of 1M-700N-800C and 2M-700N-800C with increase in the concentration of the dopant, urea. This can be related to the presence of a higher concentration of positively charged, oxidized pyridinic nitrogen in these samples (1M-700N-800C, 2M-700N-800C), hindering with the ion adsorption process, thus causing a dip in the specific capacitance and overall electrochemical performance.^{56, 178, 181} This highlights the importance of optimization of nitrogen doping and maintaining the right temperatures for enhancing the electrochemical performance. The CV curves in **Figure 5.5a** also suggest superior nature of our 0.5M-700N-800C sample, with the regular quasi rectangular curves, suggesting good reversibility and predominant electric double layer capacitance (EDLC)²⁰, whereas slight redox peaks at around -0.2 to -0.3 V reveal the pseudo-capacitive nature of the samples, typically arising from the redox reactions of active species involving the functional groups involving heteroatoms of nitrogen and oxygen.^{56, 182} Impurities of silica and silicon carbide, the difference in various annealing and activation

conditions and optimum doping could lead to conductivity differences in our samples. We thus calculated the IR drop from our charge-discharge curves at 1 Ag⁻¹ in **Figure 5.5b** in each of our samples for understanding a conductivity trend in our samples. Our best sample, 0.5M-700N-800C has the lowest IR drop of 0.055 V and the highest one of 0.204 V for 0.5M-700N. This shows the importance of optimum conditions in achieving a high electrochemical performance. **Table A4** shows the IR drop of all our samples.

Cycle life has a very significant role and is a predominant factor in deciding the performance of an electrode material. **Figure 5.5d** shows the cycle life of all our samples. Interestingly, the capacitances of all our samples have increased on testing the samples for 10000 cycles. The specific capacitance of 0.5M-700N-800C increased by 14.9% in comparison to activated carbon, whose capacitance saw an increase of 1.1 % and pure graphene hydrogel saw a decrease of 4.4% after 5000 cycles. This increase in capacitances of the carbonaceous samples has been reported and is related to the electro activation process.^{56, 183, 184} This possibly happens when a prolonged period of cycling enables ions to move around freely and intercalate in spaces which were inaccessible in the beginning, leading to more electroactive surface area and a better electrochemical performance.^{56, 60, 183} The capacitance retention for our best sample 0.5M-700N-800C was as high as 97.2 % even after 10000 cycles, highlighting its possible use for practical applications.

Table 5.2: Samples with their specific capacitances at 1 Ag⁻¹

Name of the product	Specific capacitance at 1 Ag ⁻¹
0.5M-700N	120 Fg ⁻¹
0.5M-700N-500C	200 Fg ⁻¹
0.5M-700N-800C	360.9 Fg⁻¹
1M-700N-800C	154.3 Fg ⁻¹
2M-700N-800C	118.18 Fg ⁻¹
P-700N-800C	134 Fg ⁻¹
AC	218.18 Fg ⁻¹
Pure G	305 Fg ⁻¹

A realistic comparison has also been done in our study to compare our study materials with existing literature involving other nitrogen doped and similar carbonaceous materials, mostly from different types of biomass, as shown in **Table A5**. Our material is clearly superior in terms of a high specific capacitance and a high working potential window of 0 to -1.1 V, even in a 2 M KOH solution, in comparison with a commonly 6M KOH solution. To the best of our knowledge, our material 0.5M-700N-800C has an unprecedented high performance for a biomass derived carbonaceous material, working in similar conditions. Moreover, it is worthwhile to reiterate the fact that our process involves a very facile synthesis route, involving hardly any chemicals other than urea, a non-hazardous material used for doping.

Figure 5.5 a) CV of all samples at 10 mVs^{-1} , b) GCD of all samples at 1 Ag^{-1} c) Specific capacitance Vs Current density, d) Capacitance retention- for all samples including commercial activated carbon (AC) and pure graphene hydrogel (Pure G) for comparison

5.3 Conclusions

Highly graphitized and nitrogen doped carbon has been synthesized and a detailed optimization study was conducted to understand how the parameters like the concentration of urea solution used for doping, the temperature and time of annealing etc. affect the surface functionalization and electrochemical performance of the samples. It was observed that our sample 0.5M-700N -800C, obtained by using a 0.5 M urea solution for doping, annealed at 700°C under

nitrogen (N₂) atmosphere and activated at an activation temperature of 800 °C under carbon dioxide (CO₂) atmosphere, gave an ultrahigh specific capacitance of 360.9 Fg⁻¹ in 2M KOH in the potential window of 0 to - 1.1 V and was superior in its electrochemical performance in comparison to all our other samples. It also showed an increase in its specific capacitance by 14.9 % after testing it for 5000 cycles and a capacitance retention of 97.2 % after 10000 cycles, highlighting the possibility of using it in practical applications. They are superior to commercial activated carbon and pure graphene hydrogel which we synthesized for comparison and exhibit better electrochemical performance compared to a lot of similar nitrogen doped carbonaceous products which have been discussed in literature. Thus, our simple strategy and optimization adopted for obtaining a biomass-derived highly graphitized and nitrogen doped carbon for use as negative electrode for supercapacitors, is unquestionably a facile, cheap and highly efficient method. This will pave way for substituting and reducing the use of graphene derivatives, carbon nanotubes and other carbon-based materials obtained usually by expensive and more complex procedures. It brings in to picture the possibility of using simple procedures in converting biomass-based materials into products almost in par and in some cases even better to existing materials for negative electrode for supercapacitors. A double advantageous method, it uses abundant biomass wastes for energy storage; depleting environmental wastes for an application which is most crucial in our present world of energy crisis. The results here have been used in our next chapter, to

incorporate ZIF-derived Ni, Co metal nanoparticles in the optimized coconut-leaf sheath-derived carbon framework (the best sample in this chapter).

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Chapter 6 MOF-derived Ni, Co metal nanoparticles in a N-doped biomass-derived carbon matrix for high performance supercapacitors and OER catalysis

Optimised coconut leaf sheath-derived nitrogen doped carbon framework developed in Chapter 5 is incorporated with nickel and cobalt metal nanoparticles in the carbon matrix by a facile process of growing ZIF-67 metal organic framework particles (with Ni precursors) on the graphitised carbon, followed by annealing it in inert atmosphere. Various parameters, such as the annealing and activation temperature used in the preparation of the samples and amount of nitrogen doped carbon used for loading the nickel cobalt nanoparticles, are modified to obtain three different samples. The samples obtained are then tested for high performance supercapacitors and as an oxygen evolution reaction (OER) catalyst. The optimised sample NiCo-C-1 gave an ultrahigh specific capacitance of 2471 Fg^{-1} at a current density of 1 Ag^{-1} in a 2 M KOH electrolyte. An asymmetric supercapacitor assembly prepared from NiCo-C-1 as the positive electrode and the nitrogen doped carbon as the negative electrode, exhibited an energy density of up to 31.8 WhKg^{-1} for a high-power density of 6.2 kWKg^{-1} over a potential window of 0 to 1.55 V. The two of our best samples were also tested for OER, giving good water oxidation kinetics. The process involves minimum chemicals for the pre/post treatment of the biomass and is very crucial as it yields an unprecedented performance for a material majorly developed and modified from biomass. Hence, this work opens great

avenues for biomass-derived materials for high performance supercapacitors and catalysis and is comparable to the electrochemical performance of $\text{Ni}_2\text{Co}_2\text{O}_4$ /graphene hydrogel in Chapter 4.

6.1 Materials and methods

6.1.1 Chemicals

The purchased chemicals were all analytical grade and were used without further purifications/treatments.

6.1.2 Synthesis of nitrogen doped carbon from coconut leaf sheath

The coconut leaf sheath (CLS) was well dried and the inner part of the fiber was cut into small pieces. The pieces were dipped overnight in a 0.5 M urea solution (D.I water as the solvent) with magnetic stirring and then annealed in a tube furnace, first in a N₂ atmosphere for 3 h at 700 °C and then activated in a CO₂ atmosphere for an hour at 800 °C, both at a heating rate of 5 °C/min. The pieces were then collected and powdered using mortar and pestle and were named 0.5M-700N-800C. A similar sample was prepared, 0.5M-700N-500C, which was prepared in a very similar way as mentioned above, except that it was activated at 500 °C for 3 h. These were the best samples as obtained and optimised, w.r.t their electrochemical performance, as can be seen from Chapter 5.

6.1.3 Synthesis of Ni, Co nanoparticles decorated on biomass-derived N-doped carbon

The 0.5M-700N-800C powder obtained in the above process was dispersed in a solution made from 2-methyl-imidazole in D.I water. The mixture was magnetically stirred for 30 min to properly wet the particles and enhance contact

with 2-methyl-imidazole. Thereafter, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was added to it such that the overall molar ratio of cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2-methyl-imidazole was 1:4. This was followed like the procedure in Chapter 4. The solution was then stirred for around 20 min, followed by the addition of a nickel precursor, nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), equal in amounts to the cobalt precursor. The mixture was then left undisturbed for 24 h at room temperature. The product obtained was then taken out and washed repeatedly with water and then left to dry in an oven. These powders were then subjected to annealing in a N_2 atmosphere at 700 °C for 3 h at a heating rate of 5 °C min^{-1} . NiCo-C-2 and NiCo-C-3 were also made in a similar manner, but with the following parameters changed, as shown in the **Table 6.1** and in **Table 6.2**. Here too, various ratios were tried keeping temperature fixed, but changing activation conditions; to not show a single set as the best result; instead focusing on a study of various parameters which affects the electrochemical performance, morphology, phase etc.

Table 6.1 Samples obtained with different parameters

Name of the sample	Type of carbon sample	Amount of the carbon sample (mg)	Annealing temperature (°C)	Activation temperature (°C)
NiCo-C-1	0.5M-700N-800C	10	700	-
NiCo-C-2	0.5M-700N-500C	20	700	-
NiCo-C-3	0.5M-700N-500C	10	700	800

Table 6.2 Details of sample obtained under different parameters

Type of carbon sample	Amount of the carbon sample	Annealing temperature	Activation temperature	Amount of Co precursor (mg)	Amount of Ni precursor (mg)
0.5M-700N-800C	10	700	-	100	100
0.5M-700N-800C	20	700	-	100	100
0.5M-700N-500C	10	700	800	100	100

6.1.4 Electrochemical measurements

Supercapacitors: A CHI660D potentiostat was used throughout to carry out the electrochemical characterizations for the supercapacitor study. A three-electrode setup was used to study the individual electrode performance while a two-electrode setup was used to study the asymmetric supercapacitors. The electrodes used for testing involved a platinum electrode as the counter electrode, an Ag/AgCl metro ohm double junction electrode as the reference electrode and a 2 M KOH solution as the electrolyte. Hereafter, all voltages measured and mentioned are made vs the Ag/AgCl reference electrode for all the supercapacitor tests. The samples for testing were prepared by mixing their powders with (PVDF) polyvinylidene fluoride, acetylene black in the ratio 8:1:1 and making it in to a slurry using a binder/wetting agent NMP.

The slurry is then transferred on a 1 cm² nickel foam of thickness 0.723 mm. This is left to dry overnight in a hot oven at 60 °C and the weights before and after

drying are noted to measure the active mass loading of the sample. The mass loading of the samples was averaged at 1.2-1.5 mg (total weight of the slurry (including the active material, binders and conductive agent) deposited on the nickel foam) per square centimetre of the nickel foam area. This overall weight has been used to calculate the specific capacities of the samples. The techniques used to study the electrodes are cyclic voltammetry (CV) and galvanostatic charge discharge techniques (GCD). While CV gives an account of the reversibility of the electrode, the GCD measurements give us the specific capacity and details regarding the cycle life of the material.

Specific capacitance (F g^{-1}) is calculated from the GCD measurements using the following formulas.

Three-electrode tests

$$C_s = \frac{I \times \Delta t}{\Delta V \times m} \quad (6.1)$$

Equation 6.1¹³¹ calculates the specific capacitance for a three-electrode setup, where C_s is the specific capacitance (F g^{-1}) of the electrode, I is the discharge current, ΔV is the voltage window, Δt is the discharging time and m is active mass of the electrode. The same formula allows us to give a more realistic quantity for our material, specific capacity, expressed in mAh g^{-1} ¹⁵⁶.

Two-electrode tests

Equation 6.2¹³¹ calculates the specific capacitance (F g^{-1}) of the entire cell in a two-electrode setup of asymmetric supercapacitor (ASC),

$$Cs = \frac{I \times \Delta t}{\Delta V \times M} \quad (6.2)$$

where M differs from **Equation 6.1** as $M = m^- + m^+$ where, m^+ and m^- are the active masses of the material in the positive and negative electrode, respectively. Specific capacity in mAh g^{-1} is also calculated from this equation.

Ragone plots are plotted using the energy density (Wh Kg^{-1}) and power density (kW Kg^{-1}) of the ASC, which are calculated by using **Equation 6.3** and **Equation 6.4**, respectively, which are used for the Ragone plot¹³¹

$$E = \frac{1 \times Cs \times \Delta V^2}{2} \quad (6.3)$$

$$P = \frac{E}{\Delta t} \quad (6.4)$$

Electrochemical impedance spectroscopy (EIS) helped to give us the Nyquist plots and was carried out by applying an AC voltage of 10 mV amplitude in the 0.1-10⁵ Hz frequency region.

6.1.5 OER catalysis

Electrochemical measurements towards OER were carried out using an Autolab 302N potentiostat. A three-electrode system was employed, in which coiled Pt electrode was used as the counter electrode, Hg-HgO (1 M NaOH) as the reference electrode and a glassy carbon electrode (diameter 3 mm, area 0.07 cm²)

as the working electrode. Argon saturated 1 M KOH was used as the electrolyte. Prior to the use of working electrode, the glassy carbon electrode was polished to mirror finish using alumina powder of 0.05- μm size and ultrasonically cleaned in distilled water for 10 minutes followed by drying in a N_2 stream. The catalyst ink for electrochemical studies was prepared by dispersing 5 mg of the catalyst in a water-EtOH (1:1) mixture containing 100 μl of Nafion (0.5 wt% in a solution of 1:1 water and isopropanol) to a final concentration of 5 mg mL^{-1} of the catalyst and the dispersion was made into the catalyst ink by sonicating for 30 min. Thereafter, 5 μl of the catalyst ink (0.025 mg) is loaded onto the glassy carbon electrode and allowed to dry in air. Electrochemical measurements were carried out by conducting linear sweep voltammetry (LSV) and cyclic voltammetry (CV) at a scan rate of 5 mV sec^{-1} and 10 mV sec^{-1} respectively. Before measurements, the samples were cycled at a scan rate of 10 mV sec^{-1} for 50 times to refresh the catalytic surface. All the electrochemical measurements were reported against the potential vs Reversible Hydrogen Electrode (RHE) as the reference electrode. The electrochemical potentials applied and measured using Hg-HgO reference electrode are then converted to RHE using the **Equation 6.5**¹⁸⁵

$$E_{\text{RHE}} = E_{\text{Hg-HgO}} + 0.93 \text{ V} - iR \quad (6.5)$$

In the present study, compensation was done for the current values and the value of iR 's was found by conducting impedance measurement in 1 M KOH and the value of R was in the range of 10 to 13 Ω . The temperature during the

electrochemical measurements was 25 ± 1 °C. Overpotential ‘ η ’ for oxygen evolution is calculated using the following formula in **Equation 6.6**:¹⁸⁵

$$\eta = E_{\text{RHE}} - 1.23 - iR \quad (6.6)$$

6.1.6 Materials characterisation

Field emission scanning electron microscope (FESEM, JEOL-JSM-6700F) and transmission electron microscope (TEM JEOL, 300 kV) were used to study the morphology of the samples. X-ray diffraction measurements were made using an XRD-Bruker D2 phaser diffractometer (Cu K α radiation). Bonding information and surface chemical compositions were obtained from XPS or X-ray photoelectron spectroscopy (KRATOS AXIS DLD spectrometer). Renishaw inVia Raman Microscope using an Ar⁺ ion laser (wavelength 514 nm) gave the Raman spectra of the samples

6.2 Results and discussions

6.2.1 XRD measurements

XRD measurements revealed the presence of nickel and cobalt metal nanoparticles as shown in **Figure 6.1a**. Though the cobalt and metal nanoparticle peaks are overlapping, the very sharp and well-formed peaks reveal the presence of highly crystalline pure nickel and cobalt nanoparticles, also reiterated by XPS analysis. The peaks at around 44.5°, 51.6°, and 76.2° are the major peaks corresponding to metallic fcc nickel which coincide with the planes [1 1 1], [2 0

0] and [1 6 1], respectively (JCPDS 87-07-12), while the peaks also suggest the presence of cobalt nanoparticles (JCPDS 89-4307) with the same peak positions^{116, 186, 187}. The samples also show graphitic peaks of the [0 0 2] plane at 22° (JCPDS 75-1621), stronger in NiCo-C-1, showing a good level of graphitisation¹¹⁶. It is also evident that the sample has pure nickel and cobalt particles and thus demonstrates the absence of oxides or hydroxides while in the powder form. This further shows the stability and resistance of our metal nanoparticles to oxidation in the carbon wrapped matrix.

Figure 6.1 a) XRD spectra of the samples, b) Raman spectra of the samples.

6.2.2 Raman spectroscopic measurements

Raman spectra of the samples were obtained, as shown in **Figure 6.1b**. The spectra showed typical bands of a carbon rich material, with a G band and D band. The G band in the E_{2g} mode (originating from the bond- stretching of sp² pairs in both rings and chains) is the major active mode of vibration showing up at around ~1580 cm⁻¹, while the D band in the A_{1g} mode (representing the

breathing modes of sp^2 atoms in rings, activated usually by defects in the carbon structure) is evident at $\sim 1350\text{ cm}^{-1}$ ¹⁶⁸⁻¹⁷⁰.

The I_d/I_g ratio is indicative of the defects present in the carbon framework and we calculated the I_d/I_g ratio for our samples. The samples NiCo-C-2 and Ni-Co-C-3 used with 0.5M-700N-500C as the base had slightly lower values of I_d/I_g values of around 0.88-0.9, while NiCo-C-1 which was made using 0.5M-700N-800C had a higher value of 0.92, indicating more defects in the framework. This is in line with the literature that higher temperature treatments introduce stronger D bands ¹⁶⁹⁻¹⁷¹.

Also, it is important to note here that the spectra do not show the presence of any nickel oxide/hydroxides in the lower wavelength region; in addition, metal nanoparticles of Ni and Co are not Raman active, hence they reiterate the stability of the particles and the absence of any predominant oxidation in their powder state ¹⁸⁸⁻¹⁹⁰. The Raman spectra of 0.5M-700N-500C and 0.5M-700N-800C used for loading the nanoparticles are given in **Figure A14** of the appendix and are typical of carbon materials with well-formed I_d and I_g bands.

Figure 6.2 SEM image of a) NiCo-C-1 lower magnification, b) NiCo-C-1 with higher magnification inset c) NiCo-C-2, d) NiCo-C-3, e) TEM image of NiCo-C-1 with a zoomed inset.

6.2.3 Morphological characterisations

Figure 6.2 details the morphological characterisations of the samples done by SEM and TEM. **Figure 6.2a** and **6.2b** show the lower and higher magnifications

of NiCo-C-1, respectively. The image clearly shows the multitude of nanoparticles deposited on the surface of the nitrogen doped layered carbon, forming a coral shaped assembly. The uniform and dense assembly of the particles on the carbon framework is clearly seen from the images. The average size of the nanoparticles for NiCo-C-1 is around 70.7 nm, as calculated from the Particle Size Distribution (PSD) (**Figure A16**) of **Figure 6.2e**. It is also interesting to find that the presence of the nanoparticles is not so dense on the carbon surface for NiCo-C-2 and NiCo-C-3 compared to Ni-Co-C-1 (**Figure 6.2b, 6.2c and 6.2d**), though it is higher for NiCo-C-3 compared to NiCo-C-2. One major reason for the scarce deposition of the particles on NiCo-C-2 is the higher amount of 0.5M-700N-500C taken for loading Ni Co nanoparticles, compared to the amount of carbon used for loading the nanoparticles in NiCo-C-1 and NiCo-C-3 (**Table A6**). This can also be rationalised by the fact that both Ni-Co-C-2 and Ni-Co-C-3 samples were made from 0.5M-700N-500C, which is the leaf sheath activated at 500 °C. It thus can be inferred that the sheath annealed at 800 °C has attracted and led to more ZIF-67 growth on its surface, leading to a dense population of nanoparticles on annealing. This could be because of the higher activation of the carbon activated at a higher temperature, favouring a better growth of the ZIF-67 particles on this active surface. Also, the NiCo-C-3 has a slightly thinner framework as can be seen from the SEM images, compared to the other two samples, the reason being, the whole sample after the ZIF-67 growth was not just annealed, but also activated again at 800 °C. This led to a two-stage activation process, leading to a more fine-tuned, thinner carbon

framework. A TEM image of our best sample NiCo-C-1 can also be seen in **Figure 6.2e** and it clearly shows the nanoparticles in the carbon matrix and further clarifies the successful incorporation of the particles. A digital photograph of the untreated coconut sheath, SEM images of 0.5M-700N-500C and 0.5M-700N-800C are given in **Figure A15**.

6.2.4 XPS measurements

XPS measurements conducted for our best sample NiCo-C-further clarify the incorporation of the nickel and cobalt nanoparticles in the nitrogen doped carbon matrix. **Figure 6.3** shows the C 1s, N 1s, O 1s, Co 2p and Ni 2p spectra. The carbon spectra (**Figure 6.3a**) were deconvoluted to give 4 major peaks: a graphitic C-C peak (284.2 eV), a C=N/ C-O peak (286 eV), a C-O-C/C-N peak (287.4 eV) and a O-C=O peak (291 eV)^{178, 191, 192}. The peaks support the high degree of graphitisation for the samples from the predominant C-C peak and from the low intensity carbon-oxygen bonded peaks. This is in accordance with our Raman and XRD measurements. The O 1s spectra (**Figure 6.3b**) also gave the hydroxyl, carboxyl and the metal oxide peaks^{51, 192, 193}. The successful nitrogen doping is also verified from the N 1s spectra (**Figure 6.3c**) which were deconvoluted in to three major peaks, a pyridinic nitrogen, a quaternary nitrogen and a graphitic nitrogen^{148, 192}. The nitrogen comes from both the urea used in the sheath and from the imidazolium framework used in the ZIF-67 synthesis. The cobalt and the nickel 2p spectra give clear indication of the presence of metallic nickel and cobalt particles.

Figure 6.3 XPS spectra of NiCo-C-1 with a) C 1s scan, b) O 1s scan, c) N 1s scan, d) Co 2p scan, e) Ni 2p scan.

However, XPS being a sensitive surface characterisation technique, it has also found the presence of metal oxides on the surface, mostly formed from the exposed Co Ni nanoparticles on the surface. Both the Ni 2p and Co 2p were deconvoluted to give Co⁰, Co²⁺, Ni⁰, Ni²⁺ and the respective satellite peaks of the +2 oxidation states^{187, 192, 194, 195}. There is a clear indication of a higher level of oxidation for the nickel particles, as can be seen from the higher intensity peak

of Ni^{2+} ($2p^{1/2}$ 873.4 eV and $2p^{3/2}$ 855.26 eV)^{115, 194, 196, 197}. However, for the cobalt nanoparticles, the presence of metallic cobalt Co^0 ($2p^{1/2}$ 794.15 eV and $2p^{3/2}$ 778.84 eV) is higher in comparison with its oxidised state, which is clear from a higher intensity Co^0 peak^{187, 191, 192, 198}. This can be inferred from the fact that the cobalt particles are protected by the imidazolate carbon framework during the ZIF formation and the nickel particles are more exposed in an outer layer, as they are added later during the synthesis, after sufficient time is given for a preliminary ZIF-67 formation.

6.2.5 Electrochemical characterisation

The electrochemical characterisations revealed the high capacitive properties of our samples. **Figure 6.4** gives the CV and GCD curves of all the samples. The CV curves reveal the high charge storage capacity of our material apart from the electric double layer capacitance in the samples, from the evident redox peaks. These peaks arise from the redox reactions of the nickel and cobalt oxides and hydroxide species on the surface, formed by the oxidation of the nickel and cobalt nanoparticles when in contact with the aqueous alkaline electrolyte. The maximum specific capacity obtained was 308 mAh g⁻¹ (specific capacitance equivalent of 2471 F g⁻¹) for our sample NiCo-C-1 followed by a specific capacity of 209.5 mAh g⁻¹ (specific capacitance equivalent of 1676 F g⁻¹) for NiCo-C-3 at a current density of 1 A g⁻¹. **Figure 6.5** compares all the three samples and it can be clearly seen that NiCo-C-1 is the best sample, evident from its superior electrochemical performance. The sample NiCo-C-2 with a lower

metal nanoparticle to carbon ratio, has a lower performance with a specific capacity of 152.75 mAh g⁻¹ (specific capacitance equivalent of 1222 F g⁻¹) at 1 A g⁻¹ current density. The extremely small size of the nanoparticles makes it possible for the growth of an abundant amount of the respective nickel and cobalt oxides and hydroxides species in contact with the aqueous electrolyte, leading to this very charge storage capacity¹⁹⁹. This condition is maximized in NiCo-C-1 with its abundantly grown nanoparticle system on a coral shaped carbon matrix, as previously described in the morphological studies. Another reason for a lower capacitance for NiCo-C-2 and NiCo-C-3 would be the difference in the carbon matrix, 0.5M-700N-500C, used for their preparation instead of the 0.5M-700N-800C used in the case of NiCo-C-1. The GCD and CV curves of 0.5M-700N-800C and 0.5M-700N-500C are given in **Figure A17**. The specific capacitance of 0.5M-700N-800C was 361 F g⁻¹ and that of 0.5M-700N-500C was 200 F g⁻¹. It is clear from the morphological studies that the carbon matrix obtained by activation at a higher temperature has facilitated a better and more uniform growth of the nanoparticles on its surface, thus highlighting the importance of optimising the support used for the growth of the nanoparticles. Also, the nitrogen doping helps in increasing the wettability, overall electroactivity and conductivity of the system^{21, 52, 200, 201}. It is also known that the Co and Ni nanoparticles contribute significantly to graphitisation, hence it was even more beneficial to grow the nanoparticles wrapped in a highly graphitised carbon matrix¹⁰⁶. Thus, the highly conductive nitrogen doped carbon matrix is the right base for the growth of the metal nanoparticles. The ion mobility and free

movement of electrons is highly promoted by the conductive framework as well as the metal nanoparticles. The various redox reactions taking place in these systems can be summarised by the following equations,^{23, 115, 116, 199, 202}

Ni and Co nanoparticles are first oxidised to their respective nickel and cobalt oxides in the presence of the aqueous electrolyte as in **Equation 6.7 and 6.8**. These oxides are further converted to the hydroxides through a series of redox reactions given in **Equations 6.9 to 6.12**, forming the redox peaks in the CV curves. The anodic peaks arise from the conversion of NiO and CoO to NiOOH and CoOOH and from the conversion of Ni(OH)₂/Co(OH)₂, while the cathodic peaks appear from their reverse reactions. The cyclic stability tests also show the high cycle life of our samples, especially NiCo-C-1, with a high capacitance retention of 88% even after 5000 cycles. NiCo-C-2 and NiCo-C-3 also show an impressive capacitance retention of 81% and 86% respectively as shown in **Figure 6.5d**. The efficient charge transfer ability of the samples was verified

from the Nyquist plots obtained from the electrochemical impedance spectroscopy (EIS) studies.

Figure 6.4 a) CV curves of NiCo-C-1, b) GCD curves of NiCo-C-1, c) CV curves of NiCo-C-2, d) GCD curves of NiCo-C-2, e) CV curves of NiCo-C-3, f) GCD curves of NiCo-C-3.

The charge transfer resistance, R_{ct} , calculated from the diameter of the semi-circular region in the high frequency region is due to the double layer capacitance

and also from the redox reactions taking place on the surface of the systems^{23, 109}. The R_{ct} for our samples are calculated to be roughly 0.84 Ω , 2.4 Ω and 1.4 Ω for NiCo-C-1, NiCo-C-2 and NiCo-C-3, respectively. The lowest resistance is observed for NiCo-C-1, showing its efficient charge transfer efficiency compared to the other samples and further adding the rationale for its superior electrochemical behaviour.

Figure 6.5 a) Overlap of CV curves of NiCo-C-1, NiCo-C-2 and NiCo-C-3, b) overlap of GCD curves of NiCo-C-1, NiCo-C-2 and NiCo-C-3, c) specific capacity vs current density of NiCo-C-1, NiCo-C-2 and NiCo-C-3, d) Cycle life of NiCo-C-1, NiCo-C-2 and NiCo-C-3 and an inset showing their Nyquist plots.

6.2.6 Asymmetric supercapacitor (ASC)

The optimised sample NiCo-C-1 was further employed as the positive electrode in an asymmetric supercapacitor assembly and pure 0.5M-700N-800C powder was used as the negative electrode. 0.5M-700N-800C was tested and showed a very impressive performance as a negative electrode, with a specific capacitance of 361 F g⁻¹ at 1 A g⁻¹ in 2 M KOH. **Figure A17** gives the GCD and CV curves of 0.5M-700N-800C. The ASC was tested as a two- electrode system in 2 M KOH over a potential window of 0 V to 1.55 V. **Figure 6.6** gives the details of the electrochemical tests done on our ASC NiCo-C-1//0.5M-700N-800C. Before the ASC was assembled, it is important to charge balance for the positive and negative electrodes, which have different active voltage windows and specific capacitances. For this purpose, we loaded mass for our positive and negative electrodes according to the equation given below^{23, 47}

$$\frac{m^+}{m^-} = \frac{C^- * \Delta V^-}{C^+ * \Delta V^+} \quad (6.13)$$

where m^+ and m^- are the active masses, C^+ and C^- are the specific capacitances obtained from their respective three electrode tests and ΔV^+ and ΔV^- are the working potential windows of the positive and negative electrodes, respectively. The ratio of the masses thus obtained from **Equation 6.13** was $m^+ = 0.357 m^-$. The specific capacity for the ASC was calculated and found to be 43 mAh g⁻¹ (equivalent specific capacitance of 99.25 F g⁻¹) at 1 A g⁻¹ and gave a high value of 36.3 mAh g⁻¹ (equivalent specific capacitance of 84.36 F g⁻¹) even at a high

current density of 10 A g^{-1} . It also exhibited a good cycle life with a capacitance retention of 76.6% even after 5000 cycles as shown in the inset of **Figure 6.6c**.

Figure 6.6 a) CV curves of ASC NiCo-C-1//0.5M-700N-800C, b) GCD curves of ASC NiCo-C-1//0.5M-700N-800C, c) Specific capacity vs current density of ASC NiCo-C-1//0.5M-700N-800C with an inset showing its cycle life, d) Ragone plot comparing our ASC NiCo-C-1//0.5M-700N-800C with $\text{Ni}(\text{OH})_2/\text{A.C}$ ⁴⁴, $\text{NiO}/3\text{D R.G.O}$ ¹⁵⁸, $\text{CBC-N2@LDH-0.4}/\text{CBC-N2}$ ¹⁰³, $\text{Ni}_x\text{Co}_{3-x}\text{O}_4 \text{ NW}/\text{A.C}$ ¹⁰⁸,

Ni-Co_{1.5}-O//RGO @ Fe₃O₄¹¹⁰, D-NiCo₂O₄//A.C⁴⁶, e) Nyquist plot of ASC NiCo-C-1//0.5M-700N-800C with an inset showing the high frequency region.

The Ragone plot was also plotted and the energy and power densities were compared with ASC of existing literature (**Figure 6.6d**). Our ASC obtained a very high energy density of 28.149 Wh Kg⁻¹ even at a high-power density of 7750 W Kg⁻¹. The low charge resistance of the ASC is verified by the Nyquist plots in **Figure 6.6e**, which shows a negligible charge transfer resistance in the high frequency region (inset of Figure 6e). Even though there are ASCs in literature exhibiting higher energy densities at lower power densities, there is a very high decay in the energy density at higher power densities. Our material shows an almost consistent energy density, even at higher power densities, highlighting the superiority of our samples, which can be tapped for practical applications. Lai et al. developed an ASC with a positive electrode made from nickel cobalt layered hydroxides grown on a biomass derived nitrogen doped carbon network and a nitrogen doped carbon network as the negative electrode. This gave a high energy density of 36.3 Wh Kg⁻¹ at 800.2 W Kg⁻¹, but decreased to 26 Wh/Kg even at a moderate power density of 4000 W Kg⁻¹¹⁰³.

A flower like nickel cobalt oxide vs activated carbon ASC gave a low energy density of 9.1 Wh Kg⁻¹ at 5625 W Kg⁻¹⁴⁶, whereas a complex system of multi-shelled nickel cobalt oxide vs iron oxide with reduced graphene oxide was used in another ASC yielding an energy density of 22.8 Wh Kg⁻¹ at a power density of 7600 W Kg⁻¹¹¹⁰. Wang et al. synthesised high performance porous nickel cobalt

oxide nanowires and used it against activated carbon negative electrode to form an ASC, which gave an energy density of 27 Wh Kg⁻¹ at a low power density of 2000 W Kg⁻¹ ¹⁰⁸. The ASC was also tested for EIS for knowledge about its charge transfer resistance. As can be seen from **Figure 6.6e** and its inset showing the Nyquist plots, there is only a negligible charge transfer resistance. This shows the charge transfer efficiency of the system, which is one of the main factors for its high performance.

6.2.7 OER studies

Linear sweep voltamograms (LSV) recorded after 50 CV cycles at a scan rate of 10 mV s⁻¹ are shown in **Figure 6.7a**, which reveals better OER kinetics for NiCo-C-1 and NiCo-C-3. A cathodic shift in the onset potential as well as improvement in the OER current density is observed for NiCo-C-1 and NiCo-C-3 which is ascribed to a high conductivity and the abundant space between the carbon networks. A lower Tafel slope for the electrochemical reaction is an indication of increased OER kinetics, the Tafel behavior of the catalyst is obtained from potential versus log(*J*) plot as shown in **Figure 6.7b**. The Tafel slopes for NiCo-C-1 and NiCo-C-3 are calculated to be 108 and 107 mV dec⁻¹, respectively, indicating better water oxidation kinetics. An onset potential value for producing $J = 10 \text{ mA cm}^{-2}$ is a significant parameter, since this value is considered to be matching with the 10% efficient solar to current conversion devices under 1 Sun illumination ^{185, 203, 204}. The Tafel slopes and the over potentials (η) for the water oxidation $J = 10 \text{ mA cm}^{-2}$, extracted from the LSV plot, are shown in **Table 6.2**

and a lower value of $\eta = 420$ mV is obtained for NiCo-C-3. These results thus imply a better water oxidation activity for these systems. Our Ni,Co nanoparticle-incorporated electrocatalysts are compared to other Ni,Co-based catalysts in literature, as given in **Table 6.4**. It is seen from the table that, our biomass-derived coconut leaf sheath-based product is quite comparable to graphene-based/other carbon-based Ni and Co materials. It shows the immense potential in these sustainable products and would encourage more such works to be taken up, where benign low cost biomass-derived materials more sophisticated graphene, CNT etc.

Table 6.3 Table showing OER characteristics

Sample	η to generate 10 mA cm^{-2} (mV)	Current density at $\eta=400$ mV (mA cm^{-2})	Tafel slope (mV dec^{-1})
NiCo-C-1	430	4.6	108
NiCo-C-3	420	5.8	107

Figure 6.7 a) LSV of samples, b) potential versus $\log(J)$ plot.

Table 6.4 Table showing OER characteristics of other Ni, Co, carbon-based materials

Performance of other Ni, Co, carbon-based catalysts for OER catalysis		
Catalyst	Current densities	Tafel slope
N-doped graphene/ Ni, Co double hydroxide ²⁰⁵	At $\eta = 400$ mV, $J = 145.3$ mA cm ⁻²	614 mV dec ⁻¹
N-doped graphene film with Ni nanoparticles ²⁰⁶	At $\eta = 400$ mV, $J = 16.3$ mA cm ⁻²	188.6 mV dec ⁻¹
N-doped graphene/Cobalt phosphate nanoclusters ²⁰⁷	At $\eta = 225$ mV, $J = 1$ mA cm ⁻²	550 mV dec ⁻¹
Graphene-like holey Co ₃ O ₄ nanosheets ²⁰⁸	At 0.8V vs Hg/HgO, $J = 12.26$ mA cm ⁻²	66 mV dec ⁻¹
Porous carbon fibre with cobalt-based nanoparticles ²⁰⁹	At overpotential = 314 mV, $J = 10$ mA cm ⁻²	141 mV dec ⁻¹

6.3 Conclusion

We successfully synthesised a nitrogen doped coral shaped carbon framework with nickel and cobalt nanoparticles incorporated in it. Detailed optimisation and characterisation of the samples were performed and its efficient use in supercapacitors and as an OER catalyst was demonstrated. Our samples were prepared under three different synthesis procedures, mostly differing on their carbon framework and the different temperatures they were treated in. The optimised sample NiCo-C-1 showed an exceptionally high performance for a biomass-based material, with a specific capacitance of 308 mAh g⁻¹ at a current

density of 1 A g^{-1} in a 2 M KOH electrolyte. We also tested NiCo-C-1 in an asymmetric supercapacitor, paired with a negative electrode we prepared primarily from coconut leaf sheath, 0.5M-700N-800C. It gave a very high energy density of 31.8 Wh Kg^{-1} for a high-power density of 6.2 kW Kg^{-1} over a potential window of 0 V to 1.55 V . The two best samples, NiCo-C-1 and NiCo-C-3, were also tested for OER, giving good water oxidation kinetics, revealed by their low tafel slopes in the range of 107 mV dec^{-1} and a low overpotential $[\eta]$ of around 420 mV at a current density of 10 mA cm^{-2} . Our material thus shows very commendable performance and holds promise for the energy sector. To the best of our knowledge, our material is one of the best so far in terms of its electrochemical performance for a material developed majorly from biomass. In the current scenario of energy crisis, the urgent needs for sustainable development and green solutions for our energy needs are long waiting to be answered. Our material, largely built from a biomass framework and from use of very few chemicals, shows its relevance as a key to sustainability and an environment friendly product, highlighting its potential in practical energy applications.

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Chapter 7 Conclusions and future work

7.1 Conclusions

Supercapacitors have emerged as very important energy storage systems owing to their high-power densities and energy densities. The present thesis focuses on finding carbon-based material hybrids for supercapacitor applications. Graphene hydrogel-based systems were first experimented by incorporating MnO_x /Polyaniline in our first project, followed by Nickel-Cobalt-mixed oxides in the second project. The idea was to find a better performing material composite from among the two studies. The Graphene/ MnO_x /Polyaniline electrode gave a specific capacitance of 955 Fg^{-1} at 1 Ag^{-1} in a $1 \text{ M Na}_2\text{SO}_4$ electrolyte with a cyclic stability of 89% after 1000 cycles, while the ZIF-derived NiCo_2O_4 in graphene hydrogel, $\text{GNi:Co } 1:1$, gave an ultrahigh specific capacitance of 2870.8 Fg^{-1} at 1 Ag^{-1} in a 2 M KOH and a superior cycle life with 88.1 % capacitance retention after 5000 cycles. This led to the conclusion and inference that a nickel/cobalt system performed better than a MnO_x /polyaniline system in a graphene hydrogel matrix.

To further find sustainable solutions without compromising on the electrochemical performance, we decided to extend the incorporation of a Ni/Co-based system in to a biomass-derived carbon framework instead of a graphene framework. After reading a lot of literature on biomass-based materials, coconut-leaf sheath (CLS), a type of coconut fibre, was chosen as our starting biomass material. This was decided after a rational and pragmatic evaluation of various

factors like low cost, long shelf-life, easy availability, environmental friendliness etc. Before incorporating the Ni-Co functional materials, we performed a detailed optimisation study to optimise a high-performing N-doped carbon framework from CLS. This optimisation process was based on adjusting important parameters like the annealing temperature, the concentration of urea used for nitrogen doping, the annealing time etc. The best sample, used as a negative electrode, gave a commendable specific capacitance of 360.9 F g^{-1} at 1 A g^{-1} in 2M KOH.

The optimised and best performing CLS-derived carbon was loaded with ZIF-67-derived Ni,Co nanoparticles (Since a carbonisation technique is used, we can obtain Ni, Co nanoparticles from ZIF, unlike the Ni,Co mixed oxides in the case of a graphene framework, where a hydrothermal route is used at the final step). A detailed optimisation study was then conducted to evaluate the electrochemical performance based on the mass loading of Ni, Co and the amount of carbon sample used. The best sample NiCo-C-1 gave 2471 F g^{-1} as the specific capacitance at 1 A g^{-1} in 2M KOH.

Asymmetric supercapacitors were assembled using both systems; GNi Co 1:1//Pure GH and NiCo-C-1//0.5M-700N-800C and compared with similar material hybrid works in literature (**Figure 7.1**). It was found that at higher power densities, the biomass-derived carbon systems performed better than the graphene-based systems. However, at lower energy densities, the graphene-systems performed better.

Figure 7.1 Ragone plot comparing performances of various material hybrids for supercapacitors ⁴⁷

- NiCo-C-1// N-doped CLS-derived carbon ASC: Energy density of 28.15 Wh Kg⁻¹ for a power density of 7.75 kW Kg⁻¹, $\Delta V = 0$ to 1.55 V
- GNi:Co 1:1// Pure Graphene hydrogel ASC- Energy density of 16.6 Wh Kg⁻¹ for a power density of 7.5 kW Kg⁻¹, $\Delta V = 0$ to 1.5 V

The biomass-derived systems were also tested for OER catalysis. The samples tested for OER gave good water oxidation kinetics, revealed by their low tafel slopes in the range of 107 mV dec⁻¹ and a low overpotential [η] of around 420 mV at a current density of 10 mA cm⁻². This shows the use of our biomass-derived materials for electrocatalysis and energy conversion applications further highlighting the possibility of green initiatives for energy and their commendable results.

7.2 Comparisons of all the supercapacitors assembled: Economic analysis and recommendations

We synthesised supercapacitors using these materials: Graphene, Manganese oxides, Polyaniline, Nickel Cobalt mixed oxides/nanoparticles and Coconut leaf-sheath-derived carbon. As explained in literature review, to arrange these in the order of their relative costs; coconut leaf sheath-derived carbon would be the cheapest, since it is a biomass-derived product, available in abundance in the areas of coconut plantations, in tropical and sub-tropical countries across the globe. Manganese oxides are earth abundant and environment-friendly and their relative costs are much lower compared with nickel, cobalt oxides, however, Nickel Cobalt oxides have higher theoretical capacitances, better electrical conductivities and better electrochemical stability compared to manganese oxides and polyaniline.^{8 7} In order to reduce the use of Ni, Co without compromising on the electrochemical performance and stability of the final product, we incorporated a highly optimised, conducting and high performing biomass-derived carbon with Ni Co NPs. This would reduce the final cost as it uses less Ni, Co than a product entirely built with Ni and Co products alone.

Table 7.1 Comparison of various types of supercapacitors assembled

Supercapacitors assembled	Main characteristics	Pros	Cons
Graphene-MnOx-Polyaniline system	1. 3-electrode setup, 955 Fg ⁻¹ at 1 Ag ⁻¹ , Capacitance retention- 89% after 1000 cycles in 1M Na ₂ SO ₄	1. Use of earth-abundant and cheap MnO ₂ and Polyaniline 2. Binder-free electrodes, neutral electrolyte Na ₂ SO ₄	1. Lower cyclic life and lower capacitance compared to Ni, Co-based materials 2. G.O preparation chemical intensive
Graphene/Ni-Co mixed oxide system	1. 3-electrode setup, 2870.8 Fg ⁻¹ at 1 Ag ⁻¹ 2. 2-electrode ASC setup Energy density 19 Wh Kg ⁻¹ for power density of 6 kW Kg ⁻¹ , Capacitance retention-81.1 % after 5000 cycles in 2M KOH electrolyte	1. Very high capacitance and cycle life 2. Binder-free electrodes	1. Ni, Co oxides/NPs more expensive than MnO ₂ and Polyaniline 2. G.O preparation chemical intensive.
Coconut leaf sheath derived -carbon/Ni, Co NP system	1. 3-electrode setup, 2471 F g ⁻¹ at 1 Ag ⁻¹ 2. 2-electrode ASC setup-Energy density 28.15 Wh Kg ⁻¹ for power density of 7.75 kW Kg ⁻¹ , Capacitance retention-76.6% after 5000 cycles in 2M KOH	1. Extremely cheap abundantly available biomass source-coconut leaf sheath. 2. Good substitute for graphene 3. Very high capacitance, high energy density and cycle life 4. Multi-functional- Good supercapacitor and Good OER kinetics	1. Binders added for electrodes 2. Labour-intensive- Sheath picking and sorting, from coconut farms

It is recommended that more cost-effective products like these replace the chemical-intensively produced materials like graphene, CNT etc. Also, the availability of the leaf sheath in abundance, the ease of its storage, transport and a large shelf life points to the easy ways by which the production can be upscaled. Moreover, the use of non-hazardous chemicals like urea in our synthesis and very easy pre-treatment steps for the leaf sheath would only make the scalability better. Researchers should try to bring greener chemical approaches and reduce the use of hazardous chemicals in their research. Sustainable starting materials

and use of biomass would take us a long way in dealing with the mounting environmental concerns owing to pollution, global warming etc. Efforts should also be made to have energy technologies available at a low cost, so that it will benefit people from all walks of life across the world.

7.3 Future work and perspectives

Supercapacitors have a lot of untapped potential as very fast energy storage systems due to their high-power densities, but limited energy densities make their large-scale entry to the commercial markets still very cumbersome. Firstly, it is imperative to find green solutions and synthesis techniques to find low cost, scalable and efficient carbon hybrid electrode materials for high power and high energy supercapacitors. Synthetic routes should be less chemical-oriented and less energy-intensive and more biomass-derived materials need to be developed to replace materials like graphene, carbon nanotubes etc, without compromising on the electrochemical storage performance. Use of higher performing carbon materials will reduce the use of the expensive metallic functionalities required for yielding a high pseudocapacitance.

Apart from improvements and developments in synthesis techniques, it is important to develop materials which can be easily upscaled for large scale practical applications. Recently, wearable electronics are finding a lot of attention. Supercapacitor materials which are flexible and stretchable, and which can be drawn in to yarn, have a lot of scope for powering wearable electronics. Electrolytes are an important part of a supercapacitor. Apart from improving and

testing electrode materials, importance should also be given to developing good solid-state electrolytes enabling larger voltage windows to make better devices with high energy densities.

Carbon-based hybrid material used in our Chapter 6 shows its multifunctionality by exhibiting good electrochemical performance as a supercapacitor material and as an efficient OER electrocatalyst. This highlights the importance of developing multi-functional materials and using them for diverse applications. In the current research arena, carbon-based materials are used for a wide range of applications as described in **Figure 7.2**.

Figure 7.2 Various applications for carbon-based hybrid material

The sluggish kinetics of electrocatalytic reactions where the reactions happen at nanoscale, the factors affecting fast-redox reactions and double-layer formation

in supercapacitors; all these require a strong understanding of the underlying interactions between the various molecular, atomic and sub-atomic moieties. This calls for more theoretical works to support and equip experimentalists, which could provide insights to foster better performances of materials for energy applications. For instance, hetero-atom doping, the contributions of various types of carbon-nitrogen, carbon-oxygen bonds etc, the mechanisms amounting to pseudocapacitance etc still need more clarity. More than a very specific topic-oriented study on a single material for a single application, it is imperative to incorporate a holistic approach to research works, which will enable the incorporation of these works or understandings drawn from them, for a multi-level and inter-disciplinary use. Hybrid vehicles incorporating the high-power density of supercapacitors with high-energy density of batteries are coming up for commercial use. Similarly, the rise of self-powered (electricity from fuel cells, stored in batteries/supercapacitors), self-sustaining water-electrolysers based on cost-effective, environmentally benign carbon-based material hybrids should not be far away.

Humans have vitiated ecological balance and human health in the haste of making discoveries and inventions for fulfilling their ever-increasing list of needs and wants. Carbon-based material hybrids, apart from energy applications can be effectively used for biological, biomedical and environmental applications. Non-toxic carbon-based hybrid materials will be at the forefront of future health-care systems by being useful in a plethora of diverse applications like ‘smart’ devices in regenerative medicine and tissue engineering (integrated with AI), ultra-fast

sensors which can react to their environments, controlled-drug delivery agents etc. Carbon-based materials can help to identify some of the causalities of environmental degradation and even address some of these issues; in identifying harmful pollutants like CO₂, NO_x, SO_x etc or removing harmful organic/inorganic substances like methylene blue, heavy oils etc. Gathering understanding and information from all these studies could further be used to create long-term and practical application-based multi-functional micro/nano-sensors for integrating more than one pressing issue like the detection of permissible levels of harmful substances percolating in our food chain, glucose sensors, the intensity of UV radiation, the humidity/wind speed changes to predict natural disasters like tsunami etc.

As human beings progress in to the future in all directions, it is important to incorporate a highly interdisciplinary approach to research.

APPENDIX-I Supplementary Information

Figure A1 a) SEM image of MnO₂ nanotubes, b) TEM image of MnO₂ nanotubes

Figure A2 a) XRD analysis plot of the pre-synthesised MnO₂, b) EDX spectra of PGM, c) EDX spectra of PGM- HCl, d) A typical PGM-HCl hydrogel

Figure A3 Charge Discharge plots at different current densities of a) PGM, b) PGM-HCl, c) PGM-HCl-2

Table A1: Comparison of our samples with the existing composites of Graphene/PANI/Mn₃O₄ or MnO₂

Reported By	Composite	Specific Capacitance	Binders used for electrode preparation	Capacitance retention
Our study	PGM-HCl	955 Fg ⁻¹ at 1 Ag ⁻¹	No	89% after 1000 cycles
	PGM-HCl-2	676.66 Fg ⁻¹ at 1 Ag ⁻¹		98% after 1000 cycles
	PGM	426 Fg ⁻¹ at 1 Ag ⁻¹		86% after 1000 cycles
Wang et al ¹⁴⁶	Sulfonated Graphene/Mn O ₂ /PANI	276 Fg ⁻¹ at 1 Ag ⁻¹	Yes	88.3% after 3000 cycles
Yu et al ⁹⁹	Graphene/Mn O ₂ /PANI (on 2D- graphene sheets)	755 Fg ⁻¹ at 0.5 Ag ⁻¹	Yes	87% after 1000 cycles
Ge et al ⁷⁹	Graphene/Mn O ₂	450 Fg ⁻¹ at 2 mV s ⁻¹	No	90% after 10000 cycles
Zhou et al ²¹⁰	Graphene/Mn O ₂ films	446 Fg ⁻¹ at 5 mVs ⁻¹	Yes	96% after 1000 cycles

Rakhi et al ³	CNT/Graphene/MnO ₂	308 Fg ⁻¹ at 20 mVs ⁻¹	Yes	90% after 5000 cycles
Yu et al ²⁷	3D Graphene network/PANI	751.3 Fg ⁻¹ at 1 Ag ⁻¹	No	93.2% after 1000 cycles
Zhou et al ²⁶	Graphene/PANI	250 Fg ⁻¹ at 0.5 Ag ⁻¹	Yes	73.7% after 1000 cycles
Wu et al ²¹¹	Graphene/Mn ₃ O ₄	271.5 Fg ⁻¹ at 0.1 Ag ⁻¹	Yes	100% after 20000 cycles
Raj et al ²¹²	Graphene/Mn ₃ O ₄	312 Fg ⁻¹ at 0.5 mA cm ⁻²	Yes	76% after 1000 cycles

Figure A4 XRD pattern of ZIF-67

Figure A5 Raman shift of pure graphene hydrogel (Pure G)

Figure A6 a) Rhombo dodecahedron shaped ZIF-67 crystals, b) Pure Co₃O₄ obtained by direct annealing of ZIF-67

Figure A7 a) GCD of Pure Co_3O_4 and b) CV of Pure Co_3O_4 in 2M KOH electrolyte

Figure A8 CV of a) Ni: Co-0.5:1, b) Ni: Co-1.5:1 in 2M KOH electrolyte

Table A2: I_d/I_g ratios of all samples

Name of the product	I_d/I_g
0.5M-700N	0.71
0.5M-700N-500C	0.79
P-700N-800C	0.81
0.5M-700N-800C	0.83
1M-700N-800C	0.88
2M-700N-800C	0.89

Figure A9:(a) Nitrogen adsorption isotherms of the samples synthesized at different experimental conditions, (b) Pore size distribution of samples using BJH (Barrett, Joyner, and Halenda method)

Table A3: BET surface areas of the samples

Name of the product	BET surface area (m ² g ⁻¹)
0.5M-700N	195.9
0.5M-700N-500C	324
0.5M-700N-800C	419
1M-700N-800C	434
2M-700N-800C	413
P-700N-800C	262

Figure A10: a) GCD curves, b) CV curves, both of Pure graphene hydrogel

Figure A11: a) GCD curves, b) CV curves, both of activated carbon

Figure A12: GCD curves for a) P-700N-800C, b) 0.5M-700N, c) 0.5M-700N-500C, d) 0.5M-700N-800C, e) 1M-700N-800C, f) 2M-700N-800C

Figure A13: CV curves for a) P-700N-800C, b) 0.5M-700N, c) 0.5M-700N-500C, d) 0.5M-700N-800C, e) 1M-700N-800C, f) 2M-700N-800C

Table A4 IR drop of the samples at 1 Ag⁻¹

Name of the product	IR drop (V) at 1 Ag ⁻¹
0.5M-700N	0.204
0.5M-700N-500C	0.081
0.5M-700N-800C	0.055
1M-700N-800C	0.117
2M-700N-800C	0.137
P-700N-800C	0.16

Table A5 Table showing the comparison of electrochemical performances of similar materials

Reported by	Material base	Specific capacitance (Fg ⁻¹)	Current density (Ag ⁻¹) / Scan rate (mV s ⁻¹)	Voltage window (V)	Electrolyte
Our study	Nitrogen doped graphitic carbon from coconut leaf sheath biomass	360.9	1 Ag⁻¹	0 to -1.1	2M KOH
Gharenkhani et al. ²⁰¹	Nitrogen doped activated carbon (oil palm fruit bunch biomass)	267	5 mV s ⁻¹	0 to -1	6M KOH
Li et al. ¹⁷⁸	Nitrogen doped activated carbon (corncoobs biomass)	185	0.4 Ag ⁻¹	2 to 4.5	Organic electrolyte

Dong et al. ¹⁷³	Nitrogen doped foam like carbon (pomelo peel biomass)	338	1 Ag ⁻¹	0 to 1	6M KOH
Ling et al. ⁵⁶	Boron/Nitrogen co-doped carbon (gelatin precursor)	358	0.1 Ag ⁻¹	0.2 to -0.7	1M H ₂ SO ₄
Sun et al. ⁶⁸	Porous graphene-like nano-sheets (Coconut shell biomass)	268	1 Ag ⁻¹	-0.2 to -1.1	6M KOH
Wang et al. ⁶⁷	Porous graphitic carbon nano-sheets (cornstalk biomass)	213	1 Ag ⁻¹	0.1 to -1.1	6M KOH
Qu et al. ²¹³	Nitrogen doped porous carbon (pomelo peel)	260	1 Ag ⁻¹	0.2 to -0.8	6M KOH
Wu et al. ²²	Sponge like carbonaceous hydrogel and aerogel (watermelon)	333.1	1 Ag ⁻¹	0 to -1	6M KOH
Cheng et al. ⁹	Carbon fibre aerogel (cotton)	283	1 Ag ⁻¹	-0.2 to -1.1	6M KOH
Long et al. ²¹⁴	Porous layer-stacking carbon (Fungus biomass)	339	1 Ag ⁻¹	0 to -1	6M KOH

Figure A14 Raman shift of 0.5M-700N-800C and 0.5M-700N-500C

Figure A15 a) Digital photograph of coconut leaf sheath, b) SEM image of 0.5M-700N-800C, c) SEM image of 0.5M-700N-500C

Figure A16 Particle size distribution of the TEM image in Figure 6.2e

Figure A17 a) GCD curves of 0.5M-700N-800C, b) CV curves of 0.5M-700N-800C, c) GCD curves of 0.5M-700N-500C, b) CV curves of 0.5M-700N-500C

APPENDIX- II List of publications

1. **Jayakumar, A.**; Yoon, Y.J.; Wang, R.; Lee, J.M., Novel graphene/polyaniline/MnO_x 3D-hydrogels obtained by controlled morphology of MnO_x in the graphene/polyaniline matrix for high performance binder-free supercapacitor electrodes, **RSC Advances** **2015**, 5 (114), 94388-94396, DOI:10.1039/C5RA16884H
2. R Wang, **Jayakumar, A.**, C Xu, JM Lee, Ni(OH)₂ Nanoflowers/Graphene Hydrogels: A New Assembly for Supercapacitors, **ACS Sustainable Chemistry & Engineering**, 2016, 4 (7), 3736-3742, DOI:10.1021/acssuschemeng.6b00362
3. **Jayakumar, A.**; Antony, R. P.; Wang, R.; Lee, J. M., MOF-Derived Hollow Cage Ni_xCo_(3-x)O₄ and Their Synergy with Graphene for Outstanding Supercapacitors. **Small** 13 (11) 2017, DOI:10.1002/smll.201603102
4. J Zhao, **Jayakumar, A.**, Y Yan, JM Lee, Cr-MIL-101-Encapsulated Keggin Phosphomolybdic Acid as a Catalyst for the One-Pot Synthesis of 2,5-Diformylfuran from Fructose, **ChemCatChem** 9 (7), 2017, 1187-1191, DOI:10.1002/cctc.201601546
5. **Jayakumar, A.**; J Zhao; Lee, J.M., Coconut leaf sheath- derived graphitised N-doped carbon network for high performance supercapacitors, **ChemElectroChem** 2017, DOI:10.1002/celec.2017011332/3
6. J Zhao; **Jayakumar, A.**; Hu Zhongting; Yan Yibo; Yang Yanhui; Lee J.M., MoO₃-Containing Protonated Nitrogen Doped Carbon as a Bifunctional Catalyst for One-Step Synthesis of 2, 5-Diformylfuran from Fructose, **ACS Sustainable**

Chemistry and Engineering,2017,DOI:10.1021/acssuschemeng.7b02408

7. J ZhaO; **Jayakumar, A**; Lee J.M., Bifunctional Sulfonated MoO₃-ZrO₂ Binary Oxides Catalysts for the One-Step Synthesis of 2, 5-Diformylfuran from Fructose, **ACS Sustainable Chemistry and Engineering** 2018, DOI:10.1021/acssuschemeng.7b02671

8. **Jayakumar, A**; Antony, R.P, J Zhao, Lee J.M,MOF-derived nickel and cobalt metal nanoparticles in a N-doped coral shaped carbon matrix of coconut leaf sheath origin for high performance supercapacitors and OER catalysis, **Electrochimica Acta** **2018**, DOI:10.1016/j.electacta.2018.01.210

APPENDIX III Table of Figures

Figure 1.1 Specific power against specific energy for different energy storage systems (Ragone plot). Times shown (the time constants of the devices) are obtained by dividing the energy density by the power.	4
Figure 2.1 A half-cell is shown to the left with electrolyte and electrode, in the middle a magnification of the electrode showing mesopores where the ions in the electrolyte (orange) can move freely. To the right the ions forming the double layer is shown	15
Figure 2.2 Mechanism of charge transfer in a) EDLC, explaining the electrostatic charge storage mechanism without any charge transfer b) pseudocapacitors, explaining the faradaic charge-transfer of the pseudocapacitance	17
Figure 2.3 Schematic sketch of different approaches to advance the energy density of a supercapacitor.	18
Figure 2.4 Schematic showing the self-assembly of 3D-graphene hydrogels from graphene oxide solution via a one-step hydrothermal reduction reaction	22
Figure 2.5 a) Photographs of a typical GN-GH using GO and ethylenediamine (100 mL) as precursors after hydrothermal process at 180 °C for 12 h, (b) SEM image of the typical GN-GH microstructures, (c) magnified SEM image of the typical GN-GH microstructures.....	23
Figure 2.6 (a–c) SEM images of NiOOH/GS hydrogel after vacuum freeze drying, prepared via a solvothermal reaction , d) XRD spectra of various hydrogel samples prepared in different DMF:H ₂ O ratios e) A digital photograph of NiOOH/GS hydrogels.....	24
Figure 2.7 Morphology and formation mechanism of the cork-like graphene elastomer. (a–c) Typical top-view (a,b) and side-view (c) SEM images of graphene monolith of 5.10 mg cm ⁻³ . Scale bars, (a,c) 50 mm and (b) 10 mm, (d) Schematic showing the formation mechanism of the cork-like monolith by freeze casting. Photos of the corresponding samples are presented in the insets	24
Figure 2.8 A) Schematic representation for the synthesis of Ni-MnO/ rGO aerogels via cross-linking polymer assisted hydrogel formation, b) FT-IR spectra of GO, PVA, and GO PVA aerogels. c) Schematic interaction between PVA and GO. d) XRD patterns of GO, PVA, and GO–PVA aerogels. B) Morphological and structural characterizations of Ni–MnO/rGO aerogels: a, b) SEM images; c, d,) TEM images at different magnifications e) HRTEM image; f) STEM image.....	26

Figure 2.9 (a) Thermal melting curve of dsDNA monitored by absorption spectrum and temperature-dependent curve of storage modulus (G') of SH recorded during rheological test; (b) 514 nm excited Raman spectra of GO (black), GO/ds DNA mixture before heating (red), and GO/DNA SH (blue). c) Schematic representation for the synthesis of Ni-MnO/ rGO aerogels via cross-linking polymer assisted hydrogel formation.	28
Figure 2.10 a) Optical microscope image of the emulsion made from the mixture of 2 mL hexane and 4 mL 5 mg mL ⁻¹ GO dispersion. b, c, d) Cross-sectional SEM images of MGM-5 at different magnifications; e) Cross-sectional SEM image of G-Aerogel-5. f) Photographs of MGM-5 (left) and G-Aerogel-5 (right) g) Schematic illustration of the preparation of an MGM	29
Figure 2.11 a) Photographs of the carbonaceous hydrogel monoliths with different volumes and the corresponding carbonaceous aerogel block, (b, c) SEM images, (d, e) TEM images of the carbonaceous gels	32
Figure 2.12) Schematic synthesis of Ni/NiO/NiCo ₂ O ₄ /N-CNT as electrocatalysts.	33
Figure 2.13 a) SEM image of CF (b) digital photo of aCF-6 before and after manual compression (c-e) SEM images of aCF-6 f) with different magnifications and electrical conductivity of CF and aCF measured by a standard four-probe method.	34
Figure 3.1 XRD pattern of PGM, PGM-HCl	52
Figure 3.2 a) SEM image of freeze dried PGM- HCl hydrogel, b) TEM image of PGM hydrogel c) TEM image of PGM hydrogel, d) & e) TEM image of PGM-HCl hydrogel at higher magnification	53
Figure 3.3 a) FTIR spectra of PGM, PGM-HCl at lower wavenumber, b) FTIR spectra of PGM, PGM-HCl at higher wavenumber	56
Figure 3.4 XPS spectra of various elements in PGM-HCl, a) C 1s, b) O 1s, c) N 1s, d) Mn 2p	57
Figure 3.5 Electrochemical tests conducted in a 3-electrode system using 1 M Na ₂ SO ₄ electrolyte with Pt electrode as counter electrode and Ag/AgCl as the reference electrode a) Charge discharge measurements of PGM, PGM-HCl, PGM-HCl-2 as working electrodes at 1 A g ⁻¹ , b) Specific Capacitance vs Current density data of PGM, PGM-HCl, PGM-HCl-2 as working electrodes, c) Capacity Retention Vs Number of cycles data for PGM, PGM-HCl and PGM-HCl-2 as working electrodes at 20 A g ⁻¹ , d) Ragone plot for PGM, PGM-HCl and PGM-HCl-2 as working electrodes	62

Figure 3.6 Electrochemical tests conducted in a 3-electrode system using 1 M Na ₂ SO ₄ electrolyte with Pt electrode as counter electrode and Ag/AgCl as the reference electrode a) CV curves of PGM-HCl as working electrode at various scan rates, b) CV curves of PGM as working electrode at various scan rates, c) CV curves of PGM and PGM-HCl compared at 10 mVs ⁻¹	64
Figure 4.1 Schematic representation of the GNi:Co 1:1 synthesis technique	71
Figure 4.2 XRD spectra of a) the mixed oxides and pure Co ₃ O ₄ , b) GNi:Co 1:1 and Ni:Co 1:1, Raman spectra of c) Ni:Co 1:1, Ni:Co 0.5:1, Ni:Co 1.5:1, d) Raman spectra of GNi:Co 1:1 and Ni:Co 1:1	76
Figure 4.3 SEM images of a) Ni:Co 0.5:1 with inset showing a magnified image of a smooth surfaced shell, b) Ni:Co 1:1 at lower magnification, c) Ni:Co 1:1 with inset showing a magnified image of the hollow spherical cage with a thin shell of dendrites-like surface protrusions ,d) Ni:Co 1.5:1 with inset showing the magnified image of the structure with a thickened covering of surface protrusions, e) the porous magnified structure of freeze-dried GNi:Co 1:1, f) the magnified image of a wave like graphene layer in GNi:Co 1:1 embedded with the Ni:Co 1:1 nanoparticles.....	78
Figure 4.4 TEM images of a) Ni:Co 1:1 and b) GNi:Co 1:1	80
Figure 4.5 XPS spectra of GNi:Co 1:1 with a) survey scan, b) Ni 2p scan, c) Co 2p scan, d) C 1s, e) O 1s scan	80
Figure 4.6 GCD graphs of a) Ni:Co 0.5:1, b) Ni:Co 1:1, c) Ni:Co 1.5:1, c) GNi:Co 1:1 in 2M KOH electrolyte.....	82
Figure 4.7 a) CV of Ni:Co 1:1, b) CV of GNi:Co 1:1, c) Specific capacitances of Co ₃ O ₄ , Ni:Co 0.5:1, Ni:Co 1:1, Ni:Co 1.5:1 and GNi:Co 1:1 calculated from GCD curves over current density.	83
Figure 4.8 a) log (v) vs log (i) plot to verify the linearity of current on scan rate and for calculating b values, b) obtained b-values vs potential for a cathodic scan, c) plot of v ^{0.5} vs iv V ^{0.5} for obtaining k1 and k2 values at various potentials in the cathodic sweep, d) Percentage split up of capacitance in to surface capacitive effects and diffusion controlled intercalation contributions.	85
Figure 4.9 a) GCD plot, b) CV graph , c) Specific capacitance vs current density; all of pure graphene hydrogel (negative electrode) all in 2M KOH electrolyte	89

Figure 4.10 a) GCD graph of the ASC GNi:Co 1:1// Pure G, b) CV plot of ASC GNi:Co 1:1// Pure G, c) Specific Capacitance of ASC GNi:Co 1:1// Pure G vs current density, d) cyclic stability of ASC GNi:Co 1:1// Pure G, all in 2M KOH electrolyte	90
Figure 4.11 Ragone Plot of a) Our work ASC GNi:Co 1:1// Pure G, b) Co_3O_4 // 3D P.C ¹²⁶ , c) $\text{Ni}(\text{OH})_2$ //A.C ⁴⁴ , d) NiO //Reduced graphene oxide ¹⁵⁸ , e) Aluminium substituted Nickel hydroxide($\text{Ni}(\text{OH})_2$) //A.C ¹⁶⁰ , f) Graphene-Multi-walled carbon nanotubes- MnO_2 composite // Graphene-Multi-walled carbon nanotubes ¹⁶¹	90
Figure 5.1 a) A 0.5M urea-dipped CLS piece, b) A 0.5M urea-dipped CLS piece after N_2 annealing and CO_2 activation, c) Powdered 0.5M-700N-800C, b- Different parts of the CLS fibre	98
Figure 5.2 a) XRD pattern of all samples, b) Raman shift of all samples	104
Figure 5.3 SEM images of a) Pure sheath, b) P-700N-800C, c)0.5M-700N, d)0.5M-700N-500C, e) 0.5M-700N-800C, f) 1M-700N-800C, g)2M-700N-800C, h) HRTEM image of 0.5M-700N-800C	107
Figure 5.4: XPS spectra of 0.5M-700N-800C with a) Survey scan, b) C1s spectra, c) O 1s spectra, d) N 1s spectra.....	110
Figure 5.5 a) CV of all samples at 10 mVs^{-1} , b) GCD of all samples at 1 Ag^{-1} c) Specific capacitance Vs Current density, d) Capacitance retention- for all samples including commercial activated carbon (AC) and pure graphene hydrogel (Pure G) for comparison	115
Figure 6.1 a) XRD spectra of the samples, b) Raman spectra of the samples.	128
Figure 6.2 SEM image of a) NiCo-C-1 lower magnification, b) NiCo-C-1 with higher magnification inset c) NiCo-C-2, d) NiCo-C-3, e) TEM image of NiCo-C-1 with a zoomed inset.	130
Figure 6.3 XPS spectra of NiCo-C-1 with a) C 1s scan, b) O 1s scan, c) N 1s scan, d) Co 2p scan, e) Ni 2p scan.....	133
Figure 6.4 a) CV curves of NiCo-C-1, b) GCD curves of NiCo-C-1, c) CV curves of NiCo-C-2, d) GCD curves of NiCo-C-2, e) CV curves of NiCo-C-3, f) GCD curves of NiCo-C-3.	137
Figure 6.5 a) Overlap of CV curves of NiCo-C-1, NiCo-C-2 and NiCo-C-3, b) overlap of GCD curves of NiCo-C-1, NiCo-C-2 and NiCo-C-3, c) specific capacity vs current density of NiCo-C-1, NiCo-C-2 and NiCo-C-3, d) Cycle life of NiCo-C-1, NiCo-C-2 and NiCo-C-3 and an inset showing their Nyquist plots.	138

Figure 6.6 a) CV curves of ASC NiCo-C-1//0.5M-700N-800C, b) GCD curves of ASC NiCo-C-1//0.5M-700N-800C, c) Specific capacity vs current density of ASC NiCo-C-1//0.5M-700N-800C with an inset showing its cycle life, d) Ragone plot comparing our ASC NiCo-C-1//0.5M-700N-800C with Ni(OH)₂//A.C⁴⁴, NiO//3D R.G.O¹⁵⁸, CBC-N2@LDH-0.4//CBC-N2¹⁰³, Ni_xCo_{3-x}O₄ NW//A.C¹⁰⁸, Ni-Co_{1.5}-O//RGO @ Fe₃O₄¹¹⁰, D-NiCo₂O₄//A.C⁴⁶, e) Nyquist plot of ASC NiCo-C-1//0.5M-700N-800C with an inset showing the high frequency region. 140

Figure 6.7 a) LSV of samples, b) potential versus log(*J*) plot. 143

Figure 7.1 Ragone plot comparing performances of various material hybrids for supercapacitors
..... 149

Figure 7.2 Various applications for carbon-based hybrid material 153

APPENDIX IV Abbreviations

3D-	Three-dimensional
APS-	Ammonium persulfate
ASC-	Asymmetric Supercapacitor
BET-	Brunauer–Emmett–Teller
BJH-	Barrett–Joyner–Halenda
CF-	Carbon Fibre
CLS-	Coconut Leaf Sheath
CNT-	C carbon Nanotubes
CV-	Cyclic Voltammetry
D.I-	De-ionised water
DNA-	Deoxyribo nucleic acid
DMF-	N, N-dimethylformamide
EC-	Electrochemical Capacitors
EDLC-	Electrochemical Double Layer Capacitors
EDX-	Energy Dispersive X-ray Spectroscopy
EIS-	Electrochemical Impedance Spectroscopy
FTIR-	Fourier Transform Infrared Spectroscopy
GCD-	Galvanostatic Charge Discharge measurements
G.O-	Graphene oxide
LSV-	Linear Sweep Voltammetry
MGM-	Microporous Graphene Monoliths
MOF-	Metal Organic Frameworks
NMP-	N-methyl Pyrrolidone
OER-	Oxygen Evolution Reaction
PANI-	Polyaniline
PGM-	Polyaniline-Graphene-Manganese oxide
PPy-	Polypyrrole

PVA- Polyvinyl alcohol
PVDF- Polyvinylidene Fluoride
PVP- Poly Vinyl Pyrrolidone
PSD- Pore Size distribution
 R_{ct} - Charge Transfer Resistance
rG.O- Reduced Graphene Oxide
RHE- Reversible Hydrogen Electrode
SEM- Scanning Electron Microscope
SSA- Specific Surface Area
TEM- Transmission Electron Electroscope
XPS- X-ray Photoelectron Spectroscopy
XRD- X-ray diffraction
ZIF- Zeolite Imidazole Frameworks

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