

Multifunctioning Electrocatalytic Cathodes for Lithium-Air and Lithium-Oxygen Batteries

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ABSTRACT

Despite its historical success, currently, the limited energy density in Li-ion batteries restricts the electrifying of transportation into small and medium-scale vehicles. On the contrary, Li-O₂ batteries (LOBs) and Li-air batteries (LABs) with larger theoretical energy density are capable of powering heavy-duty transportation, given they overcome the sluggish oxygen kinetics. One of the possible ways to achieve this goal is by introducing novel bifunctional electrocatalysts at the battery cathode, enhancing the cycle life and the discharge capacity of the LABs and LOBs via promoting oxygen reaction kinetics. My PhD study is focused on developing transition metal derivative-based novel bifunctional catalysts to achieve superior charge densities and cyclability in LABs with relatively lower expenses. Following the mentioned rationale, self-standing cathode structures were developed by grafting binary oxide of NiCo₂O₄, sulfide of NiCo₂S₄, phosphide of NiCoP, and their heterogeneous phases on Ni foam. During the study, different physicochemical, morphological, and electrochemical analytical techniques were analysed to determine the suitability of the synthesised materials for catalysing oxygen kinetics. The performance of developed cathode structures was mainly assessed by cycling the assembled aprotic LABs with different current ratings, while CV and EIS studies were also conducted to obtain a further understanding of the battery performance. The examined strategy of optimization of eg-orbital occupancy in binary metal oxides through stoichiometric adjustments was found to be effective in enhancing the electrocatalytic activity in binary oxides. During the study, the highest discharge capacity of 25162 mAgh⁻¹ at a current density of 400 mAg⁻¹ was obtained for the heterogeneous hollow catalytic microstructure of NiCoP/ NiCo2S4/ NiCo2O4. The in-situ synthesized NiCo₂O₄/ NiCoP hybrid structure lasted exceeding 400 cycles at a current density as high as 800 mAg⁻¹ highlighting the success of the study advancing beyond the state-of-theart knowledge. In both cases, morphology and the orientation of the discharged Li_2O_2 were able to be altered through the modulation of the electronic structure of the catalyst, allowing undisturbed diffusion of Li+ towards the cathode, allowing high discharge depths and extended cyclability.

LIST OF PUBLICATIONS

Journal publications exclusively related to this thesis:

- Shadeepa Karunarathne, Chanaka Sandaruwan, François Orange, Yasun Y. Kannangara, Alice Mija, Ali Reza Kamai, Amr M. Abdelkader, "Tri-phase heterogeneous electrocatalysts of Ni and Co for high-performing Li-O₂ batteries", *EcoMat*, Volume 7, 3, 2025, <u>https://doi.org/10.1002/eom2.70002</u>
- Shadeepa Karunarathne, Gabriel E. Pérez, W.P.S.L. Wijesinghe, François Orange, Yasun Y. Kannangara, Chirag R. Ratwani, Chanaka Sandaruwan, Alice Mija, Ali Reza Kamai, Amr M. Abdelkader, "Hetero-nanostructured NiCoP/NiCo2O4 for sustainable Li-O₂ battery operation through optimised discharged product morphology", (In Production- *Journal of Material Chemistry A*)
- 3. Shadeepa Karunarathne, Yasun Y. Kannangara, Chirag R. Ratwani, Chanaka Wijesinghe, Sandaruwan. W.P.S.L. Ali Kamali. Amr M. Abdelkader. "Stoichiometrically optimized eg orbital occupancy of Ni-Co oxide catalysts for Li-air Nanoscale, Volume 16. 2024, Pages batteries", 7937-7950, https://doi.org/10.1039/D4NR00518J
- 4. Shadeepa Karunarathne, Chamali K. Malaarachchi, Amr M. Abdelkader, Ali Reza Kamali, "Advances in bifunctional electrocatalysts towards high-performing Li-air batteries", *Journal of Power Sources*, Volume 607, 2024, Pages 234553, <u>https://doi.org/10.1016/j.jpowsour.2024.234553</u>

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- Chirag R. Ratwani, Shadeepa Karunarathne, Ali Kamali, Amr M. Abdelkader, "Transforming Nature's Bath Sponge into stacking faults enhanced Ag Nanorings decorated Catalyst support for Hydrogen Evolution Reaction", ACS Applied Materials & Interfaces, Volume 16, 2024, Pages 5847-5856, <u>https://doi.org/10.1021/acsami.3c16115</u>
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- 8. Shadeepa Karunarathne et al. "Rapid Exfoliated GNP and 2D-Silica for High Performing Concrete", Graphene Week (2022), Munich, Germany

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List of Abbreviations

ALD	Atomic layer deposition		
CB	Carbon black		
CNF	Carbon nanofiber		
CNT	Carbon nanotube		
CV	Cyclic voltammetry		
СТ	Carbon textile		
CVD	Chemical vapor deposition		
DBBQ	di-tert-butyl-1,4-benzoquinone		
DFT	Density function theory		
GDL	Gas diffusion layer		
GNP	Graphene nanoplatelets		
GO	Graphene oxide		
HER	Hydrogen emission reaction		
LAB	Lithium-air battery		
LIB	Lithium-ion battery		
LOB	Lithium-oxygen battery		
LSV	Linear sweep voltammetry		
MAB	Metal-air battery		
NCO	Nickel cobalt oxide		
NCP	Nickel cobalt phosphide		
NCS	Nickel cobalt sulfide		
NP	Nanoparticle		
NS	Nanosheet		
OER	Oxygen evolution reaction		
OLC	Onion-like carbon		
ORR	Oxygen reduction reaction		
PBA	Prussian blue analogues		
PDA	Polydopamine		
PTFE	Polytetrafluoroethylene		
PVD	Physical vapor deposition		
rGO	reduced graphene oxide		

RRDE	Rotating ring disk electrode		
SAXS	Small-angle X-ray spectroscopy		
SEI	Solid-electrolyte interface		
SEM	Scanning electron microscopy		
TEM	Transmission electron microscopy		
TEMPO	tetramethylpiperidinyloxyl		
ТМО	Transition metal oxide		
TMN	Transition metal nitride		
TMP	Transition metal phosphide		
TMS	Transition metal sulphide		
XPS	X-tray photon spectroscopy		
XRD	X-ray diffractometry		

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I would like to express my gratitude to my parents, who have always stood by me throughout my life. I would never have gone so far without their selfless dedication and unwavering belief.

Finally, I would like to thank everyone important to the success of my PhD study at Bournemouth University.

XXIII

Dedication

To my beloved wife, Eshani Fernando.

Your unwavering belief in my potential was the spark that encouraged me to embark on this challenging journey. Thank you for being my steadfast supporter, my motivator, and my source of strength during every stage of this PhD. Your patience, sacrifices, and endless encouragement made even the most difficult moments bearable. This accomplishment is as much yours as it is mine, and I am forever grateful for your love and dedication.

With all my heart, thank you.

Chapter 1: Introduction

1.1. General Background

Fossil fuels have met the majority of energy requirements over the last century, significantly elevating human living standards. However, the ongoing reliance on fossil fuels must be curtailed, not only due to resource depletion but primarily because of the environmental harm it inflicts through global warming, air pollution, and other factors. Consequently, there is an urgent call for scientific and technological advancements to develop advanced energy storage systems with high efficiencies and minimal or zero carbon emissions. This is crucial for maximizing the utilization of energy generated from renewable sources [2,3].

Lithium-ion batteries (LIBs) currently stand as the most widely used energy storage devices, already serving as an essential component of daily human life by powering numerous consumer electronics and communication devices. Furthermore, LIBs can be recognized as the most successful electrochemical energy storage technology in history. Despite their historical success, LIBs are currently facing challenges in meeting the necessary energy storage demands to achieve the ambitious goal of electrifying transportation. This entails replacing gasoline engines in automobiles with packs of secondary batteries. The limited gravimetric energy density in commercial LIBs (≈200 Wh kg⁻¹) hinders their effective use for long-range drives in medium to heavy vehicles [4,5]. The current bottleneck resides in the cathode, where the commonly used graphite anode has a capacity of 372 mAh g⁻¹, while the most advanced nickel-rich layered NMC (LiNi_xCo_yMn_zO₂, x≥0.8) cathodes can only achieve capacities up to 240 mA h g⁻¹ [6]. Other developments in LIBs such as Li-rich or Mn-rich NMC cathodes, Si-coated graphite anodes, and Li metal chips as anodes report suffering from respective issues related to electrolyte instability, unstable SEI formation, and safety concerns [7,8]. Consequently, significant advancements in LIB technology in terms of capacity are challenging to anticipate shortly.

According to the calculations made by the International Energy Agency (IEA), the usage of energy storage devices increased by 2023. The demand expected to grow exponentially, with global requirements forecasted to exceed 2.5 TWh by 2030 and potentially reaching 15 TWh by 2050, driven primarily by electric vehicles (EVs), renewable energy integration, and grid storage [9–11]. A projected lithium supply of 2,348 kt will be required by 2030 to meet the anticipated demand. However, even with the most optimistic growth in the lithium supply chain, a substantial supply shortfall is anticipated, along with the potential for an exponential increase in lithium prices from the current range of \$25–30/kg [10]. Hence, with energy densities ranging from 150–250 Wh/kg, and with the above-mentioned limitations, it's a steep task for LIBs to meet the forecasted demands. To meet future demands, especially for heavy-duty applications and long-duration storage, advanced battery chemistries with higher energy densities (>400 Wh/kg) and reduced environmental impact will be essential. These factors, coupled with the projected increase in energy demand [9–11], exert substantial pressure on battery researchers to advance battery technology beyond LIBs.

1.2. Emerging Battery Technologies

With concerns about potential shortages in lithium resources, the exploration of other metalion battery technologies has gained momentum in recent times, with sodium-ion batteries, in particular, making substantial progress [12]. Alongside metallic anodes, oxygen, and sulfur cathodes have demonstrated the capability to deliver higher energy densities within a broader operational window compared to metal-ion batteries [13,14]. Metal-sulfur batteries represent an intriguing field of research, with lithium-sulfur (Li-S) battery technology identified as the most mature technology beyond LIBs [15,16]. However, despite their promising progress, challenges related to polysulfide shuttling, currently hinder the commercialization of Li-S batteries. In this context, it is anticipated that metal-air batteries (MABs) have the potential to emerge as pivotal contenders, demonstrating significant promise as a battery technology poised to achieve substantially higher theoretical energy densities ranging from 500 to 3500 Wh kg⁻¹ [17]. This positions MABs in proximity to the energy density levels of fossil fuels (13,000 Wh kg⁻¹) [18], signifying their potential to approach comparable performance.

1.3. Li-air batteries, and associated challenges

Currently, most studies are focusing on developing an efficient Li-air battery (LAB) system mainly due to its very high theoretical energy density of 3500 W h kg⁻¹ during discharge and 11 600 W h kg⁻¹ during charging [19], which is an order of magnitude higher than the current delivery of existing LIB technology. Therefore, the LAB technology is predicted to be the main energy source for future electronic devices, electric vehicles, and grid storage [20]. However, despite these promising features, LABs are not commercially available, mainly due to technical issues related to their short cycle life and discharge capacity, owing to poor oxygen kinetics at the battery cathode and fast degradation of cathode and electrolytes as exposed to reactive species generated during the charging and the discharging steps.

Batteries	Theoretical Voltage (V)	Theoretical specific capacity (A h kg ⁻¹)	Theoretical energy density (kW h kg ⁻¹)	Practical operating voltage (V)
Zn–air [15]	1.65	658	1.35	0.5–1.6
Mg–air [30]	1.81	920	6.81	0.5–2.5
Na-air [31]	2.27/2.33	487/687	2.65	1.5-4.5
K-air [32]	2.48	377	1.70	1.5-3.0
Fe-air [33]	1.3	300	1.13	0.3- 1.6
Al-air [16]	1.2	1030	8.1	0.5–1.6
Li–air [34]	2.91	1170	11.6	2.4-4.3

A LAB mainly consists of a lithium anode, an electrolyte, and a porous cathode. Its working mechanism is based on the successive lithium oxidation and reduction at the anode, accompanied by the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) at the cathode during the discharge and charge processes, respectively unless redox mediators are involved [21]. Figure 1.1 illustrates this schematic outlook of the Li-air battery and its mechanism.

As mentioned, the sluggish oxygen kinetics (ORR and OER) at the cathode is one of the main causes of the poor performances of LABs [22]. Additionally, the decomposition of the cathode and electrolyte as exposed to various reactive oxygen species such as superoxide radicals, singlet oxygen radicals, and other protonated radicals is another cause for the fast decay in LAB performances [23,24]. Therefore, the selection of both the electrolyte and cathode material, along with the architecture of the latter, is crucial in defining the underlying reaction mechanism for battery operation. While properties of electrolytes, such as ionic conductivity, donor number (DN), stability, and electrochemical window, are important factors in determining cell performance, the characteristics of cathodes, including their conductivity, surface area, pore size/volume, and, more importantly, the affinity of the cathode surface for oxygen and reduced oxygen species, are also critical in determining LAB performance and governing mechanisms.



Figure 1.1: Schematic diagram of a typical Li-Air Battery.

1.4. Aims and Objectives

My doctoral studies were aimed at upgrading the performances in Li-air and Li-O₂ batteries by developing highly efficient battery cathodes through the incorporation of advanced bifunctional catalysts.

The following objectives were planned to be achieved by the completion of the research.

- Understand of role of the catalysts in LABs and develop strategies to overcome the shortcomings in existing technologies.
- Design and engineer a suitable environment (test bed) for characterizing LAB performances.
- Obtain a high-performing transition metal oxide-based electrocatalysts suitable for LABs through d-orbital electron occupancy modulation via optimizing the synthesis parameters.
- Convert the transition metal oxides to respective phosphides, sulfides, and their heterogeneous structures to yield superior LAB performances via faster charge-transferring kinetics in the synthesized semiconducting catalysts.

As this research focuses on developing effective catalytic cathodes, to simplify the battery systems and reduce potential complexities, pure O₂ gas was used in some of the studies instead of air. While the primary reactions remain unchanged, batteries operating under these conditions are referred to as Li-O₂ batteries (LOBs).

1.5. Outline of the thesis

A summary and the scope of the individual chapters of the doctoral dissertation is given below.

Chapter 1 provides a general introduction to emerging battery technologies and discusses more specific challenges associated with Li-air battery technology. An introduction to the aims and objectives of my doctoral studies was also provided in the chapter.

2nd chapter is focused on discussing the fundamentals of Li-air battery technology and historical developments, working mechanisms and side reactions, advantages and shortcomings in state-of-the-art catalyst technologies, and the opportunities in developing high-performing electrocatalysts and associated challenges.

Chapter 3 provided details on the chemicals and experimental techniques used during the doctoral studies. Methods used during the material synthesis, material analysis, battery assembly, and electrochemical analysis were discussed individually for better clarity.

Chapter 4 introduces an alternative simple strategy for modulating e_g orbital occupancy of binary metal oxide catalysts to obtain superior Li-air battery performances. During the study, an optimal d-band electron structure was obtained by optimizing the stoichiometric ratio in Ni: Co oxides by controlling the hydrothermal reaction conditions. The assembled LAB cells employing this cathode demonstrate an exceptional lifespan, operating for 3,460 hours and completing 173 cycles while achieving the highest discharge capacity of 13,759 mAhg⁻¹ and low charging overpotentials.

Chapter 5 introduced the study on the groundsel flower-like hierarchical microsphere network of NiCoP/NiCo₂O₄. The material was synthesized by in-situ grafting the microstructures on a nickel foam. Benefiting from the surface electron transfer through heterogeneous surface phases of NiCoP and NiCo₂O₄, enhanced oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics were observed. The assembled LOB cells demonstrated an exceptional lifespan, withstanding over 400 cycles under a very high charge rate of 800 mAg⁻¹ while achieving the highest discharge/ charging capacities of 15710/ 14632 mAh g⁻¹ at 100 mAg⁻¹ and low charging overpotentials. Interestingly, the discharge capacity was only reduced by 10% to 14092 mAh g⁻¹ even after the charge rate increased by 6 times, where the capacity of the studied pure metal phosphide and metal oxide cathodes faded substantially.

Chapter 6 discusses the undertaken approach to improve the catalytic performances in binary transition metal sulfide catalysts by hybridizing the structure with corresponding phosphide and oxide phases. The introduced tri-phase heterogeneous catalyst containing the phases of NiCoP, NiCo₂S₄, and NiCo₂O₄ assembled into a hierarchical hollow-microstructure architecture was found to be efficient in modulating the discharge product morphology and the orientation, facilitating the sheets-like growth of Li₂O₂ perpendicular to the surface of the cathode. The properties of the discharge product support the assembled batteries to reach deeper discharge depths recording 25162 mAhg⁻¹ at 400 mAg⁻¹, and an impressive cyclability of 270 cycles at 400 mAg⁻¹ under a limited discharge depth of 1000 mAhg⁻¹, exceeding 1350 hours of continuous operation. In comparison, the heterogeneous catalytic system produced at least thrice and twice high respective specific capacity and cyclability than the LOBs assembled with the individual catalytic structures integrated at the heterogeneous catalyst. The presence of individual electrophilic and nucleophilic phases within the heterogenous microstructure is supposed to promote the sheet-like growth of Li₂O₂.

Chapter 7 provides an overall comparison of the electrocatalytic performances of the derived catalytic structures. Certain perspectives provide future research directions based on the conclusions made at the end of the doctoral studies.

References are followed by the introduced main chapters.

Chapter 2: Literature Survey

The literature review covers a wide range of topics, offering an in-depth discussion on fundamentals and historical developments, battery configurations, operational mechanisms, parasitic reactions, catalytic cathodes, as well as perspectives and existing research gaps. Some sections of the literature survey are based on one of my first author publications, a recently published review article titled "Advances in bifunctional electrocatalysts towards high-performing Li-air batteries", published in the Journal of Power Sources [25].

2.1. Introduction to Li-Air Battery and Historical Developments

A LAB cell contains a lithium anode, an air cathode, a membrane separator, and an electrolyte [26]. Even though different combinations of materials were experimented to improve the LAB performances, the basis categorization of Li-air batteries was made based on the electrolyte. Hence LABs are distinguished by the four different types of electrolytes: aqueous, non-aqueous (aprotic organic solvents or ionic liquids), hybrid of aqueous and non-aqueous engineered configuration, and all-solid-state electrolytes [27].

Li-air battery technology has now matured nearly three decades since its first discovery. It should be mentioned that Abraham et al [28] invented the Li-O₂ batteries in 1996 as O₂ was accidentally pumped into a Li-graphite cell. It took another decade to unravel the basic electrochemistry of the Li-O₂ batteries, where J. Read, D. Foster, P.G. Bruce, and T. Ogasawara made substantial early contributions.[29,30] Early research on LABs used alkali carbonates-based aprotic electrolytes with the influence of the already developed LIB technology. However, the batteries failed to cycle over 100 cycles maintaining full coulombic efficiency, and the reported charging overpotentials were very high. The findings related to the instability of carbonates against the discharge products such as LiO₂ and Li₂O₂, subjecting the electrolytes to nucleophilic attack by the reduced oxygen species forming Li₂CO₃ as a non-reversible product, well explained the mentioned observations [31,32].

2.2. Li-Air Battery Configuration

The above-mentioned components of lithium anode, air cathode, membrane separator, and electrolyte are assembled to produce the Li-air battery electrochemical system. The following section will discuss the main responsibilities, and state-of-the-art developments in fabrication and material selection, providing directions to address the critical challenges justifying their utilization in LABs.

2.2.1. Electrolyte

The electrolyte is a key component in Li-air/Li-O₂ technology, determining the operational window and the associated reaction mechanisms involved in energy storage and release. An ideal electrolyte is expected to have all the required features, including high ionic conductivity with suitable viscosity and polarity, allowing ions to move without much hassle and enabling a sufficient amount of salts to dissolve in the solvent. Other desirable characteristics include appropriate stability against reactive species in the system, without any side reactions occurring, stability in the electrolyte for the full operational window of the electrochemical system, allowing all the necessary reactions to take place, and low volatility, high purity, and flame retardancy, ensuring safe operation [33,34].

The experimental and theoretical studies conducted to date favour aprotic electrolytes, in which the presence of a Li salt in combination with other additives satisfies most of the mentioned criteria, whereas, in contrast, fast corrosion of the Li anodes remains as major drawback against aqueous LABs raising concerns against the stability and the safety of the batteries [35]. The hybrid systems aim to protect the Li anode by placing an additional solid-state, or aprotic electrolyte next to the Li anode and utilizing an aqueous electrolyte towards the cathode terminal. Despite numerous efforts with several polymer and ceramic conductive membranes [36] and hybrid electrolyte architectures [37], none of the techniques have yet reached the expected success. In addition, there has been great enthusiasm in the last few

years toward solid-state electrolytes in the overall battery community, including LABs [38,39]. However, in addition to several challenges associated with solid-state electrolyte conductivity, complexities related to reaction mechanisms, and storage of Li₂O₂ in Li-air/Li-O₂ need to be addressed as the technology matures, since currently, the properties of electrolytes mostly define the reaction pathways. Furthermore, it's difficult to incorporate redox mediators into such systems, and in such a scenario, the discharge capacity and the reversibility of Li-air/Li-O₂ batteries will solely depend on the properties of the cathode. On a positive note, most of the currently known parasitic reactions can be disregarded, and the least damage to the electrolytes and Li anode can be expected from contaminants in the air [36]. Therefore, aprotic electrolytes may be considered the most studied electrolytes to date. More recent studies favour organic ethers due to their stability toward highly reactive discharge products. Specially glyme-based electrolytes have shown increased stability in the presence of reduced oxygen species, and greater resistance was exhibited against nucleophilic attacks. Based on this, tetraethylene glycol dimethyl ether (TEGDME) is the most common electrolyte used in Li-air systems [40,41], even though the recent in-situ infrared spectroscopy studies suggest that diglyme (DG) is more stable compared to TEGDME [42].

2.2.2. Separator

Separators are employed in battery technologies to electrically isolate the anode and the cathode, ensuring no short circuits in the cell. The separator should also facilitate the migration of Li ions with minimal ionic resistance. Furthermore, the wettability of the electrolyte, electrochemical stability, thickness, pore structure, and porosity of separators are critical parameters affecting the long-term stability and the maximum current density of the battery cell [43]. Typically, glass fiber [44], polyamide (PA) [45], polyethylene (PE) [45] and polypropylene (PP) [46] membrane filters are used in LABs as the separator. Some attempts
to use advanced membranes like polyvinylidene difluoride hexafluoropropylene (PVDF-HFP) with engineered pore structures are reported to allow fast Li⁺ ion migration [47].

2.2.3. Lithium Anode

The typical choice for the anode material in a LAB is lithium, providing a very high theoretical capacity of 3860 mA h g⁻¹, lightweight, and a very low potential of -3.04V [48]. Such a low potential allows a larger operational window and fast kinetics, while the mentioned properties make Li extremely reactive, raising safety and efficiency concerns. Other challenges with Li anodes include the high impedance during cycling due to the instability of the solid-electrolyte-interface (SEI) layer [26,49], the accumulation of shuttled discharge products at the anode surface [49], the Li dendrite growth [50] and low coulombic efficiency of the cell due to irreversible consumption of the Li anode and the electrolyte. In that sense, strategies such as incorporating protective films that limit the crossover of O_2 , ROC, and other contaminants [51], utilizing lithiated Si, Al, and C anodes [52,53], and promoting the growth of protective layers, including artificial SEI [49, 50] have already delivered promising results, but still need further fine-tuning for a better-performing anode. One other outstanding problem associated with Li anode is the morphological roughness introduced due to the continuous stripping and plating processes, particularly charging at higher current densities [56]. Therefore, typically aprotic electrolytes are recommended for use with Li metal anodes which minimize the damage to the anode material [50]. However, if other requirements are satisfied, using a solid electrolyte may be more protective for Li anodes in the future, since it limits most of the unwanted interactions with the Li metallic anode.

2.2.4. Air Cathode

The oxygen evolution reaction (OER), and the oxygen reduction reaction (ORR) are two sets of key reactions occurring at the cathode of a LAB. The oxygen is supplied from the

atmospheric air, and generally, an electrocatalyst is required to support such reactions. The cathode covers functions as a current collector, a catalyst layer, and a diffusion layer during the operation as three main responsibilities.

As the current collector, the structure should support the electron transport outward and inward from the cathode. Porous metal foams of either Ni [57], Cu [58], Al [59] or metallic composites [60] or porous carbon-based materials [61] have been reported as the non-metallic current collecting layers. Further, the cathode structure should be engineered in a way that it supports swift oxygen diffusion through it while preventing the electrolyte is leaking out. Hence mesoporous carbon structures are popular choices. Recently more sophisticated cathodic structures were engineered with linear pore gradients with increasing pore sizes towards the air side as indicated in Figure 2.1 [62], yielding more satisfying battery performances.



Figure 2.1: Effect of the cathode's porosity on the electrochemical performances of LAB where carbon-based cathodes were compared with three single porosities and with gradient porosity increasing towards air side [62], Reprinted with permission from Ref. [62]. Copyright 2020 IOP Publishing

In the cathode compartment of a typical LAB, the catalytic layer is of specific importance. Even though the theoretical overpotential of Li₂O₂ is around 0.2 V, it can be as high as 1.5 V, as reported in several empirical studies [63,64]. Many factors, including poor reaction kinetics, the formation of large crystals of insulating Li₂O₂, and poor interfacial properties, contribute to the high overpotential. Therefore, the bi-functional catalysts have been efficiently used to improve the reaction kinetics in LABs [65]. While the OER and ORR kinetics are naturally slow, a catalyst layer can significantly enhance the kinetics of reactions. The catalysts supporting OER, and ORR reactions are called "bi-functional" catalysts. One of the key objectives of this literature review is to review the performances of different types of bifunctional catalysts used for LAB electrodes in recent years and to highlight the ones with standout performances among them, while identifying a potential research gap.

2.3. Principal and the Working Mechanisms

As discussed, the basic aprotic cells consist of the Li anode, electrolyte, separator, and cathode. The cathode and the electrolyte involve the main chemical reactions occurring in a LAB cell, and an ideal cathode should provide favourable conditions for fast reaction kinetics and long-lasting performances [66]. Typical, LAB cells identified as batteries consist of Li metallic anode, aprotic electrolyte, and lightweight carbon [67,68] or metallic [49,69] conductive porous cathode unless mentioned otherwise, and the reaction mechanisms discussed is associated with such a system.

2.3.1. Mechanisms on discharge

As the LAB discharges, O_2 molecules diffuse into the battery through the porous cathodic network and undergo a single electron reduction forming superoxide radical as indicated in Equation 2.1, which was followed by Li-ion coupling as shown in Equation 2.2.

$$0_2 + e \rightleftharpoons 0_2^{-} \tag{2.1}$$

$$0_2^- + Li^+ \rightleftharpoons Li0_2 \tag{2.2}$$

Current understanding is the initial one-electron reduction of the oxygen molecule doesn't go through a chemisorption [70]. But the fate of the produced superoxide radical (O_2^{-}) is determined by the properties of the cathode surface and the electrolyte. It's hard to determine which effect the other, since most studies conducted, neglect the effect of the other while reporting.

From the perspective of the electrolyte, the stability of the superoxide in the electrolyte depends on the counteraction [71]. As observed in K-O₂ batteries, since K_2O_2 is not highly stable, long-life stability can be found with the superoxide (KO₂) [72]. In contrast, peroxides with smaller cations are more stable. Hence, the intermediate product of lithium superoxide has a shorter lifetime in the electrolyte before converting into lithium peroxide (Li₂O₂) via disproportionation as indicated in Equation 2.3.

$$2LiO_{2(sol)} \rightleftharpoons Li_2O_{2(s)} + O_{2(g)}$$

$$(2.3)$$

The produced Li_2O_2 is an insoluble solid product, and it's known to assemble as large toroidlike particles at the pores of the cathode, providing decent discharge capacity. The mentioned mechanism is well established as the "solution mechanism". A sizeable quantity of LiO_2 needs to be dissolved at the electrolyte to favour the solution mechanism, and the donor number (DN) of the solvent needs to be high to facilitate such a mechanism. Alternatively, solvents with low DN promote the superoxide to stay attached to the surface of the cathode till it subsequently reduces to the solid deposit of lithium peroxide. The overall process is called the "surface mechanism", and in addition to the DN of the electrolyte, the availability of the surface defects and the energy of the facet also contributed to governing superoxide reduction pathways at the cathode surface. Hence, surface adsorbed LiO_2 can undergo the following reaction pathways, (1) disproportionate into Li_2O_2 as indicated in Equation 2.3, (2) electrochemically reduce into Li_2O_2 by obtaining another electron as presented in Equation 2.4, (3) stabilized on the surface as LiO_2 without further reduction. The third mechanism is yet to be fully accepted across the wide battery community, but it was reported that defect sites presented at the cathode surface could stabilize the superoxide [73].

$$Li^{+} + LiO_{2(ads)} + e \rightarrow Li_2O_{2(ads)}$$

$$(2.4)$$

Most of the pioneers in Li-air/Li-O₂ battery research, who are now interested in solutionbased redox mediators, are recommending avoiding the surface-mediated process, which is known to deposit Li₂O₂ on the surface of the electrode as a film-like layer [74]. Despite, the arguments that the growth of a film-like layer could passivate the electrode surface, ineffectiveness in solid catalysts, and limit the discharge capacity, many researchers have published their findings, acknowledging decent LAB performance owing to surface-grown Li₂O₂ layers [75]. Figure 2.2 summarises the above discussion through graphical illustrations explaining different oxygen reduction pathways that could occur during the battery discharge.



Figure 2.2: Surface- and solution-based mechanism involved in reactions taking place at the cathode of LABs. Reaction pathways illustration of the formation of toroid-like structures with a SEM image of a formed toroidal-shaped Li₂O₂ at the surface of the cathode after discharge [76], and an illustration of the formation of layered structure covering the cathode surface with a SEM of such a foamed Li₂O₂ thin film at the surface of LAB cathode after discharging [77]. Reprinted with permission from ref [76]. Copyright 2017 John Wiley and Sons.

The above reaction mechanisms are mostly valid for the Li-O_2 batteries under room temperature operation. The reaction mechanisms could be drifted towards either way with the varying temperature. As the temperature lowers, reaction kinetics as well as the solubility in the electrolyte also lowers promoting a more surface-mediated mechanism. While operating the Li-O₂ batteries at high temperatures benefiting from faster reaction kinetics [78], lowtemperature operation helps suppress the side reactions [78]. The battery operation becomes more complicated in Li-air batteries, as the different components in the air could make a large number of non-reversible side reactions consuming Li, as well as blocking the pores in the cathode unless molecules find a way to shuttle towards the Li anode. Even though, moisture and CO₂, and NO_x are known as culprits, forming non-reversible parasite products such as Li₂CO₃ and LiNO₃. recent studies suggested that small quantities of moisture could benefit the performance of Li-O₂/Li-air batteries [79]. For example, it was mentioned that the presence of small percentages of water in electrolytes could act as an AN (acceptor number) additive, improving the solubility of LiO₂ and helping to form larger Li₂O₂ toroids, increasing the discharge capacity [79]. Recent findings by Clare P. Grey's group also support the existence of water/ moisture in LABs in the presence of solid or redox catalysts, where the successful reversibility of LiOH was demonstrated [80,81].

2.3.2. Mechanisms on charge

During the charging step, the solid discharge product decomposes, releasing O_2 into the air, known as the Oxygen Evolution Reaction (OER) [82]. The overall response can be written as Equation 2.5, for which the open-circuit voltage can be calculated as 2.96 V vs Li/Li⁺ [48].

$$2 Li_{(s)} + O_{2(g)} \rightleftharpoons Li_2 O_{2(s)}$$
 $(E_{OCV} = 2.96 V vs Li/Li^+)$ (2.5)

In a practical scenario, the specific discharge capacity varies from the theoretical value of $3500 \text{ W} \text{ h kg}^{-1}$, and a charging overpotential ~of 1 V is typically observed. It is believed that the discharge mechanism and the nature of the discharge product, including its morphology, crystallinity, and affinity to the cathode surface, are critical to determining the charging overpotential and the discharge capacity of the cell [50].

The current understanding is that the LiO_2 , surface-grown Li_2O_2 , or the Li_2O_2 with an amorphous nature can easily be decomposable with lower charging overpotentials, and the generalized oxygen evolution reaction can be found in Equation 2.6.

$$Li_{(2-x)}O_{2(s)} \rightarrow xLi^{+} + x e + O_{2} \qquad (2.6)$$

Since the discharged product $(Li_{2-x}O_2)$ is in good contact with the cathode surface, the interface resistance is reported to be low. With that, the cell's ability to be fully recovered without high charging overpotentials will keep the electrolyte and the carbonaceous components of the cathode safe without being decomposed, which are known to be susceptible to high potentials, ensuring a longer lifespan for the battery.

In contrast, the bulk Li_2O_2 toroid need a higher charging potential to get decomposed, showing a greater hysteresis in between discharging and charging voltage profiles. The weaker bonding between the active cathode material and the discharged product is the main reason for higher overpotentials upon charging, as the interfacial resistance is much higher in such instances [83]. Under the mentioned scenario, in some cases, the recovery of Li ions can only be partially possible after a full charge.

Generally, in a practical scenario, the charging profile contains both domains explained earlier at varying proportions, expanding the charging profile from 3.0V to 4.5V. However fast decomposition can be expected if the discharging mechanism is dominated by the surface-mediated route. Currently, there is a dispute about whether the defect density or the facet energy of the solid catalyst surface is more important for the reliable LAB operation, in addition to the conductivity, stability, stability of the electrolyte in the presence of the catalyst, and the scarcity and commercial viability of using the catalytic material. Before discussing individual domains of the solid catalyst and their performances, it's important to be aware of the possible parasitic reaction pathways limiting battery performances, and eventually ending the life span of the LAB cell.

2.3.2. Parasitic Reactions and Degradation Mechanisms

Reduced oxygen species (ROC), lithiated oxygen species (Li_xO_2), protonated oxygen radicals, singlet oxygen (1O_2), and some catalysts are now identified as the main culprits in promoting parasitic reactions in Li-air/Li-O₂ batteries.

Early studies on LAB degradation suggest that LiO₂ is the main source of parasitic reactions due to its high reactivity. The C and H atoms next to heteroatoms in organic electrolytes were found to be susceptible to nucleophilic attacks by O^{2-} , LiO₂, and Li₂O₂, but recent studies have identified singlet oxygen $({}^{1}O_{2})$ is most responsible for the battery degradation through parasitic reactions, which is currently known to be produced during the chemical disproportionation of superoxide radicals, and the oxidation of Li₂O₂ [84]. Even though the thermodynamics and the kinetics of the mentioned singlet oxygen-generating reaction pathways are still under discussion [85], the increased singlet oxygen generation during the high overpotentials during the oxidation of the peroxides is believed to be the reason for fast battery degradation as battery charges over 3.8V [84]. Currently, further research is progressing toward understanding reaction pathways and reliable detection of singlet oxygen [86] and quenching the generated singlet oxygen via physical quenchers [87]. The carbon electrode materials and binders were found to be reacting with the mentioned ROC and singlet oxygen primarily forming Li₂CO₃, which needs potentials above 3.8V to decompose [88]. The degradation is reported to be intensified in the presence of moisture, which helps form more reactive protonated reduced oxygen compounds that could lead to chain reactions via H atom or H⁺ abstraction [88,89]. Studies on the degradation mechanisms of noncarbonaceous cathode materials and their contribution to degradation mechanisms are yet to make significant progress. But we cannot rule out the possibility of catalysts becoming inactive in contact with the mentioned radicals, and the potential ability of catalysts like transition metal phosphides to promote the singlet oxygen generation by oxidating protonated/ non-protonated reduced oxygen radicals as reported elsewhere[90], which needed a careful study to be conducted soon.

2.4. Bifunctional catalysts for Li-air battery cathodes

Noble metals like platinum, silver, and palladium are known to catalyze the chemical reactions including the ones taking place at the air cathode of LABs. These catalysts, however, have limited practicality due to their high cost, susceptibility to gas poisoning, and poor durability. Therefore, an intensive research effort is being taken to develop bifunctional catalysts based on less expensive materials with matching or better cell efficiency and durability.

2.4.1. Carbon and doped carbon structures

Carbon, a non-metallic tetravalent element with several allotropes, is one of the most abundant elements in the universe with a wide range of applications in energy-related sectors. The lightweight, high conductive, low-cost flexible carbon structures with high porosity and high surface match most of the requirements needed for a LAB cathode. Early studies used non-fully crystalline types of carbon black as Super P, Ketjen Black, and Vulcan XC-72, with limited success [91,92]. In comparison, more crystalline carbon as carbon nanotubes (CNT), reduced graphene oxide (rGO), graphene nanoplatelets (GNP), and hierarchical 3D graphitic structures were more successful as cathodes, allowing a larger Li_2O_2 accumulation and longer life span [93]. The paper-like cathode prepared by Kim et. Al. By mixing GNP and graphene oxide (GO) with a sulfonic acid stabilizer can be identified as one of the finest carbon cathodes reported in recent years, which delivered a discharge capacity of 9760 mA h g⁻¹ at 100 mA g⁻¹ current rate [94]. In addition, a successful attempt was reported by hybridizing two graphene structures via hydrothermal activation of glucose and GO by Xin et al., and a large discharge capacity (9760 mA h g⁻¹) and an extended cycle life (170 cycles) were reported during the study [95]. Many of the above-mentioned studies focused on achieving the optimized pore structure with a superior inter-connected network of mesopores and macropores, where better support towards Li^+/O_2 diffusion and storing large amounts of discharge products was expected. Further, the presented defect sites at the graphitic surfaces are expected to provide a greater catalytic activity lowering the charging overpotential.

Belova et al. provided further insight into the mechanisms involving carbon cathodes in Li-O₂ batteries, through a series of cyclic voltametric and X-ray absorption near edge structure (XANES) analyses, determining the reaction pathways involving LiO₂ are strongly affected surface properties of the cathode electrodes even in the systems with high DN electrolytes as DMSO [70]. As illustrates in Figure 2.3 (a), the study further reveals that the pure graphitic basal plane supports the electrochemical reduction of the lithium superoxide as previously presented in equation 4, and the defective carbon structures as glassy carbon or the edge planes of the pyrolytic carbon are promoting the solution-mediated process. The study further warns against engineering materials with high defect concentrations, revealing that deformations could lead to surface stabilization of LiO₂, and it could result in reacting with carbon substrate forming the parasitic product of Li₂CO₃. With the results from the above study, a reasonable explanation can be provided for the high performances in the graphitic carbon allotropes as CNT, GNP, and rGO, over the carbon black-like amorphous structures, where the supportive crystal facet is important at supporting the reactions with higher binding energies.

Many techniques have been investigated to improve the performance of carbon-based electrocatalysts, including doping the carbon materials lattice, functionalizing the surface, and hybridizing with other non-carbonaceous materials. Heteroatom doping on carbon is an interesting approach to modulating the electronic structure, which could be used to enhance the electrokinetic performances of the LAB cathodes.

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Figure 2.3: (a) Effect of the purity in graphitic basal plane on ORR mechanism of carbon cathodes [70], mono-doped Carbon Cathodes for LABs (b) N-doped CNT synthesized by using seed-impregnated CVD technique [96], (c) TEM image of N-doped OLC prepared by thermal annealing of nanodiamonds in Ar and Ammonia environments respectively [97], and (d) N-doped Graphitic Carbon developed through heat treatment of PDA [98]

2.4.1.1. Mono atom doped carbon structures.

Various approaches have been used in the literature to replace the atoms in a carbon skeleton with foreign atoms of different sizes and electronegativity. This replacement is known as doping, and when the dopant is of a single type of heteroatom, it is called mono-atom-doping. The heteroatom doping helps to enhance the catalytic activity of the carbon structure by introducing alterations to existing energy states. Verifying the concept through theoretical means via density function theory (DFT) calculations, Novcic et al. found that doped- - graphene provides better support for oxygen kinetics as doped-graphene surfaces favour fast adsorption of oxygen, intermediates, and discharge products [99].

Even though several atoms like N [100], B [101,102], and S [103] can be used for doping purposes, nitrogen dominates among them as the most frequently reported dopant [104–106]. Due to the comparable atomic size (155 pm for nitrogen and 170 pm for carbon), nitrogen can easily be incorporated into the basal plane of carbon materials. With five electron valances, nitrogen can tune the physical and chemical properties of the carbon materials, leading to enhanced electro-catalytic performance. Upon doping, the lone pair electrons in nitrogen (with higher electron negativity) render the adjacent carbon atoms more attractive to negatively charged particles since the electron density of carbon is lower than nitrogen [107]. This phenomenon increases the catalytic activity of the doped carbon. Moreover, N-doping further increases the electrical conductivity of carbon materials, with a profound impact on the electrochemical performance of nanoparticles such as N-doped CNT and N-doped graphene, as discussed in a review article by Peng et al. [104]. In addition, Shin and his group [108] identified that the higher number of defects that occurred in nitrogen-doped CNT could provide additional support for ion and electrolyte diffusion. Moreover, Wang and his co-workers [109] discovered that the oxygen reduction reaction (ORR) takes place more

effectively at the edges of graphitic structures than in the basal plane due to the high level of defects on the edges, not quite agreeing with the previously introduced concepts.

N-doped CNT catalysts were commonly prepared by chemical vapour deposition (CVD) techniques. The vertically grown parallel porous array of N-doped CNT-based integrated air cathode reported by Li et al. as shown in Figure 2.3 (b) [96] by the impregnated CVD method, and N-doped CNT prepared by floating-catalyst CVD method, are two such examples [105]. Thermal treatment processes with nitrogen-containing gases are frequently used to dope graphene. In this regard, Li et al. [110] used high-purity ammonia mixed with Ar at 900 °C to produce N-doped graphene. Even though the researchers were able to achieve an initial discharge capacity of 11,660 mA h g⁻¹, at a current density of 75 mA g⁻¹ for the N-doped graphene nanosheets, which is about 40% higher than undoped graphene nanosheets (8530 mA h g⁻¹), a reasonable cycle stability was not achieved.

Apart from CNT and graphene, heteroatom-doped 3D carbon networks are by pyrolyzing/annealing the selected polymer or biochar structures [111]. For example, N-doped Onion-like Carbon (N-OLC) (see Figure 2.3 (c)) prepared by two step annealing process produced an effective cathodic catalyst, which produced a very high specific capacity (~12180 mA h g⁻¹carbon), lower overpotential (0.88V), and reasonably good round-trip efficiency of 70.0% even after 194 cycles [97]. Typically, precursors as dopamine [98] and polyester fibers [112] like precursors with large number of ammine groups were used to achieve high N-doping concentrations, and a typical synthesis process illustrates in Figure 2.3 (d). It was also discovered that the type of N doping in carbon structures could be varied depending on the starting material and the annealing temperature [98]. Typically, at lower annealing temperatures (~600- 700 $^{\circ}$ C), the formation of pyrrolic and pyridinic types of N is more favourable. As the temperature increases, the pyrrolic and pyridinic N tend to convert to graphitic N. Hence, the catalytic activity will also depend on the annealing/pyrolyzing

temperature, and several experimental studies verified that pyridinic N is most suited to catalyzing oxygen kinetics in Li-O₂ batteries [98,113].

In addition to N, other heteroatoms were also used for doping graphitic structure, and doping with B has also yielded successful results owing to the electron-deficient nature of B-doped carbon as theoretically and experimental studies verified [114,115]. The synergy of two or more heteroatoms doped at once, could yield better performance in carbon cathodes, providing enhanced catalytic support promoting ORR and OER kinetics at LABs.

2.4.1.2. Dual atom doped carbon structures.

Co-doping of carbon with more than one element can further increase the catalytic activity of the carbon-based cathodes used in LABs. Dual, or multi-doping with heteroatoms is mostly reported using sulfur [116], phosphorous [117], iodine [118] and boron [119] along with nitrogen. Commonly, the dopants have approximately similar sizes as carbon. However, if the dopant atom size is larger than the carbon atom, there would be a higher possibility of generating structural defects in carbon [117]. Different heteroatom doping affects the catalytic properties differently depending on their physical and electronic structural properties. Moreover, a synergistic effect can be expected when two or multiple doping atoms are simultaneously applied [120,121].

With the high electronegativity of nitrogen and comparably the larger atomic size of sulfur, the induction of structural distortions, modification of charge, and spin densities in the carbon structure are commonly observed in N and S-doped Carbon, and frequently thiourea was used as the source of both sulfur and nitrogen during the heteroatom doping stage, and efficient doping was achieved by annealing the green body at 700 ^oC - 1000 ^oC [122]. For example, graphene oxide annealed in presence of thiourea at 900 ^oC was performed as a good

bifunctional catalyst for LABs achieving the discharge capacity of 11252 mA h g^{-1} at 200 mA g^{-1} current density [123].

Additionally, B and N co-doped [119], I and N co-doped [118], O and N co-doped [124] bifunctional carbon catalysts for Li-O_2 batteries were also reported. Iodine was selected to co-dope with N because of its ability to create free hole carriers within the carbon material that improve the density of free charge carriers, accelerating the electron transport.

 Table 2.1: Summary of design parameters and output properties of LABs made using advanced carbon structures-based cathodes.

Туре	Catalyst	Shape	Substr ate	Method	Surfa ce area (m ² g ⁻ ¹)	Por e Size (nm)	Dischar ge Capacit y (mA h g ⁻¹)	Rate (mAg ⁻¹)	Cycle Numb er	Rate/Li mit	Over Potent ial (V)	Li ₂ O ₂ shape	Ref
Mon o Dope d Carb on	N- doped CNT	Bamb oo-like	CNT	CVD	40.92		866	75			1.7		[10 5]
"	N- doped CNT	Paralle l- array	CB/ Carbo n Paper	CVD			2203	60	5	60	1.81		[96]
"	N- doped Graphe ne	NS	Celgar d 3500 GDL	Annealing			11,660	75				Particl e	[11 0]
	N- doped GNP/ N- doped CB	Porous 3D	Ni foam	Annealing	900	11. 86	1687.3						[12 5]
cc	N- doped Onion- like Carbon	shells	carbon paper	Annealing	406.4	20	12180	25	196	50	0.88	film- like	[97]
Dual dope d carbo n	N and S co- doped graphen e nanoshe ets	NS	35BC GDL	Hydrother mal/ Annealing	1730	4	11 431	100	38	100	1.3	Film- like	[12 6]

N and S	NS	Sigrac	Annealing	310	10-	22252	200	20	200	0.88	-	[12
co-		et			25							3]
doped		GDL										
graphen		10 BC										
e												
nanoshe												
ets												
N J I	20	Carla	I I due dh u	417	2	14017	200	225	500	0.76	T	F1.1
IN and I	3D	Carbo	Hydrother	41/	2-	14017	200	225	500	0.76	1 oro1	[11
co-	porous	n	mal /		10						dal	2]
doped		paper	Annealing									
graphen												
e												

Table 2.1 provides a summary of key material properties, synthesis conditions, and design parameters used for the cell assembly, as well as the main electrochemical performances of the LABs, which discussed various advanced carbon structures-based LABs. In summary, the studies conducted up to date produced enough theoretical and experimental proof to verify the effectiveness in carbonous structures with many advantages as the cathode material for Li-air/Li-O₂ batteries with a suitable pore structure and oxygen reduction support. The oxygen adsorption capabilities at the graphitic surface are found to be pivotal in providing superior catalytic support towards oxygen reduction, and the derivation of more favourable surface properties via heteroatom doping was also found to be effective at promoting oxygen kinetics. Even though a solid mechanism favouring the OER kinetics is yet to be introduced with carbon cathodes, the discharged product could be easily decomposed on occasions where it is well attached to the cathode surface avoiding the branched growth. Irrespective of the obtained initial capacity, the lifetime of the battery is limited to a small number of cycles in many studies, and the occurrence of side reactions could be the main cause of premature death. In particular, the instability of C in contact with Li₂O₂, producing a layer of Li₂CO₃ in between the cathode and Li₂O₂, as observed by Gallant et al. [127], is the main obstacle facing carbon cathodes against succeeding. Despite the support at initial discharge capacity, the presence of defects and deformations could worsen the degradation by retaining the more reactive lithium superoxide at the cathode surface. The mentioned vulnerability of carbon cathode against parasitic reactions forced the researchers to search for more stable alternatives.

2.4.2. Noble metal/ metal oxide-based catalysts

Over the years, noble metals have been used to catalyze various electrochemical reactions. The limited performance, electrolyte decomposition, and the high cost of using the catalyst were found to be the main obstacles to using them in LABs on a commercial scale. But the recent development of nanotechnology and the novel synthesis routes of developing noble metal structures with desired physicochemical properties at low cost again turns noble metals and noble metal derivatives attractive among Li-air application researchers [33,128–131]. The successful utilization of noble metal nanoparticles in related applications encouraged further studies on LABs using noble metal-based bifunctional electrocatalysts [130,132,133]. Further, the recent understanding in surface modulations to reach high O₂ adsorption, and to tailor the size, shape, nucleation. and the growth routes of Li₂O₂ via high energy metallic facets and optimizing the e_g orbital occupancy via alloying are promising techniques for improving LAB performances.

Pt is the most exploded noble metal catalyst in LABs as well as in other energy applications. In-depth analysis conducted by Song et al. [134] has found the catalytic activity of Pt is dependent on its structure, where Pt catalysts with anisotropic structures exposing high-indexed (411) facets are found to be significantly reactive than low-indexed facets. Atomic steps as step-edge, kink, and ledge sites in the facet as presents in Figure 2.4 (a) were found to have high surface energies and strong bindings with O, supporting enhanced OER and ORR activity. The Li-O₂ battery exhibited a stable catalytic performance with a large discharge capacity (12,985 mA h g_{carbon}^{-1}) and the growth of Li₂O₂ as sub-micron-sized

pellets allow easy decomposition with the low charge overpotential and the cycle retention for 70 cycles.

In addition to Pt, feasibility of Ru and Au is also extensively studied as catalysts could promote O_2 kinetics in Li-air batteries. Ru nanoparticles decorated on vertically grown graphene nanosheets on Ni foam (VGNS@Ni) helped to yield an inspiring electrochemical performance on the assembled LAB with specific discharge capacity was reported as 23864 mA h g⁻¹ at a current density of 200 mA g⁻¹. Interestingly, the cells could be cycled over 200 cycles under a discharge depth limit of 1000 mA h g⁻¹ and at the rate of 200 mA g⁻¹. According to researchers, the enhanced performance of the catalysis was referred to the abundance of nanoparticles on the surface, the large surface area of the vertically aligned graphene sheets, and the voids provided by the Ni foam. [135]. The electrochemical stability of Ni foam against parasitic reactions may also play a critical role in the extended stability of the cell.

In addition to scrunty and the expenses regarding noble metals as catalysts, the main other issues regarding noble metal catalysts are that they promote the degradation of the electrolyte, carbon cathode, and the binder by promoting the nucleophilic attack by O^{2-} and singlets oxygen as identified by McCloskey et al. [136] and Samojlov et al. [137] Recently, it was identified that the catalytic activity of noble metals can be controlled by alloying them with another metal.

2.4.2.1. Bimetallic/ alloyed catalysts

Several research groups experimented with bimetallic noble metal nanostructures to optimize the catalytic activity. One possible way of enhancing the OER activity of a catalyst is by improving the adsorption energy with an intermediate of LiO_2 , and altering the e_g occupancy in transition metals can be used to tune the adsorption properties [138]. Pt has a high e_g occupancy, causing a weak OER performance as well as a high charging overpotential. But since Pt (generally transition metals) has a tuneable d-orbital structure, it was realized that the e_g occupancy can be altered by alloying Pt with other metals to obtain an improved catalytic activity.



Figure 2.4: Noble metal-based cathodes for LABs, (a) Pt catalysts with anisotropic structures exposing high-indexed (411) facets [134], (b) The full discharge–charge profiles and (c) galvanostatic curves of the PtAu and PtRu catalysts at a current density of 0.1 A g⁻¹ [139]

Zhou et al. recently reported e_g engineered Pt as an efficient catalyst promoting oxygen kinetics at Li-O₂ batteries, by modifying e_g occupancy of Pt by alloying with Ru and Au. It was found that alloying with Au is more fruitful, where the electronegativity of Au helped to attract electrons from Pt, lowering the electron occupancy in e_g , which allows having a higher binding energy with LiO₂ intermediate, as proven by XPS and DFT studies. The effect of

alloying with Au helped to have high discharge capacity with lower the charging overpotential as demonstrates in Figure 2.4 (b, c) and to have a decent cycle performance with 220 cycle stability in the assembled batteries.

Up to date, the conducted limited studies with bimetallic structures delivered mixed results, where the PtAu core-shell nanoparticle incorporated LAB cathode derived by Cheng Chao Li only helped to survive 30 cycles [139], while the LAB constructed on Pt₂Ru/Vulcan XC-72 on Ni foam cathode by Yao Yang et al. [140] barely lasted 10 cycles indicating the necessity of optimizing the alloying/e_g engineering process with suitable materials at correct ratios to obtain more maturity and reliability over the technique.

2.4.2.2. Noble metal oxide catalysts

Other than the pure metal itself, noble metal oxides, especially RuO₂, were also effective as bifunctional catalysts. Several composites were tested, including SWCNT/RuO₂ composite [141], CNTs decorated by RuO₂[142], Ketajan Black/RuO₂ composite [143], RuO₂.nH₂O clusters anchored on carbon nanofibers [144], and porous RuO₂ nanosheets anchored on carbon fibers [77].

Among the mentioned works, the study conducted by Jiaqiang et al. [77] demonstrated extraordinary cycle ability where the LAB cells survived for 200 cycles at a very high current rate of 1000 mA g⁻¹. The discharge product was in the form of a thin film, which, together with the low charging overpotential (0.71V), contributed to the long-stable behavior. The study conducted by Liyuan et al. [144] with RuO₂.nH₂O clusters anchored on electro-spun carbon nanofibers (CNFs) also yielded promising results. Excellent OER activity was observed with the decomposition of Li₂O₂ and Li₂CO₃ to a greater extent, and this is one of the very few incidents where successful decomposition of Li₂CO₃ was recorded. The assembled LAB could run up to 300 cycles at a 200 mA g⁻¹ rate after replacing the anode after 200 cycles.

Theoretical studies also have provided insights into parameters involving in the performance of RuO₂-based electrocatalysts. As explained in section 2.3 the oxygen adsorption energy influences the rate at which the LiO₂ intermediate forms, and its affinity on the electrode surface. If the adsorption energy is too low, the intermediate may desorb from the catalyst surface before completing the reaction, leading to poor stability and efficiency of the battery. Conversely, if the adsorption energy is too high, it may hinder the release of reaction products, affecting the reversibility of the battery [145-148]. Hence, a catalyst with an appropriate adsorption energy can facilitate the adsorption of intermediate species and subsequently promote their decomposition, enhancing the overall reaction kinetics. As found through DFT calculations, RuO₂ strongly adsorbs LiO₂ with adsorption energy (ΔE_{ads}) of -4.26 eV. But, by hybridizing RuO₂ with Co (-2.17 eV), RuO₂/Co-N-C hybrid obtained a moderate ΔE_{ads} of -3.13 eV for the adsorption of LiO₂ due to the cooperative interaction between RuO₂ and Co-N-C [146]. Since RuO₂/Co-N-C exhibits an increased adsorption energy for intermediates compared to Co-N-C, but a reduced value than RuO₂, which becomes beneficial to the desorption of LiO₂ [147]. Therefore, an appropriate intermediate adsorption energy is an important parameter to consider, diminishing the impedance by the RuO₂-based cathodes throughout the charging process [148].

Even though the doped carbon structures mostly supported the ORR activity, noble metals., especially e_g engineered bimetallic structures and oxides like RuO_2 evidenced to provide better support towards OER performances. Hence, noble metals and their derivatives provide better overall bifunctional activity over the previously discussed non-metallic catalysts.

First block transition metal-based bifunctional catalysts were introduced at LABs as a costeffective replacement for noble metals. But in recent years, some transition derivatives and their hybrids started to overperform the noble metal catalysts.

2.4.3. Transition metal oxide catalysts

Several transition metal oxides (TMO) structures have been tested as bifunctional catalysts for LABs and related energy applications, including metal oxides [149], ferrites [150], binary spinel structures [151], perovskites [152] and their hybrids. MnO_2 and Co_3O_4 are two examples of TMO that are repeatedly reported for their better catalytic activity, low cost, and natural abundance[141–144].

2.4.3.1. Mixed unary catalysts

The low electrical conductivity of most TMOs is the major concern since it leads to fast capacity degradation [153]. One strategy introduced in the literature to overcome some of the TMO-based cathode problems is to develop conductive binder-free electrodes. In-situ hybridization techniques can be adapted to typical TMO synthesis techniques such as hydrothermal [154,155] and electrochemical synthesis [156] to minimize the charge transfer resistance and the production of undesired side products during the Lab operation. In one of the attempts, Park and co-workers produced MnO₂ and Co₃O₄ co-catalyst anchors on Ni foam yielding 9690 mA h g⁻¹ initial discharge capacity and 66 cycles at a high rate of 400mAg⁻¹ [157].

2.4.3.2. Binary catalysts

Compared to unary transition metal oxides, the presence of metallic cations in multiple valances and a large number of unsaturated coordination sites makes binary oxides more attractive as solid catalysts in Li-air batteries [158]. NiCo₂O₄[159] CoFe₂O₄ [160], and NiFe₂O₄ [47] are some of binary oxides used in LABs. As in alloyed noble metals, electron

structure modulation was found to be an attractive strategy for enhancing the catalytic activity and the electronic properties in the binary oxides.

DFT calculations provide evidence on σ -bond formed through strong overlapping between 3d e_g orbitals of transition metals and 2p orbitals in oxygen is having a significant impact on the electronic structure of the intermediate discharged products associated with the ORR and the OER processes, compared to the π -bond occurs in between the 3d t_{2g}- 2p orbitals in transition metals and oxygen respectively [161]. Further, the theoretical calculations suggest semi-filled e_g orbitals are benefited, leaving room for oxygen to get adsorbed at the valent sites [162] as schematically illustrates in Figure 2.5 (a).

2.4.3.3. Doped-binary and ternary catalysts

Doping with a foreign element was found to be an effective strategy to modify orbital electron occupancy, where ternary structures prepared by Pd-impregnation on NiCo₂O₄ [163] and Fe-doping on Ni-Co oxides [164] modifying the eg orbital occupancy were yielded with improved outcomes. Ren and co-workers observed the near-unity eg occupancy in the Fe-doped NiCo₂O₄ (NiCoFeO), which was prepared through respective hydrothermal and calcination steps [164]. As the authors describe, Fe³⁺ replaces some of the Co³⁺ at octahedral sites, and as an effect, the surface Ni³⁺/Ni²⁺ ratio increases while the Co³⁺/Co²⁺ ratio decreases, allowing high occupancy of Ni³⁺ ($t_{2g}^{6}e_{g}^{1}$) at the surface making sure a strong covalent metal-oxygen bond occurs, facilitating a high electrochemical activity in the material. The large carrier concentration and the high intrinsic conductivity with electronic states concentrates near the fermi level leads to fast oxygen transport in NiCoFeO. Furthermore, the increased adsorption capacity of oxygen in NiCoFeO (E_{ad} = -1.189 eV) compared to that of -0.547 eV of NiCoO demonstrated the contribution in Fe doping to enhance the oxygen adsorption, while strong adsorption of LiO₂ (E_{ad} = -1.407 eV) to the

surface of the NiCoFeO catalyst as illustrated in Figure 2.5 (b) was found to be favouring the surface mediated mechanism.



Figure 2.5: (a) ORR and OER catalytic support in semi filled eg orbitals in transition metals [165], (b) high adsorption of LiO₂ at the surface of NiCoFeO catalyst [164], (c) TEM image of silica-coated ZnFe₂O₄ catalyst with a shell thickness of 11 nm [150], and (d) schematic of the synthesis steps of the CNL composite and its ORR mechanism [166].

2.4.3.4. Protective coating on catalysts

Following the successful attempts with using protective alumina [167] and silica [168] coating on LIB cathodes enabling high-capacity retention and protection against HF, an attempt to enhance the catalytic activity of the ZnFe₂O₄-based catalyst by adding a coating

silica layer was reported by Metin et al. [150]. The TEM image in Figure 2.5 (c) verified the successful formation of silica coating over ferrite nanoparticles, where optimum results were obtained with an 11nm coating thickness.

2.4.3.5. Perovskites catalysts

In recent years, highly improved photovoltaic performances have been shown by perovskites. Perovskites, ABO3-like metal oxide structures were found to be similarly effective as electrocatalysts to promote ORR and OER reactions, especially when an early transitional metal occupies the B site. The transition metal enhances the electrical conductivity by altering the electronic structure and providing numerous reaction sites for enhanced catalytic activity [169,170]. Zhang. Y et al. developed a hybrid catalyst by mixing graphitic carbon nitride (g-C₃N₄) with LaNiO₃ [166]. g-C₃N₄ is a layered structure where every C atom is bonded with three N atoms, either as graphitic or pyridinic nitrogen. The lone-pair electrons in the pyridinic structure are ideal for bonding with oxide ions, and they also help to alter the electronic structure [171]. Further, it was understood that the presence of Ni³⁺ at the B site of the LaNiO₃ perovskite enhanced both ORR and OER by introducing favourable binding energies with semi-filled eg orbit, verifying the effectiveness in the concept discussed related to ternary oxides. During the study, the researchers were able to enhance the bifunctional catalytic activity of LaNiO₃ by elevating the Ni³⁺/Ni²⁺ ratio as it composites with g-C₃N₄ and producing the composite catalyst called CNL. The g-C₃N₄ was produced by pyrolyzing melamine at 550 ⁰C and LaNiO₃ nanoparticles were produced by calcining the previously produced metal citrate gel via a sol-gel method. The final composite was prepared by heating the ultrasonicated g-C₃N₄ and LaNiO₃ dispersion at 550 ⁰C for 2 hours in an N₂ atmosphere as shown in the schematic diagram in Figure 2.5 (d). The composite with 10% g-C₃N₄ loading delivered the best outcome with lower ORR and OER polarization potentials, discharge

capacity over 5000 mA h g^{-1} , and cycling stability over 65 charge/ discharge cycles at a high current of 250 mA g^{-1} .

In a more recent development, the catalytic reaction kinetics of the perovskite structures has been enhanced by replacing the B site with two transitional metals. The cathode produced with wrinkled $La_{0.9}Mn_{0.6}Ni_{0.4}O_{3-\delta}$ nanofibers demonstrated excellent rate capability and could withstand 100 cycles under 300 mAg⁻¹ current density. Doping the B sits with different valence ions has improved the conductivities and introduced numerous active sites that promote the oxygen reaction kinetics [75]. A similar study was conducted by Cheng et al. with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ nanoparticle-based cathode. Even though an impressive discharge capacity of 13,979 mA h g⁻¹ was recorded, the assembled batteries could not survive more than 20 charge/ discharge cycles[172].

2.4.3.6. Facet engineered metal-oxide catalysts

Up to date fairly limited facet engineering studies were conducted on identifying highperforming crystal facets and engineer the cathode structure in a way of maximizes the exposure of oxygen and discharged products to achieve enhanced oxygen kinetics in Li-air/ Li-O₂ batteries. Lai et al. provided useful insight in this regard through the analysis of OER activity of different facets of Cr₂O₃, and they found high OER activity in Li-O₂ batteries can be achieved by inhibiting the growth of low-energy facets of Cr₂O₃ [83]. Researchers were able to inhibit the growth of (012) low-energy facet by adding anatase TiO₂ into the synthesis mixture and achieved impressive OER activity during the battery charging (0.12 V lower than Ru/C) owing to strong interactions between uncoordinated sites on the high-energy facets (ex. 116 and 110) and the intermediates as $Li_{2-x}O_2$. It's worth investigating the strategy further with better-performing catalysts as MnO₂, and Co₃O₄ and their complex structures. Table 2.2 provides a summary of key material properties, synthesis conditions, and design parameters used for the catalyst synthesis, as well as the main electrochemical performances of the discussed TMO-based LABs. Overall, high resistance is one of the critical drawbacks repeatedly reported in the literature regarding metal oxides as bifunctional catalysts for Li-air batteries. In general, binary oxides and perovskites with mixed valances provided improved catalytic activity. Even though the techniques were yet to mature, the novel design strategies focusing on the surface energy of metal oxides e_g orbital occupation modulation via inhibiting the low energy facet growth, and heteroatom doping started to be proven as vital approaches in addressing the shortcomings in TMOs. As synthesis approaches, the hydrothermal technique was more frequently used to synthesize binary and ternary metal oxides, and perovskites were mostly synthesized through carbonizing the electrospun nanofibers.

 Table 2.2: Summary of design parameters and output properties of LABs made using transition metal oxide-based cathodes.

Tuno	Cotolyst	Shape	Subat	Mathad	Surf	Dor	Dicah	Do	Cual	Data/I	Over	Lie	Do
Type	Cataryst	Shape	Subst	Method	Suri	POr	Disch	Ka	Cycl	Kate/L	Dver	L1202	Ke c
			rate		ace	e	arge	te	e	imit	Poten	Shap	İ
					Area	Siz	Capac	,	Num		tial	Shap	
					(m ² g	e	ity	(m	ber		(V)	e	
					⁻¹)	(N		A					
						m)	(mA h	g ⁻¹					
							g ⁻¹))					
Transit	Mn/Co	Spherica	Ni	Hydrothermal/	105.	12.	9690	20	66	400	1.04	Semi	[15
ion	Oxide	1	Foam	Annealing	71	55		0				-	7]
Metal		Flower-										Circ	
Oxides		Like										ular	
/													
Deriva	CoFe ₂ O ₄ /	Spherica	Copp	Chemical			7510	10	4	100	1.0	-	[16
tivos	Vulcan C	1	er	Conversion/				0					01
uves			Foil	Self-Assembly				-					
			1011	Sen rissemory									
	Silica	Nanopar	Carb	Cmc / Reverse	-	-	6200	10	45	1000	0.85	Toro	[15
	Coated	ticles	on	Microemulsion				0				idal	01
	ZnFe ₂ O ₄	lieles	Paper	1. Inter o e Interiori				Ŭ				ruur	01
	Ziii 0204		1 aper										
	NiFe ₂ O ₄	Spinel-	Ketje	Hydrothermal/	105.	25.	10830	50	100	50	0.85	Toro	
		Structur	n	Calcination	2	1						idal	
		ed	Black	Cultilution	-	-						ruur	
		cu	Didek										
	G-C3n4-	Lavered	Carb	Pvrolvsis/	-	-	5000	25	65	250	1.2	-	[16
	LaNiO ₂		on	Calcination				0					6]
	Luitio		Dopor	Culcillation				Ŭ					01
			1 aper										
	Fe ₃ O ₄ / CoO	Core-	Nicke	Hydrothermal/	-	20	5100	10	50	100	0.45	Toro	[17
	2-4	Shell	1										
	1	Shen	1 1	1	1	1							1

	Nanostr ucture	Foam	Calcination		0		0				idal	3]
La _{0.9} Mn _{0.6} Ni _{0.4} O ₃₋ <i>8</i>	Nanofib ers	Carb on Paper	Sol-Gel / Electrospinning	29	35	9959	10 0	100	300	1.11	Film -Like	[75]
$\frac{La_{0.6}Sr_{0.4}Co_{0.}}{{}_2Fe_{0.8}O_3}$	Spherica 1	Nicke 1 Foam	Sol-Gel /Calcination	10.6 9		13979	20 0	20	200	0.89	Leaf- Like	[17 2]
LaCo _{0.6} Ni _{0.4} O ₃ / Co ₃ O ₄	Nanofib ers	Toray Carb on Paper	Electrospinning / Hydrothermal	30.7	50	11288	10 00	116	1000	0.97	Shee t- Like	[17 4]

2.4.4. Transition metal sulfide and selenide catalysts

Transition metal Sulfides (TMSs), selenide (TMSes), and TMOs have similar physicochemical properties due to the similarity in their electronic structure [175]. However, TMSs have the advantage of high electrical and lower tuneable optical bandgap. Many TMSs and TMSes, such as CdSe and SnS₂, are ideal semiconductors for applications like solar cells, photocatalytic processes, and energy storage applications [175–178]. Therefore, TMSs can overcome the previously mentioned shortcomings observed with TMOs associated with their poor electrical conductivity. Moreover, loosely stacked structures and 2D structures of TMSs such as 2D MoS₂ can provide enough spacing to accommodate discharge products such as Li₂O₂ with low volume expansion. They can also act as the cathode, eliminating electrochemically unstable carbonous electrodes and binders [179]. Furthermore, the verification of the support of TMSs towards ORR kinetics in fuel cell applications [180,181] and OER kinetics in water splitting applications [1,182,183] are a few other facts that favour the applications of TMSs in LABs.

2.4.4.1. Unary Transition metal sulfides

The first study with a metal sulfide catalyst in aprotic LABs was reported in 2015 by Zhang, Z. et al. [184]. researchers synthesized flower-like (f-NiS) and rod-like (r-NiS) nickel sulfide electrocatalysts via a hydrothermal method. During this initial study, f-NiS performed better over r-NiS, showing a higher discharge capacity and cycling stability with 6733 mA h g⁻¹ and 30 cycles, respectively, at 75 mA g⁻¹. The later studies conducted on Ni₃S₂ [185] demonstrated superior performances, achieving stability over 100 cycles. Among various cobalt sulfide catalysts investigated [186], CoS₂ nanocage catalysts reported synthesized using a zeolitic imidazolate framework (ZIF-67) as a precursor [187] exhibited a superior conductive network. However, the battery performances were ultimately limited. The identified parasitic products as LiCO₃ and HCO₂Li are believed to be responsible for the early decay in performances. In comparison, DFT calculations conducted by Lin et al [188] reveal that Co₉S₈ exhibits a high adsorption tendency towards O₂, and intermediate discharged products compared to cobalt oxides such as CoO. The experimental evidence appears to corroborate the theoretical observations, as a closely arranged distribution of small hydrangea-like Li₂O₂ particles was observed in significant quantities deposited along the edge sites of Co₉S₈ on the discharged cathode [188].

In one of the instances where MoS_2 used in Li-air batteries, MoS_2 nanosheets were in-situ grown on hollow carbon spheres (HCS) using a hydrothermal reaction (at 200 °C for 24 h) using thiourea and $(NH_4)_6Mo_7O_{24}$ ·4H₂O as sulfur and molybdenum precursors, respectively as illustrates in Figure 2.6 (a). The cathode with 4–9 layers thick MoS_2 sheets on HCS performed well in the assembled LAB with a good discharge capacity of 4010 mA h g⁻¹ and long cycling stability of 105 cycles. In addition, Asadi et al. experimented with using the naturally occurring 2D transition metal dichalcogenides as Li-O₂ battery cathode by using the exfoliated MoS_2 [179]. Another transition metal sulfide of MnS is also found to be useful in Li-air batteries, where Shuling Li et al. synthesized γ -MnS using a solvothermal technique, and α -MnS was also produced by heating γ -MnS at 450 °C for 10 hours under an argon environment as shown in the schematic presented in Figure 2.6 (b) [189] An outstanding discharge capacity (14017 mA h g⁻¹ at 100 mA g⁻¹ current rate) and stable cycle performance

(87 cycles at 400 mA g⁻¹ current rate for a discharge depth of 900 mA h g⁻¹) verified the strong bifunctional catalytic activity of α -MnS. The researchers suggested; that (a) the unique cross-linked cashew-like and spherical pellets-like morphologies of the discharged product (Li₂O₂) and (b) the high conductivity of large lattice volume accounted for the improved performance.



Figure 2.6: Binary Sulfides used at LAB cathodes (a) In-situ growth of MoS_2 nanosheets on hollow carbon spheres (HCS) using a hydrothermal reaction [179], (b) Schematic diagram for solvothermal synthesis of γ -MnS and the production of α -MnS via heat treatment of γ -MnS at 450 ⁰C under argon environment [189]

2.4.4.2. Binary Transition metal sulfides

In addition to monometallic transition metal sulfides, few studies reported binary sulfides, such as NiCo₂S₄ [190], CoNi₂S₄ nanorods [191], ZnCo₂S₄ nanosheets [192], and MnCo₂S₄ nanosheets [193] as suitable cathode materials for Li-O₂/Li-air batteries. Compared with TMOs and monometallic TMS, binary sulfides have high electric conductivities and a larger number of redox catalyst sites, which could enhance the catalytic performance [194].

In one of the highlighted studies [191], remarkable cycling stability of 588 cycles (at 500 mA g^{-1} current rate for a limited capacity of 1000 mA h g^{-1}) was achieved by anchoring 3D mesoporous CoNi₂S₄ nanorods on a carbon textile (CNS-RAs/CT) as the cathode of LAB. As the article describes, CNS-RAs/CT showed very good electrical conductivity and open spaces in the cathodic structure, which contributed to the superior stability of the cell.

2.4.4.3. Hybrid Transition metal sulfide-based catalysts

The hybrid cathode prepared by P. Ramakrishnan et al. by wrapping FeS nanoparticles with N and S doped 3D nanofoam (FeS-C) delivered a high discharge capacity of 14 777.5 mA h g⁻¹ at 0.1 mA cm⁻² current rate [195]. The cell survived for 100 cycles and, the uniformly distributed FeS nanoparticles promoted the OER reaction by oxidizing Li₂O₂ while the 3D carbon provides the necessary support for gas diffusion, electron transfer, and accommodating Li₂O₂. The dopant sites promote ORR reaction by adsorbing Li⁺. The low percentage of carbon (< 5%) in cathode could help the battery to survive against side reactions, which leads to deuterating the Li-O₂ battery performance and cycle life.

Further proving the effectiveness in the synergy of doped-carbon and TMS, a cathode based on Co₉S₈ nanoparticles encapsulated by S and N dual-doped graphitic shells (Co₉S₈@G/NS-PCNF) [196] showed a high discharge capacity of 8269 mA h g⁻¹, and a small polarization gap (1.52 V). In addition, NiCo₂S₄ nanoparticles anchored on S-doped porous carbon nanostructure [197] achieved a high discharge capacity of 14173 mA hg⁻¹ at 150 mAg⁻¹ and considerably high cyclability over 100 cycles for 1704 h were achieved.

It was noteworthy to mention that, during the studies by Anjun Hu et al. [191] and Yuan Cao et al. [196], the researchers were careful about exposing the least amount of carbon materials to the discharged and intermediate products, and it seems to work in favour of the researchers. This could be another strategy that could be experimented with in future studies not limited to TMS. Further, Zhou et al. were successfully able to enhance the Li-O₂ battery performances by modulating the e_g occupancy of NiS by forming a hierarchical heterostructure with MoS₂ [198], using the similar strategy of increasing the availability of unsaturated eg orbitals as discussed previously.

Table 2.3 provides a summary of key material properties, synthesis conditions, and design parameters used for the catalyst synthesis, as well as the main electrochemical performances of the discussed TMS-based LABs. Among different TMS, manganese-based catalysts produced better catalytic activity. In contrast to unary sulfides, the binary and hybrid catalyst-based batteries exhibited much-improved performances. The relatively higher conductivity of such compounds may reduce the interfacial resistance between the electrolyte and the current collector, allowing the cell to operate at a relatively lower potential window, which minimizes the decomposition of the electrolyte and the supportive carbon network. But the long-term stability of the catalyst doesn't report to be as strong as the oxides. A distinguishable improvement in electrocatalytic performances was observed as a minimum portion of the carbon scaffold is exposed, and also through the eg orbital occupation modulation, and it's noticeable that further research in the mentioned topics is essential to uncover the successful pathways of designing advanced LAB technology.

T	Catal	C1	C1t	M-411	Confe	Den	Direl	Data	Cruel	Data /I.	0	I:O	D.f
гуре	Cataly	Snape	Substr	wiethod	Surra	Por	Discha	Kate	Cycle	Rate/L1	Over	$L1_2O_2$	Ker
	st		ate		ce	e	rge	(A	Num	mit	Potent	-1	
					area	Siz	Capaci	(mA	ber		ial	snape	
					(m ² g	e	ty	g ⁻¹)			(V)		
					⁻¹)	(nm							
)	(mA h						
						,	g ⁻¹)						
Transit	NiS	Flower-	Carbo	Hydrothe	-	-	6733	75	30	75	1.38	toroidal	[18
ion		like	n	rmal									4]
metal			paper										
sulfide													
s													
	Ni ₃ S ₂	Porous	Ni	Hydrothe	171.	10.	7478	300	100	300	1.36	Lamina	[18
		Foam	foam	rmal	1	3						r-2D	51
													1
	Co ₃ S ₄	nanoshee	Ni	Hydrothe	23.2	15-	6990	200	25	100	0.92	-	[18
		ts	Mesh	rmal	1	24							6]
													-
	CoS ₂ /	nanocage	Celgar	Hydrothe	-	-	2400	188.5	52	188.5	1.05	Film-	[18
	CNT	s	d	rmal								like	7]
			3500										_
			GDL										
	Co ₉ S ₈	Flower-	Porou	Hydrothe	14.5	-	6875	50	105	100	0.57	hydrang	[18
		like	s	rmal								ea-like	81
			carbo										1
			n film										
			in ruun										

Table 2.3: Summary of design parameters and output properties of LABs made using transition metal sulfide-based cathodes

MoS ₂ / hollo w carbon sphere s	nanoshee ts	Carbo n paper	Hydrothe rmal	244. 98	7.6 6	4010	200	105	200	1.44	Film- like	[19 9]
MoS ₂	nanoshee t	Carbo n Paper	Exfoliatio n	-	-	1450	222	50	222	0.8	Film- like	[17 9]
α- MnS	Rock salt-like	Nickel Foam	Solvother mal	17.9 3	-	14017	100	87	400	0.693	Pellets- like	[18 9]
MnCo ₂ S ₄	nanoshee t	Carbo n paper	Hydrothe rmal	55.4	14. 36	10760	200	96	200	0.90	Film- like/ pellets- like	[19 3]
CoNi ₂ S ₄	nanorods	Carbo n textile	Hydrothe rmal	19.9 3	6.2 1	5438	500	588	500	1.54	Film- like	[19 1]
FeS	nanoparti cles	N, S doped 3D carbo n foam	MOF/ Carbonisa tion	88.5	18. 3	14 777. 5	0.1 mA c m ⁻²	100	0.3 mA cm -2	0.73	Toroida 1	[19 5]
Co ₉ S ₈	nanoparti cles	N, S doped graphi tic sheets	Electrospi n/ Pyrolysis	204. 71	6- 12	8269	100	60	200	1.52	Film- like	[19 6]
NiCo ₂ S ₄	nanoflak es	S doped porou s carbo n	hydrother mal	461	2.9	14173	150	100	150	1.32	Toroida 1	[19 7]

2.4.5. Transition metal phosphide catalysts

Despite continued improvements, the cathodes based on TMOs and TMSs and their hybrids still have many challenges to overcome related to cyclability and charging overpotential mainly due to the relatively low conductivities. As an alternative, Transition Metal Phosphides (TMPs) were started to be utilized as LAB cathodes since they are known for higher electrical conductivity and better stability elsewhere related to anticorrosive studies and water-splitting applications. As a fact, TMPs have shown promising results in watersplitting studies as bifunctional catalysts for HER and OER reactions in the last couple of years. The most common methods to prepare the catalysts are the thermal treatment with PH_3 gas, the thermal decomposition of NaH_2PO_2 [195,200–202] or the treatment with red phosphorous[203,204].

2.4.5.1. Unary Transition metal phosphides

Nanoflakes of MoP was one of the first TMPs tested in LAB functionality. During the study conducted by Minghui Wei et al., hydrothermally produced MoO₃ was converted into MoO₂ and MoP nanoflakes by thermal phosphodising using NaH₂PO₂ [205]. In another study by the same group, MoP quantum dots were anchored on N, P co-doped hollow carbon fibers (MoP QD@HCF) as illustrates in Figure 2.7 (e-g) [206]. However, any of the batteries didn't last over 30 cycles raising the concerns over the durability of metal phosphide catalysts. In a more encouraging note, LAB with CoP microspheres derived via a hydrothermal process using CTAB as the soft template and Co(NO₃)₃.6H₂O, and NaH₂PO₄.2H₂O as Co and P sources, respectively, (see Figures 2.7 (a, b)) lasted up to 80 cycles [207].

2.4.5.2. Binary Transition metal phosphides

Similar to bimetallic sulfides and oxides, binary phosphides could provide better OER activity over the monometallic due to the improved conductivities and abundance of the active sites. Bimetallic Co and Fe were amongst the first TMPs to be investigated [208,209]. Kailing Sun et al. developed a LAB cathode using CoFeP nanodots as the active catalytic layer [210]. The three-step is illustrated in Figure 2.7 (c), and the LAB assembled sustained up to 141 cycles and delivered a maximum specific discharge capacity of 11969 mA h g⁻¹ at 100 mA g⁻¹ displaying better cycle stability. During the study conducted by Huagen Liang at el., a Li-O₂ battery was assembled using a self-standing cathode prepared using NiFeP nanoparticles deposited on a 3D biochar network, shown in Figure 2.7 (d) [211]. The battery with NiFe-PBA-based catalyst survived over 90 charge-discharge cycles and provided a specific discharge capacity of 10.9 mA h g⁻¹ cathode at a current density of 0.05 mA cm⁻².


Figure 2.7: (a)XRD (b)SEM of hydrothermally synthesized CoP microspheres [207], (c) synthesizing procedure of CoFeP bimetallic phosphide [210], (d)SEM image of NiFeP nanoparticles deposited on 3D biochar network [211], (e- g) SEM and HRTEM images of MoP quantum dots on N, P doped carbon fiber [206].

With limited literature, it's difficult yet to conclude the performances of TMPs as LAB cathodes. However, based on reports on impressive outcomes in related fields, betterperforming TMPs could expected to be reported sooner if the previously discussed catalytic activity boosting strategies could effectively tune the properties of TMPs.

2.4.6. Hybrid catalysts

In recent years, various hybrid bifunctional catalysts were tested at the cathode of LABs expecting better functionality over individual catalyst materials. In addition to the hybridization of the active materials with carbon skeleton, which has been discussed in previous sections, there are attempts to use more than one catalytically active material per cathode.

Lulu Huang et al. reported a hybrid bifunctional catalyst suitable for LABs produced by insitu synthesizing yucca-like CoN- CoO nanoarrays on top of a pre-treated carbon paper. The catalyst was produced by partial nitriding the hydrothermally synthesized Co(OH)F nanoarray precursor. The assembled Li-O₂ cell sustained 200 cycles at 100 mA g^{-1} with a limited capacity of 500 mA h g^{-1} and delivered a discharge capacity of 5423 mA h g^{-1} at 50 mA g^{-1} . The authors highlighted that partial nitridation is critical for enhanced cell performance. The additional oxygen vacancies and nitridation provided the required support to obtain enhanced OER and ORR performances. The 3D mesoporous morphology of the cathode provided enough space for gas diffusion and to accommodate the discharge products [212].

Similarly, a better-performing hybrid cathode for LABs was reported by Zonghuai Zhang et al. The catalyst was produced by decorating the Ni₃S₂ layer on top of electrospun fibers of double perovskite $PrBa_{0.5}Sr_{0.5}Co_2O_{5-\delta}$ (PBSC) [213]. The synergy of two catalysts and the high amount of surface oxygen vacancies (O₂²⁻ and O⁻) generated as the sulfide was deposited were recognized to be responsible for the enhanced performances of the LAB.

Peng Wang et al. developed a hybrid cathode where the noble metal Ru and TMP (Co_2P) were anchored on N-doped CNT. The assembled cell outperformed previously reported cells with a TMP catalyst-based cathode with a discharge capacity of 18 048 mA h g⁻¹ at 100 mA

 g^{-1} (12800 mA h g^{-1}). The cell exhibited good cycle stability of 185 cycles at 100 mA g^{-1} . The low ORR/OER overpotential (0.75V) and high peak currents further verified the effectiveness of the synergy of Co₂P and Ru in promoting oxygen kinetics[214].

Outstanding cyclic stability of more than 300 cycles (with 1000 mA h g⁻¹ limited discharge depth at 200 mA h g⁻¹) was reported by Peng Wang et al. for a composite of NiO and NiCo₂S₄ [215]. NiO nanotubes were hydrothermally grown on NiCo₂S₄ nanoarrays, which were also synthesized hydrothermally on pre-treated carbon paper. The developed three-phase hybrid heterostructure was used as a binder-free self-standing air cathode. Interestingly the relatively large 3-5 μ m length peasecod-like Li₂O₂ particles were successfully decomposed during the subsequent charging. This is one of the few instances where large Li₂O₂ particles could be successfully recycled, including the previously discussed study of Xiaodong Lin et al. with hydrangea-like large Li₂O₂ deposits [188,216].

A few other articles can also be found that achieved a similar outcome by hybridizing two or few noble metal derivatives, transition metal compounds, and doped porous carbon structures. For example, stability of over 200 cycles could be achieved on a cathode fabricated with RuO₂ nanoparticles and NiO nanosheet catalyst [217]. In another example, a low overpotential (0.32V), outstanding discharge capacity (26 833 mA h g⁻¹), and remarkable cycling stability (200 cycles at 300 mA g⁻¹) were recorded for Sr and Fe co-doped LaCoO₃ perovskite-based cathode. [218] Overall, hybrid catalysts were shown to improve discharge capacity as well as cycle stability.

It's wonderful to observe some better-performing catalysts can be derived through hybridizing two or more individual catalysts. But also, it has been witnessed above that a hybrid catalyst does not guarantee an enhanced LAB performance, and the individual materials need to be selected carefully with a meaningful rationale. Further, it's essential to develop an in-depth and solid theoretical understanding of the role of solid catalysts on Li-O₂ battery cathode, and associated concepts related to molecular orbit theory need to be studied to depth to understand the possible combinations of catalysts that could work together. With such an understanding, the electronic structure of the hybrid structure can be modulated to obtain a useful e_g orbital occupancy, enabling enhanced interactions with oxygen and reduced oxygen compounds.

It's further important to adhere to the Sabatier principle in constructing catalyst heterostructures. It's a very popular concept related to HER catalysts [219], and it could align with Li-O₂ batteries meaning that the ideal ORR/OER catalyst should have balanced adsorption of the oxygenated intermediates neither too strong nor too weak to achieve a greater balance between the adsorption and desorption of adsorbates. Tian et al. recently obtained a volcano-type correlation between the catalytic activity and the d-band centre, indicating the applicability of the Sabatier principle as a general guidance to develop highperforming catalysts for the Li-O2 battery applications [220]. Table 2.4 summaries key material properties, synthesis conditions, and design parameters used for the catalyst synthesis, as well as the main electrochemical performances of the discussed Hybrid Catalysts-based LABs discussed above.

Тур	Catalyst	Shape	Substr	Method	Surf	Por	Discha	Ra	Cycl	Rate/Li	Over	Li ₂ O ₂	Ref
e			ate		ace	e	rge	te	e	mit	Poten		
					area	Siz	Capaci		Num		tial	shape	
					(m ² g	e	ty	(m	ber		(V)		
					⁻¹)	(n		A					
						m)	(mA h	g ⁻¹					
							g ⁻¹))					
** 1	C O/C N		<u> </u>	TT 1 .1		1	5 400	50	200	100	1.00	T"1	50.1
Hyb	CoO/ CoN	nanoarray	Carbo	Hydrotherm		1-	5423	50	200	100	1.30	Film-	[21
rid		8	n	al/ Partial		30						like	2]
			Paper	nitridation									
			-										
	Ni ₃ S ₂ /	Nanoparti	Carbo	Electrospin/	10.7	1-	12784	10	120	100	0.68	toroida	[21
	PrBa _{0.5} Sr _{0.5}	cles/	n	ALD	9	20		0				1	3]
	Co ₂ O _{5-δ}	nanotubes	Paper										
			-										
	Ru/ Co ₂ P/	Nanoparti	Carbo	pyrolyzing	105	4-	18 048	10	185	100	0.75		[21
	N-doped	cles/	n									nanosh	

Table 2.4: Summary of design parameters and output properties of LABs made using hybrid catalysts-based cathodes

CNT	nanotubes	Paper			30		0				eets	4]
NiO/ NiCo ₂ S ₄	Nanotube s/ nanoarray s	Carbo n Paper	Hydrotherm al/ Annealing			10050	20 0	300	200	0.88	peasec od - like	[21 5]
α-MnO ₂ / Co ₃ O ₄	Nanorods / nanosheet s	Carbo n paper	Hydrotherm al / electrodepo sition/ annealing	71.1 8		5940	51	55	103	0.95	Particle s/ film- like	[21 6]
RuO ₂ / NiO	Nanoparti cles/ Nanoshee ts	Ni foam	Chemical conversion/ Heat treatment	5.92		3240	25 0	200	500	1.18	toroida 1	[21 7]
Sr, Fe- doped LaCoO ₃		Carbo n cloth	Sol-gel/ annealing	49.6	24. 16	26 833	50	200	300	0.32	large granule -like	[21 8]
Fe3O4/ PtRu/ C	nanoparti cles	Ni foam	Hydrotherm al/ Chemical reduction	44.3 6	2-3	7996	20 0	32	200	1.16	Film- like	[22 1]
Co/ N- doped CNF	Nanoparti cle/ nanofiber	-	Electrospin/ Calcination	301. 5	2- 25	4583	10 0	40	100	1.22	Film- like	[22 2]
Co/ N, S- doped CNF	Nanoparti cle/ nanofiber	-	Electrospin/ Calcination	121. 3	1.7 - 38. 8	6995	10 0	34	200	0.97	Film- like	[22 3]

The literature review delves into recent advancements in bifunctional catalysts for lithium-air (Li-air) batteries (LABs), with a focus on catalysis and degradation mechanisms. In the initial sections, it introduces LAB technology and examines critical challenges, including rapid passivation of catalytic sites, high charging overpotentials, and the pressing need for viable solutions. It provides a comprehensive discussion on battery components, the chemistry of oxygen reduction (ORR) and oxygen evolution reactions (OER), as well as parasitic reactions and degradation mechanisms.

The primary emphasis of the literature review is on electrocatalysts, categorizing six types of bifunctional catalysts: carbon-based nanostructures, noble metals, transition metal oxides (TMOs), sulfides, nitrides, and phosphides. Carbon catalysts demonstrate potential due to their high conductivity and oxygen reduction properties but face limitations in stability

against Li₂O₂. Noble metals exhibit excellent catalytic performance but are constrained by high costs and resource scarcity. TMOs display notable OER activity, particularly with binary and ternary oxides, where further improvements are achievable through doping and orbital engineering techniques. Emerging catalysts, such as transition metal sulfides, nitrides, and phosphides, show promise in addressing conductivity and charging overpotential limitations to a certain extent. The review concludes that future research should focus on advanced metal sulfide and phosphide electrocatalysts, as well as their heterogeneous structures, to achieve enhanced LAB/LOB performance through optimized catalytic activity and improved discharge product morphology.

Chapter 3: Experimental

During the doctoral studies, various in-situ grafted catalytic structures of Ni-Co oxide, NiCo₂S₄, NiCoP, and their heterogeneous structures were synthesized. The crystallographic, morphological, and physiochemical properties of the as-synthesized catalytic compounds were analyzed using various analytical techniques. The electrochemical properties of the free-standing catalytic cathodes were analysed using a standard three-electrode setup, and by assembling as CR2032 meshed Li-air/ Li-O₂ battery coin cells inside an Ar-filled glovebox. Finally, associated battery operational mechanisms and possible battery degradation pathways were analyzed by studying the components of the de-assembled battery after selected stages of the battery operation. Figure 3.1 presents a general overview of the experimental process carried out during doctoral studies.



gure 5.1. Outline of the experimental procedure during the doctoral stud

3.1. Materials and Chemicals

The following list in Table 3.1 provides a list of chemicals and materials used during the doctoral studies.

Table 3.1: Chemicals and materials used during doctoral studies.

Chemical	Formula	Supplier			
Urea	NH ₂ CONH ₂	Sigma-Aldrich			
Thiourea	NH ₂ SNH ₂	Sigma-Aldrich			
Melamine	$C_3H_6N_6$	Sigma-Aldrich			
Red Phosphorus	Р	Sigma-Aldrich			
Sodium hypophosphite hydrate	NaH ₂ PO ₂ .H ₂ O	Fisher Scientific			
Nickel (II) nitrate hexahydrate	Ni $(NO_3)_2 \cdot 6H_2O$	Fisher Scientific			
Vanadium (III) chloride	VCl ₃	Fisher Scientific			
Manganese (II) nitrate		Fisher Scientific			
tetrahydrate	$Mn (NO_3)_2 \cdot 4H_2O$				
Cobalt (III) nitrate hexahydrate	Co (NO ₃) ₂ · 6H ₂ O	Fisher Scientific			
Lithium bis(trifluoromethane)		Sigma-Aldrich			
sulfonimide (LiTFSI)	$LiC_2F_6NO_4S_2$				
Tetraethylene glycol dimethyl		Sigma-Aldrich			
ether (TEGDME)	C ₁₀ H ₂₂ O ₅				
Ammonia solution (25%)	NH4OH	Sigma-Aldrich			
Nitric Acid (70%)	HNO ₃	Fisher Scientific			
Sulfuric Acid (95-98%)	H_2SO_4	Fisher Scientific			
Hydrochloric Acid (37%)	HCl	Fisher Scientific			
Toray Carbon paper 060	С	Fuel Cell Store			
Isopropanol	(CH ₃) ₂ CHOH	Fisher Scientific			
Carbon black (Ketjen EC600-JD)	С	Fuel Cell Store			
Polyvinylidene fluoride (PVDF)	$-(C_2H_2F_2)_n-$	Fisher Scientific			
Li disk electrode	Li	MTI corp.			
Ethanol	C ₂ H ₅ OH	Fisher Scientific			
Zinc trifluoromethane sulfonate	$ZnC_2F_6O_6S_2$	Fisher Scientific			
(98%)					
Zinc sulfate heptahydrate	$ZnSO_4 \cdot 7H_2O$	Fisher Scientific			
Zn disk electrode		MTI corp.			

3.2. Material Synthesis

3.2.1. Hydrothermal Synthesis

A bottom-up, solution reaction-based technique commonly used for the preparation of crystalline nanomaterials. A nutrient mineral dissolved in the solvent under high pressure and high-temperature conditions, and desired crystal morphologies can be achieved through controlling the parameters associated with the nucleation and crystal growth.

In a typical synthesis, synthesis, well well-dissolved nutrient solution is transferred into a Teflon-lined stainless steel autoclave vessel filling $2/3^{rd}$ of the vessel. The autoclave chamber was then heated to allow the nucleation to initiate and kept at a suitable temperature allowing sufficient time for the crystal growth. Then, the chamber was cooled down, and the resultant product was collected as sedimented powder, or as in-situ grown compounds. The resultant product is washed thoroughly with ethanol and DI water before drying overnight at 60 °C before further processing.

The hydrothermal process was frequently used during my doctoral studies to prepare catalyst precursors, which will be extensively discussed in chapters 4, 5, and 6.

3.2.2. Calcination

Calcination is a thermal treatment, carried out to remove the moisture and other volatile impurities of the subject compounds. The heating temperature could vary with sample properties, however always the temperatures kept below the melting temperature of the subject compound.

During the doctoral studies, calcination was used to produce the required transition metal oxide compounds by calcining the pre-synthesized hydrothermal product.

3.2.3. Sulfurization

Sulfurization is a chemical treatment, that allows to formation of sulfur-containing bonds as the subject reacts with S. Typically, sulfurization is used to synthesize S-containing organic structures by allowing S to react with hydrocarbons. However, during my doctoral studies, sulfurization was used to convert the hydrothermally produced transition metal hydroxide compounds to corresponding transition metal sulfides.

In a typical synthesis, thiourea is used as the source of sulfur, and the target compound is placed downstream inside an Ar-filled horizontal tube furnace as illustrated in Figure 3.2. As the tube furnace is heated above the decomposition temperature of thiourea (above 220 0 C), the produced H₂S travels downstream under the produced Ar flow and reacts with the target compound converting the hydroxide structures into corresponding transition metal sulfides.



Figure 3.2: Sulfurization process

3.2.4. Phosphorization

Phosphorization is a similar chemical process to sulfurization, which forms P-containing bonds instead of S. Phosphorization was used during my doctoral studies to convert the precursor catalysts into corresponding transition metal phosphides and to synthesize Pcontaining hybrid structures. The experimental setup looks identical to the one present in Figure 3.2 with the only modification of sodium hypophosphite hydrate (NaH₂PO₂.H₂O) replacing the thiourea. As the temperature elevates above the decomposition temperature of sodium hypophosphite hydrate, the hydrothermal product kept downstream will start to react with the in-situ generated PH_3 gas forming the desired transition metal phosphide compounds.

The harmful gaseous compounds that could travel downstream during the experiments discussed in sections 3.2.2- 3.2.4 are collected by bubbling it through mineral oil and NaOH-filled waste collectors ensuring maximum safety during the experimental procedure.



Figure 3.3: Scanning Electron Microscopes (a) Hitachi SU6600 FE-SEM, (b) Hitachi JSM-6010PLUS/LV), Transition Electron Microscopes (c) HRTEM, JEM-2000F, JOEL, Japan, Powder X-ray Diffractometer (d) XRD, Siemens D5000

3.3. Morphological, structural, and physiochemical characterization

3.3.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a microscopy technique, which uses a focused high energy electron beam to analyze the morphological properties of the material under observation. Primarily, back-scattering electrons (BSE), secondary electrons (SE), and characteristic energy dispersive X-rays (EDX) are the types of signals could be generated providing information on the material composition and the surface topographical properties as the as the highly energetic electrons interact with the subject substance during an SEM analysis.

During the doctoral studies, the topographical images generated by mapping the surface/ near-surface generated secondary electrons as a result of inelastic scattering in between the primary electrons and sample were extensively used to identify the morphological features of the synthesized catalytic microstructures. Further, characteristic EDX signals were also tremendously helpful in determining the elemental composition and the distribution of the synthesized microstructures.

During the sample preparation, samples were attached on a conductive carbon tape, which was mounted on an aluminium sample holder, and the loosely attached particles were removed by using a rubber bulb dust blower cleaner. A 5nm of gold coating was applied on samples to prevent static charge build up before inserting the samples into the SEM chamber. Electron microscope of Hitachi JSM-6010PLUS/LV and field emission scanning electron microscope (FESEM) of Hitachi SU6600 FE-SEM attached with EDS probes as presented in Figure 3.3 (a, b) were used for the SEM analysis during my doctoral studies, and both instruments were capable of accelerating electrons up to 20kV energy.

3.3.2. Transition Electron Microscopy (TEM)

Transition electron microscopy (SEM) is also a microscopy technique, which uses electrons with a significantly high energy electron to analyze the properties of the samples as morphology, lattice structure, and crystal orientation. In contrast to SEM, transmitted electrons through the sample are used for the TEM analysis, and the imaging resolution is typically in the sub-nanometre range. Selected area electron diffraction (SAED) is a useful crystallographic experimental technique usually coupled with the TEM equipment, which uses the diffracted electrons on the crystal lattice. The generated SAD patterns can be used to identify the crystal structures, crystal orientation, and crystal defects.

During the doctoral studies, TEM analysis, along with SAED analysis was used to determine polycrystalline properties and to identify the heterogeneous surface facets present in the synthesized catalytic structures. Unlike SEM analysis, the specimen needs to be ultra-thin for a substantial electron beam to be passed through the sample during the TEM imaging. Hence, the samples were ultrasonically dispersed in ethanol before loading them into a holey carbon support film on a copper grid for observation. High-resolution transmission electron microscope (HRTEM, JEM-2000F, JOEL, Japan) as presented in Figure 3.3 (c) was used for TEM and SAED analysis, and Gatan digital microscope software was used for TEM imaging and in-depth crystallographic analysis during the doctoral studies. The expert support provided by Dr. W.P.S.L Wijesinghe, Associate Prof. Amor Abdelkader, and Prof. Ali Kamali as authorized TEM users are appreciated.

3.3.3. Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) is a rapid, non-destructive, crystallography technique that could be used to determine the identity, crystallinity, and polycrystalline phases present in the sample. In comparison to SAED, XRD uses the diffraction of X-rays, and the crystallographic properties of a larger sample volume are considered in the generated X-ray diffraction pattern. The operation of the XRD instrument is based on Bragg's law, which describes the following relationship between the wavelength of the X-ray beam (λ), the angle of the incident beam (θ), and the lattice spacing (d).

 $n\lambda = 2dsin\theta$, where *n* is an integer.

During the operation, a coherent beam of X-ray radiation (from a Cu k_{α} source with λ = 1.5406 Å) is directed into the sample (as illustrated in Figure 3.3 (d)), and the diffracted X-ray radiation from the crystal planes of the sample is captured by the detector. The experiment continues for a desired range of incident angle, and the plot of the intensity of the detected X-rays vs. 2 θ is used for identification of the material identification, and the obtained XRD data was further refined using FullProf software to quantify the crystalline phases with greater precision.

3.3.4. X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is an accurate analytical technique to analyze the surface chemistry of a given substance. XPS relies upon the basics of the photoelectric effect, where the kinetic energy (E_{Kin}) of the ejected electrons from the surface of the material is dependent on the energy of the incident X-ray photon energy (hv), and the binding energy of the electron (E_B) as the equation follows.

$$E_B = E_{Kin} - h\nu$$

During XPS analysis, samples are exposed to X-rays from a known wavelength, and the emitted electrons from the surface of the material is guided towards a hemispherical electron energy analyzer (see Figure 3.4), and the multichannel detectors in it help identify the binding energies of the electrons through the measurements of the associated kinetic energies.



Figure 3.4: Schematic cross-sectional view of a hemispherical electron energy analyzer[224].

During the doctoral studies, XPS was also performed to identify the information about elemental composition, chemical state, and the electronic state of the elements. All the samples were kept inside Ar-filled containers. All XPS tests are carried out using ESCALB 250Xi spectrophotometer (Thermo Fisher, USA) by an authorized XPS user, Dr. Chanaka Sandaruwan. For the analysis, samples were mounted onto a standard 60×60 mm K-Alpha System sample plate by pressing onto conductive carbon tape. Then, the samples were loaded into the airlock, and samples were automatically transferred into the analysis chamber as the sufficient vacuum level was reached inside the intermediate chamber. Samples were first analyzed for the elemental composition for the full bandwidth. Based on the findings of the survey scan, high-resolution narrow-band scans were conducted to identify more precise information on the chemical properties of the compounds. Al k α radiation was used with

EXCALABXi⁺ hemispherical electron energy analyzer (Thermo-Scientific Company, US) to determine the chemical state of the as-synthesized catalyst materials, and Thermo Fisher Scientific commercial software (Advantage Data Systems) and CasaXPS software were used to analyze the surface chemical properties of the materials.

3.3.5. Raman Spectroscopy

Raman spectroscopy is a non-destructive analytical technique that could be useful in identifying the chemical and structural composition of the compounds. As a coherent beam of light beam (Laser beam) is directed at a sample, a vast majority of the beam scattered with the same colour frequency (Rayleigh scattering), and only a tiny part of light is interacts with the materials by exchanging energy and the frequency of the scattered light is shifted as a result of the interaction (Raman Scattering). Raman scattering could be stroke or anti-stroke depending on the energy shift as illustrated by a Jablonski diagram in Figure 3.5.



Figure 3.5: Joblonski diagram illustrating scattering modes of an exited electron [225].

In Raman spectroscopy, the instrument filters out the Rayleigh scattered light using a bandpass/ notch filter and provides a plot of light intensity vs. Raman shift. Since the Raman shift is directly co-related with the frequency of in-plane and out-of-plane vibrational

energies of atoms in the molecules or lattices, spectroscopy is useful in determining the chemical and structural composition of the compounds. During the doctoral studies, the samples were analyzed with a fully confocal Horiba XploRATM Raman microscope using 5mW powered 532 nm and 785 nm lasers.

3.3.6. Brunauer-Emmett-Teller (BET) Analysis

BET analysis is known for accurate measurements of the surface area of the porous structures. The instrument uses N_2 isotherms to determine the surface properties of the materials by quantifying the amount of gas molecules adsorbed on the surface of the material. During the doctoral studies, the BET analysis was used to determine the specific surface area and the pore size distribution of the synthesized catalysts, and BET surface area was measured using N_2 adsorption/desorption at 77.3 K on an Autosorb iQ Station after the samples were degassed at 150 $^{\circ}$ C for 12 h under vacuum before physisorption measurements, and Dr. Yasun Y. Kannangara provided technical support during the analysis.

3.4. Battery Assembly and Electrochemical Characterization

3.4.1. Preparation of Electrodes

Two types of catalyst-loaded electrodes were used during my doctoral studies. The initial assessments on Li-air batteries were conducted using a tape-casted catalytic cathode by applying a thin catalytic layer on a gas diffusion layer/ current collector (Toray carbon sheet) using the doctor blade technique. Figure 3.6 (a, b) presents the coating steps, where roughly 1 mg cm⁻² catalyst-loaded cathodic material was prepared. In a typical procedure, 0.25 g catalyst powder is mixed with 0.032 g carbon black (CB) using a motor and pestle. In parallel, 0.032 g PVDF dissolved in 1g NMP by stirring for 1 hr. Next, the catalyst and CB mixture was added into the NMP and PVDF solution and stirred for another 3 hrs until a viscous uniform slurry was obtained, and the gravimetric ratio of catalyst: CB: PVDF ratio is

8:1:1 in the final slurry. Once an even layer of slurry was applied, the coated substrate was kept in an oven for 24 hrs to remove the solvent of NMP.

In addition, the catalytic cathodes were prepared by processing the in-situ grafted catalytic microstructures on the current collector substrates during the hydrothermal process as presented in Figure 3.6 (c, d). During the doctoral studies, in-situ grafted microstructure-based cathodes were found to be more advantageous due to the low interfacial resistance present in such uniformly distributed, self-assembled hierarchical networks of catalytic microstructures.



Figure 3.6: (a) Applying a catalytic layer on a current collector by doctor-blade method and (b) cathode material after drying for 24 hours, (c) In-situ hydrothermal synthesis of catalyst loaded current collector, (d) Photographs taken at different stages of in-situ catalyst loaded cathode preparation where steps 1, 2, and 3 presents cleaned Ni foam, catalyst precursor in-situ coated Ni foam after hydrothermal reaction, and the final catalytic cathode respectively.



Figure 3.7: (a) Li-air battery components, (b) Three-electrode setup[1], (c) Li-air meshed coin-cell under testing

3.4.2. Li-air/ Li-O₂ Battery Assembly

CR-2032 type meshed Li-air and Li-O₂ battery coin cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany), and the H₂O and O₂ levels inside the glovebox were maintained at <1ppm. As synthesized catalyst-loaded Ni foams cut into disks with 13 mm diameter were used as battery cathodes, where the active material loading of individual cells was measured to vary 0.8- 1.0 mg cm⁻². A Li metal foil and a celguard 2500 membrane were used as the battery anode and the separator, while 1 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) solution was used as the battery electrolyte. All components used for LAB assembly are presented in Figure 3.7 (a). All electrochemical measurements were conducted after allowing the batteries to reach equilibrium conditions by keeping them in an oxygen-filled container for 12 hours.

3.4.3. Linear Sweep Voltammetry (LSV) Analysis

LSV is a simple voltage sweep between pre-determined voltages, and LSV plots the measured current vs. voltage. The recorded current at a given voltage depends on the rate at which the voltage changes (scan rate), the rate of the electron transfer during a reaction, and the chemical activity of the material under test.

During the doctoral studies, the OER and ORR electrocatalytic performances of the asprepared catalytic microstructures were evaluated using a three-electrode setup attached to the IviumStat system. During the experiment, the catalyst-grafted Ni foams were used as the working electrode, while Pt foil and saturated calomel electrodes were used as counter and reference electrodes respectively. 1 M KOH electrolyte was used as the electrolyte as presented in Figure 3.7 (b), and all the measured potentials were transformed to the standard reversible hydrogen electrode (RHE) following the formula of E (RHE) = E (SCE) + 0.241 + $0.059 \times pH$. The working electrodes were activated through cyclic voltammetry (CV) tests at 100 mVs⁻¹ before linear sweep voltammetry (LSV) measurements. The OER LSV measurements were carried out at a rate of 10 mV s⁻¹ in a saturated Ar atmosphere, while ORR LSV polarisation curves were recorded at a scan rate of 5 mV s⁻¹ in a saturated O₂ environment.

3.4.4. Cyclic Voltammetry (CV) Analysis

Cyclic Voltammetry is a powerful electrochemical analytical technique commonly used for studying the reaction kinetics involved with the reduction and oxidation processes, which involves electron transfer. During the CV analysis, voltage sweeps between two selected voltages in both forward and reverse directions, and the process repeats (cycles) for as many number of cycles as necessary for the analysis. The analysis is capable of providing information on the electrochemical activity, onset potentials and the reversibility of redox reactions, and chemical/ thermodynamic stability of the products obtained by the electrochemical reactions. During the doctoral studies, CV analysis for the assembled LABs/LOBs was conducted at 0.2 mVs^{-1} scan rate for a potential window of 2.0- 4.5 V Vs Li/Li⁺ using the IviumStat system.

3.4.5. Galvanostatic Charge/ Discharge (GCD) Analysis

Galvanostatic Charge Discharge is a common technique of battery analysis, which discharges and charges the battery with a predetermined current density. Hence this technique can be used to determine the specific discharge/ charge capacities simply by multiplying the current density (*J*) over the operational time (*t*). The experiment can be further extended to determine various other analytical studies. During my doctoral studies, GCD analysis was used to determine the discharge/ charge capacity, cycle stability, rate performance, energy efficiency, and couloumbic efficiency of assembled LAB and LOB cells. All analyses were conducted with the use of a Neware battery analyzer to different depths of discharge and charge at a range of current densities from 100 mAg⁻¹ to 800 mAg⁻¹, and the amount of active material present in the cathode was used for the calculation of the corresponding specific capacities and current densities. Figure 3.7 (c) presents a LOB cell under evaluation.

3.4.6. Electrochemical Impedance Spectroscopy (EIS) Analysis

EIS is a very versatile technique that models the electrochemical systems with the use of common passive components and with other complex components (if necessary) representing the referred electrochemical system with an equivalent electrical circuit. EIS provides a range of information on the mechanistic and kinetic properties, such as lead resistance, charge transfer resistance in the electrolyte, mass transfer resistance in the electrode interface, as well as the time constants associated with certain processes [226]. In EIS analysis, the differences in the output AC signal are analyzed compared with the input AC signal (typically a sinusoidal signal with low amplitude, which does not disturb the equilibrium of the system) over a range of frequencies, and a suitable equivalent circuit is fitted to the resulting Nyquist plot. During my doctoral studies, the IviumStat system was used for electrochemical impedance spectroscopy (EIS) analysis, where a sinusoidal signal with 5 mV amplitude was used in the frequency range of 1 MHz to 0.01 Hz for the study, and fitted equivalence circuits for the obtained results were used for further analysis.

3.4.7. Discharged/ Charged Product Analysis

Understanding the morphology, crystallinity, and the nature of contact with the cathode surface of discharged products is critical to determining the redox reaction pathways, and battery degradation mechanisms. Furthermore, it's vital to make sure that all the discharged products are decomposed upon charging, to achieve a sustainable LAB operation. Hence, during the doctoral studies, the dissembled LAB cathodes were examined with XRD, RAMAN, and SEM analytical techniques by disassembling the batteries at selected stages of discharge and charge to gather the mentioned information.

Chapter 4: Stoichiometrically Optimized eg Orbital Occupancy of Ni-Co Oxide Catalysts for Li-Air Batteries

4.1. Preface

High-density renewable energy storage is becoming increasingly important due to the limited availability of fossil fuels and the global demand for renewable energy sources [2,5], and aprotic Li-Air batteries (LABs), considered the best possible alternative, is still struggling to make meaningful progress owing to its sluggish air cathode reaction kinetics and related parasitic reactions [227,228].

As a better-performing bifunctional catalyst, noble metals provided a decent LAB performance with a good cyclability and a low charging overpotential as discussed in detail previously in section 2.4.2 [131,133]. However, excessive costs limit the practical usage of noble metals and their derivatives in LABs [229]. Numerous low-cost alternatives have shown promising results, such as doped/ undoped carbon [126] and derivatives of nonprecious transition metals, including its oxides [230], and sulfides [186]. Despite their decent ORR activity owing to their suitable pore structure and high conductivity, carbonaceous materials were found to be susceptible to reduced oxygen compounds (ROC) and singlet oxygen (¹O₂) generated during the charging cycle [231]. As revealed during the literature survey section 2.4.3, TMOs demonstrated encouraging performances in the last few years, specifically due to their high stability during OER [232], motivating further research in the field[160]. Among many TMOs explored, binary spinel structures like CoFe₂O₄ [160], and NiFe₂O₄ [233] produced decent bifunctional activity for Li-air batteries, where the mixed valences in AB₂O₄ spinel structures contribute to enhancing the catalytic activity and obtaining good electrical conductivity, overcoming the inherent insulative nature of TMOs [151]. In particular, NiCo₂O₄ has gained considerable attention due to its excellent electrochemical properties [234].

Nevertheless, the high intrinsic resistivity and the limited catalytic activity of TMOs limit their performances as a long-lasting stable catalyst, and using carbon-rich highly resistive binders further amplifies the instability as commonly using binders such as PVDF, PAN, PVC, and PVP was found to be unstable to Li_2O_2 [235], hence, binder-free cathodes were preferred [236]. Further, recently it was identified that the catalytic activity in transition metal-based catalysts can be enhanced by tuning the eg orbital occupation, where a low occupancy in eg orbit with a higher number of unsaturated coordination cations is found to be forming a strong bonding between reaction intermediates, improving the oxygen reaction kinetics. Different orbital engineering and facet engineering techniques such as alloying [140], doping [164], selective facet growth [83], and forming heterostructures [198] were found to be successful up to date in altering the orbital occupancy in transition metal-based catalysts used in LABs.

Important parameters that have yet to receive adequate attention in the existing literature pertain to the impact of the spinel binary oxide stoichiometry, the associated stoichiometric defects towards the electronic properties of the catalyst, and its effects on the electrode's electrochemical performance. In this research, we explore this gap by producing three distinct Ni-Co oxide stoichiometries with dissimilar morphological features, achieved through precise control of nucleation and crystal growth during hydrothermal conditions. Amongst the tested structures, interestingly, the defect-rich inverted spinel structure, formed into a hierarchical groundsel flower-like microstructure directly anchored on the fur-like surface grown on the Ni foam, yielded the best catalytic activity. This structure, having a 1.38 Ni: Co stoichiometry and high Ni³⁺/Ni²⁺ and Co²⁺/Co³⁺ ratios, with plentiful unsaturated coordination cations exhibited exceptional OER and ORR performances in both aqueous and aprotic mediums, with only 1.56 V to reach 10 mA cm⁻² current density and a halfwave potential of 0.89 V in the respective OER and ORR studies in the aqueous medium. Additionally, it displayed an

excellent Li-air battery performance, boasting a specific discharge capacity of 13759 mAhg⁻¹ and a remarkable cyclability of 173 cycles, further demonstrating the key attributes by the synthesized porous binary oxide 3D network with favourable e_g orbital occupation, stoichiometry, and facets supporting fast oxygen redox kinetics and large depositions of the discharged product. Further analysis into the discharged and recharged electrodes found that the high diffusivity and the easy decomposability of the formed amorphous discharge product helped the efficient and durable cyclability of the battery, while the resistance shown by the binder-free binary oxide cathode against the parasitic reaction involving ROC and singlet oxygen helped the sustainable operation with full recovery. These findings highlight the importance of the study, providing deeper insight into optimizing the stoichiometry of binary oxides to obtain favourable eg orbital occupation for enhanced Li-air battery operation.

4.2. Experimental

4.2.1. Synthesis of in-situ electrocatalyst-loaded electrodes

The electrocatalysts of NiCo₂O₄ were directly grown on the surface of a Ni foam using a hydrothermal method. In a typical synthesis, 2.5 mmol Ni (NO₃)₂·6H₂O, 5 mmol of Co (NO₃)₂·6H₂O, and 10 mmol of urea were dissolved into 100 ml deionized water, and 70 ml of it transferred into a 100 ml Teflon-lined stainless steel autoclave vessel. The surface of the Ni foam was prepared suitable for catalyst growth by degreasing the surface via ultrasonic cleaning in an ethanol/ DI (deionized) water mixture, followed by etching out the surface oxide layer using diluted HCl and HNO₃ acid solutions. A 5×2 cm well-cleaned freshly prepared Ni foam was vertically immersed in the precursor-filled autoclave vessel, and it heated at 5 0 C min⁻¹ before maintaining at 120 0 C for 12 h. After letting the autoclave vessel cool down to room temperature, the catalyst-coated Ni foams were collected and washed thoroughly with DI water before air drying at 60 0 C for 12 hours. The dried samples were calcined for 4 hours at 400 0 C with a ramping rate of 5 0 C min⁻¹ in the air to obtain the final

product of NCO 120, which was found to be loaded with catalyst material ~0.8 mg cm⁻². For comparison, two other catalysts were synthesized under different thermodynamic environments by maintaining the autoclave at 150 $^{\circ}$ C (NCO 150) and 180 $^{\circ}$ C (NCO180) for 12 hours, respectively, as shown in Fig. 4.1 while keeping the other parameters the same.



Figure 4.1: Schematic illustration of the growth of different Ni-Co oxide morphologies on Ni foam under different reaction environments

4.2.2. Material Characterization

Crystalline phases of synthesized materials were identified using X-ray powder diffraction (XRD) on a Siemens D5000 diffractometer with Cu K_{α} radiation (Siemens, Germany). The morphology of the synthesized NiCo₂O₄ catalysts was examined using scanning electron microscopy (SEM, HITACHI SU6600), and the microstructure and crystallinity of samples were further examined using transition electron microscopy (TEM, JEOL JEM-2100) combined with selected area electron diffraction (SAED) and inverse- fast Fourier transform (FFT). Brunauer–Emmett–Teller (BET) surface area was measured using N_2 adsorption/desorption at 77.3 K on an Autosorb iQ Station 1 after the samples were degassed at 150 °C for 12 h under vacuum before physisorption measurements. X-ray photoelectron Spectroscopy (XPS) was performed using ESCALB 250Xi spectrophotometer (Thermo Fisher, USA). Al k α radiation was used with the spot size of 900 μ m with the monitored beam values of 14.4 kV (Anode HT), and 18.08 mA (Beam current). All XPS measurements were performed in constant analyzer energy (CAE) mode and 2000 eV of ion energy with the midrange current used for 30 seconds to clean the surface.

4.2.3. Electrochemical Measurements

The OER and ORR performances of the as-prepared in-situ coated electrocatalysts were evaluated using a three-electrode setup attached to the IviumStat system, where the catalyst grafted Ni foam were used as the working electrode while Pt foil and saturated calomel electrodes were used as counter and reference electrodes respectively. 1 M KOH electrolyte was used as the electrolyte, and all the measured potentials were transformed at RHE following the formula of E _(RHE) = E _(SCE) + 0.241 + 0.059*pH. The working electrodes were activated through cyclic voltammetry (CV) tests at 100 mVs⁻¹ before CV and linear sweep voltammetry (LSV) measurements. The OER LSV measurements were carried out at a rate of 10 mV s⁻¹ in a saturated Ar atmosphere, while ORR LSV polarisation curves were recorded at a scan rate of 5 mV s⁻¹ with rotation rates ranging from 0 to 1500 rpm in a saturated O₂ environment. Electrochemical impedance spectroscopy (EIS) was performed for the frequency range of 1 MHz to 0.01 Hz with a 5 mV sinusoidal signal. Further, the catalyst's long-term stability was studied with chronopotentiometric measurements with a current density of 10 mA cm⁻².

The Li-air battery CR-2032 type meshed coin cells were assembled in an Ar-filled glovebox, where 13 mm disks of 0.5- 0.8 mg cm⁻² catalyst loaded Ni foam was used as the battery cathode while 1 mm thick Li foil, celgard 2500 membrane, and 1 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) solution were used as the anode, separator, and the electrolyte respectively. Assembled batteries were kept in a sealed dry air environment at 1 atm for 5 h before electrochemical analysis. CV analysis for Li-air cell was conducted at 2.0-

4.5 V Vs Li/Li⁺ potential window with 0.5 mV s⁻¹ using IviumStat system, and galvanostatic discharge/charge analysis was performed using a Neware battery analyzer where the specific capacities and current densities were calculated considering the amount of active material present in the battery cathode. All the electrochemical analysis were triplicated and averaged to ensure the reliability and the repeatability of the test results. EIS, SEM, and Raman microscopy techniques were utilized for discharge product analysis.

4.3. Results and Discussion

4.3.1. Material Characterization

The Ni-Co oxide catalyst nanostructures were in-situ grafted on the Ni foam using the hydrothermal technique. The synthesis technique is known to produce non-stoichiometric hydroxide structures with crystal imperfections [237] mostly in terms of substitutional disorder (atoms in the given site are replaced by another atom) leading to the occurrence of point defects or extended defects in the calcined binary oxide nano-crystalline structure. Hence, the process helped to optimize the stoichiometry of the derived Ni-Co oxide spinel structure, forming a favourable electronic structure for faster oxygen kinetics.

Scanning electron microscopy (SEM) images identified differently synthesized NCOs' distinct morphological and structural features. Figure 4.2 (a)-(d) indicates that the NCO 120 structure has well-interconnected groundsel flower-like 3D morphology directly anchored on the Ni foam, and the remaining surface of the Ni foam is well covered with fur-like grown NiCo₂O₄ as depicted in Figure 4.2 (d). Further, SEM images of NCO 120 in Figure 4.2 (b, c) and the histogram presented in Figure 4.3 verify the hierarchical growth nature of catalyst microstructures on the Ni foam with a narrow particle size distribution (5.28 \pm 1.19 μ m), in addition to the identified petal diameter of ~30 nm (see Figure 4.2 (c)). This hierarchical structure can provide a high surface area to exploit many exposed active sites and simultaneously leave enough voids for improved O₂/air diffusion. Figure 4.2 (c) further

indicates that the given reaction parameters promote the unidirectional growth of the crystal to form the final groundsel flower-like structure by assembling many needle-like nanostructures.



Figure 4.2: SEM images of different Ni-Co oxide structures anchored on Ni foam, (a-d) low and high magnifications of NCO 120 structure, (e) NCO 150, (f) NCO 180, and (g-j) EDX analysis of NCO 120 structure.

As the hydrothermal reaction temperature increased to 150 °C, even though it looks similar to the one in Figure 4.2 (a) with low magnification, it is observed that the structure of the material (NCO 150) is further opened to form a chrysanthemum flower-like morphology as indicated in Figure 4.2 (e), where the crystal growth seems to expand towards the second direction while keeping the well-interconnected architecture (see Figure 4.4). The SEM images in Figure 4.2 (f) and Figure 4.5 suggest further expansion of the structure as the reaction temperature increased to 180 ^oC by exfoliating individual petals into lamellar-like 2D morphology, where bidirectional crystal growth is well exhibited. The modification in the morphology closely follows the dissolution-precipitation mechanism related to nucleation and crystal growth in hydrothermal synthesis [238]. The increase in crystal size, accompanied by a more open architectural structure (leading to a 2D morphology), can be attributed to the higher convection and diffusion rates resulting from elevated reaction temperatures and ramping rates in both NCO150 and NCO180. These various temperature regimes induce granular growth in different directions, allowing shifts in crystal facets and stoichiometries. EDS elemental mapping (refer to Figure 4.2, panels g-j) confirms the uniform presence of Ni, Co, and O within the synthesized NCO120 structure, whereas the fur-like coating and particles exhibit a comparatively lower concentration of Ni than the Ni foam.





Figure. 4.3: Particle size distribution of NCO 120 catalyst

Figure 4.4: SEM image of NCO 150



Figure 4.5: SEM image of NCO 180

XRD patterns of various as-synthesized NCO structures were analyzed to identify their characteristic crystalline phases. The NCO powder was first detached from the Ni substrate to prevent any overlap with the diffraction signals from the substrate, as previously reported. [157] The XRD pattern in Figure 4.6 (a) shows that all synthesized materials have a similar nano-crystalline cubic spinel structure. The diffraction peaks presented at $2\Theta = 19.0^{\circ}$, 31.1° , 36.8° , 44.7° , 55.5° , 59.1° , and 65.1° could be assigned to (111), (220), (311), (422), (400), (511), and (440) planes respectively, mostly agree with the typical XRD pattern for spinel cubic NiCo₂O₄ (JCPDS No.20-0781, a = b = c = 8.11 ⁰A), consistent with the previous reports. [239] The other small diffraction peak present in the spectrum around 43.8° is due to the presence of residual Ni from the Ni foam. It is worth noting that the XRD spectrum is more diffused for NCO 120, and much sharper diffraction peaks can be observed for NCO 180. Further, a small mismatch in the 311 peak, more distinctly with the NCO 120 structure, can be observed, and it could be due to an offset in the Ni: Co stoichiometry. The shift of the diffraction peak towards the higher angles with lower temperatures could refer to form more Ni-rich compounds, possibly by replacing Co^{2+} with Ni^{3+} ions with a smaller ionic radius. Such a phenomenon aligns with the concept of the partial inversion of spinel crystal structures, where peak shifts and the decrease in intensity are related to a low crystalline material with the increased disorder [240] as the tetrahedral Co²⁺ sites exchanged with octahedral Ni³⁺, reducing the symmetry of the structure [241].

TEM, HR-TEM, SAED, and inverse-FFT were used to further evolute the microstructures of the NCO samples, including their morphological and crystalline lattice properties. The TEM image of an individual petal of the NCO 120 microstructure (Figure 4.6 (c)) shows that the petals are assemblies of small crystals of size varying from 25-40 nm in diameter. The selected-area diffraction (SAED) pattern with well-defined diffraction spots in Figure 4.6 (e) reveals the presence of crystalline Ni-Co oxides. In contrast, the recognized diffraction spots

aligned well with the planes indexed during the XRD studies. The high-resolution TEM of the same structure identified the lattice fringes with d-spacing at about 0.24 nm and 0.47 nm, corresponding to 311 and 111 crystallographic planes of NiCo₂O₄, respectively (Figure 4.6 (d)). As indicated in the inverse-FFT analysis presented in Figure 4.6 (f, g), the calculated interplanar distances of 0.243 nm and 0.467 nm for respective 311 and 111 planes are marginally lower than the reported d-spacing in JCPDS No.20-0781, in agreement with the observed peak shift in the XRD analysis. The dominant surface planes of 111 and 311 are rare for NiCo₂O₄, providing indirect evidence of stoichiometric shifts, where the surface is known to be dominated by the 220 plane along with the 111 plane in most cases (including NCO 150 presented in Figure 4.7) for NiCo₂O₄. [242] More importantly, the image in Figure 4.6 (h) identifies the frequent presence of point defects (or extended defects) on the crystal facets. The defects could arise by substituting Co²⁺ ions at octahedral sites of the spinel structure with Ni³⁺ ions. In such a scenario, since the substituted Ni³⁺ ion at the octahedral site prefers to have tetrahedral coordination, the surrounding oxygen anion matrix can get distorted, and extended defects could rise by missing one or two out of six oxygen anion coordinates. The observations were in line with the XRD results discussed previously and will be further discussed along with the XPS studies.



Figure 4.6: a) XRD patterns of the synthesized NiCo₂O₄ structures on Ni foam, b) Nitrogen adsorption/desorption isotherms and pore size distribution curve of NiCo₂O₄ structures, (c)TEM image, (d) HRTEM image, (e) corresponding SAED pattern, (f, g) inverse-FFT analysis for NCO 120 structure, and (h) crystal defects



Figure 4.7: HR-TEM image of NCO150

The characteristic N₂ adsorption-desorption isotherm curves obtained at 77.3 K for the three NCO materials are presented in Figure 4.6 (b). All materials present type IV isotherm H3 hysteresis behaviour with calculated BET surface areas of 62.31, 45.21, and 39.02 m² g⁻¹ for NCO 120, NCO 150, and NCO 180, respectively. Further, the NCO 120 catalyst contains a large number of mesopores with pore diameters ranging from ~ 5-30 nm with a large pore volume of 54.11 cm³ g⁻¹. This mesoporous structure with higher pore volume is reported to support high discharge capacity by accommodating a large quantity of the discharged products. Also, the mesoporous structure with a higher surface area promotes full reversibility of LAB cells with lower interfacial resistance by keeping the discharged products well attached and within the structure of the cathode surface [174].



Figure 4.8: XPS analysis: (a) survey spectra, (b) Co 2p spectra, (c) O 1s spectra, (d) Ni 2p spectra of as-synthesized NiCo₂O₄ catalysts on Ni foam, and (e) extrapolated co-relations via peak area analysis

Surface chemical states and the composition of synthesized three different Ni-Co oxide catalyst materials were studied using the XPS analysis. The survey scan in Figures 4.8 (a) and 4.9 confirmed the presence of Ni, Co, and O in all three synthesized structures. As indicated
in Figure 4.8 (b), Co 2p spectra of all three samples can be deconvoluted into well-fitted two spin-orbit doublets and shakeup satellites, where the peaks fitted at 779.7 and 794.5 eV correspond to Co^{3+} valance, while the peaks at 780.9 and 795.9 eV are assigned to Co^{2+} .[159] Similarly, the high-resolution Ni 2p spectra in Figure 4.8 (d) can also be fitted with two spin-orbit doubles and shakeup satellites. The peaks at 853.7 and 871.1 eV are assigned to Ni²⁺. The peaks at 855.9 and 873.0 eV can be assigned to Ni³⁺ valance.[243] The peaks positioned at 529.5, 531.1, and 532.6 eV in O 1s spectra in Figure 4.8 (c) typically correspond to metal-bonded oxygen, defect sites with low oxygen coordination, and surface adsorbed hydroxyl groups in water molecules, respectively [155].



Figure 4.9: XPS survey scans for NCO 150 and NCO 180

As indicated in Figure 4.8 (e), NCO 120 poses the highest amount of oxygen vacancies, corresponding to 38% of the total envelope. Further, XPS results provide evidence

confirming that defects could arise by the substitution of Co^{2+} ions at octahedral sites of the spinel structure by Ni³⁺ ions, where a high Ni³⁺/Ni²⁺ ratio and Co^{2+}/Co^{3+} ratios can be observed in the NCO 120 structure. As mentioned, the preference for tetrahedral coordinates of the substituted Ni³⁺ ions at octahedral sites, distorting the surrounding oxygen anion matrix by missing one or two out of six oxygen anion coordinates, is understood to be the mechanism of the formation of the vacancy sites. These differences in the metallic ion ratios in the derived spinel structure were achieved by altering the reaction conditions during the hydrothermal synthesis. The NCO 180 catalyst with the least substitutions and closer stoichiometry (1.74) to standard 2.0 Co/Ni stoichiometry for NiCo₂O₄ structure was synthesized at a relatively higher temperature of 180 ⁰C with more favourable thermodynamic conditions, while low-temperature synthesized NCO 150 and NCO120 catalysts were found to form defect-rich non-stoichiometric complexes with respective Co/Ni stoichiometry of 1.39, and 1.55.

While knowing the identified defect sites could act as the catalyst centres promoting oxygen kinetics as previous literature suggests [244], the main objective of the current study is to understand the effect of alternation in the stoichiometry towards the catalytic activity and the battery performance. Following the concepts in molecular orbital theory, a strong interaction between the atomic orbitals of the catalyst site and the atomic orbitals of the reduced oxygen intermediates is needed to have strong adsorption of the intermediate reduced oxygen compounds (Li_{2-x}O₂) to the surface, facilitating a highly efficient Li-O₂ battery operation [139]. According to the crystal field theory, as the transition metals coordinate with anionic groups as oxides, the d-band splits into two energy levels, where low energy threefold (d_{xy} , d_{yz} , and d_{xz}) t_{2g} base called the bonding orbitals, and the other two degenerates at a higher energy level (e_g base) called as the anti-bonding orbitals. According to Lund's rule and the Aufbau principle, electrons start to fill from the t_{2g} orbitals, and if only the bonding orbitals

were filled in the catalyst site, the reduced oxygen intermediates could bond at the vacant e_g anti-bonding orbitals, making it challenging to acquire strong adsorption at scenarios where the e_g orbitals are highly occupied. Accordingly, a high catalytic activity can be expected $Ni^{3+}(t_{2g}^{}e_g^{1})$ with its unsaturated e_g orbital occupation, compared to highly e_g orbital filled $Ni^{2+}(t_{2g}^{}e_g^{2})$ and $Co^{2+}(t_{2g}^{}e_g^{2})$ ions. Amongst the three derived Ni-Co oxides, NCO 120 presents the highest. Ni^{3+}/Ni^{2+} ratio (2.49) based on the deconvoluted peak area, compared to the ratios of 1.73 and 2.27 for NCO 150 and NCO 180 spinel structures, respectively. Hence, a high catalytic activity can be expected from the engineered NCO 120 structure with favourable e_g occupation, as graphically illustrates in Figure 4.10. The overall summary of the key material characteristics of the three distinctive catalysts are provided in Table 4.1.



Figure 4.10 Graphical illustration for the Stoichiometric Optimization of the d-band e_g orbital occupation for higher catalytic activity

	Table 4.1: Key	/ Material	Characteristics	of the	Catalysts	s against :	synthesis	parameters
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Label	Hydrothermal	Shape	Dominant	Co: Ni	O vacancy/
	Conditions	_	Crystal Planes		Total
			-		Envelope
NCO 120	120 °C -12 h	Groundsel	311, 111	1.39	0.38
		flower-like			
NCO 150	150 °C -12h	Chrysanthemum	111	1.55	0.32
		flower-like			
NCO 180	180 °C -12h	Sheets	111	1.74	0.33

4.3.2. Electrocatalytic activity in aqueous medium

Before constructing Li-air battery cells, the OER and ORR catalytic activity of the synthesized NCOs were evaluated using a three-electrode configuration with a 1M KOH aqueous electrolyte. Figures 4.11 (a), and (b) present the LSV polarisation curves and the associated Tafel slopes, respectively. NCO 120 possesses the lowest onset potential of 1.56 V vs RHE at 10 mA cm⁻² current density and the smallest Tafel slope of 71 mV dec ⁻¹, presenting a superior oxygen evolution activity over the other two synthesized catalysts of NCO 150 and NCO 180. In addition to the faster kinetics, the NCO 120 catalyst exhibits long-term stability, as can be concluded from the galvanostatic chronopotentiometry in Figure 4.12. The stability of the catalyst over 50 hours of exposure to protonated reduced oxygen species as a OH^- , OH^+ , OOH^+ and O₂ verifies the stability of the catalyst against possible parasitic reactions that could occur in aprotic Li-air batteries.



Figure 4.11: (A) Linear sweep voltammetric curves of NCO 120; NCO 150 and NCO 180 for OER in 0.1M KOH at a scan rate of 5 mV s⁻¹, and (B) respective Tafel slopes, (C) ORR polarisation curves at O_2 saturated 0.1M KOH at a scan rate of 5 mV s⁻¹, and (D) respective Tafel slopes



Fig 4.12: Galvanostatic Chronopotentiometry at current density of 10 mAg⁻¹ for NCO 120

Following the OER assessments, the catalytic support towards ORR kinetics was also studied for all three synthesized materials. As indicated in Figure 4.13, all three materials draw higher reduction currents under an O₂-saturated environment, and the NCO 120 catalyst showed better activity with higher ORR current densities and peaks presenting at relatively higher potentials. The LSV curves are presented in Figure 4.13 (c). Again, NCO 120 exhibits the best performance with the highest onset potential of 0.94V vs RHE, the highest halfwave potential of 0.88 V, and the highest current density of 0.47 mA cm⁻² at 0.9 V, outperforming the other two NCO catalysts. The ORR performance of NCO 120 also outperforms many other reported catalysts in the literature [245,246]. It is even higher than the commercial Pt/C catalyst, which was reported to have 0.89 V, 0.836 V, and 0.38 mA cm⁻² of ORR onset potential, halfwave potential, and the current density at 0.9V, respectively [247].



Figure 4.13: ORR CV for NCO 120, NCO 150, and NCO 180 under Ar- saturated and O2-

saturated environments

The Tafel plots in Figure 4.11 (d) show a two-step gradient. The smaller gradient at lower current densities closer to the equilibrium is mostly kinetically driven, while the larger gradients at higher current densities are further away from the equilibrium, where the diffusion effects also contribute to the gradient of the Tafel plot [248]. The lowest Tafel slopes of -31 mV dec $^{-1}$ and 135 mV dec $^{-1}$ were obtained with NCO 120, at least two times smaller than NCO150 and NCO 180 catalysts. Although the ORR Tafel slopes can vary with the catalyst loading and the region of interest, it is safe to mention that NCO 120 is one of the most active ORR catalysts reported so far, where it's exposed 311 and 111 facets, allowing fast adsorption of O₂ into its surface, supporting fast oxygen reduction kinetics. The Pt nanoparticles, commonly believed to be amongst the best catalysts, are reported with the

Tafel slopes of -65 to -82 mV dec⁻¹ at lower current densities and in -100 to -300 mV dec⁻¹ at higher current densities.[249] Further, NCO 120 exhibits only a 0.62 V gap between OER and ORR onset potential with lower Tafel slopes, suggesting it can serve as an efficient bifunctional catalyst, whereas NCO 150 and NCO 180 exhibited larger potential gaps of 0.75 V and 0.77V.

The conducted experiments reveal the high amount of Ni³⁺ present in the electrode surface could significantly enhance the water electrolysis process, where both OER and ORR efficiencies follow the same order of Ni^{3+}/Ni^{2+} atomic ratios, with NCO 120 exhibiting the highest catalytic activity, followed by NCO 180 and NCO 150 catalysts, respectively. The study further implied the significance of the conducted stoichiometric sweep in Ni-Co oxides, which could be used as a simple technique to derive high-performing electrocatalysts. Moreover, the high surface area and the binder-free, well-interconnected unique surface structure of NCO 120 may further enhance oxygen kinetics by exposing more reactive sites.

4.3.3. Aprotic Li-air battery analysis

Following impressive ORR and OER performances in an aqueous medium, aprotic Li-air batteries were assembled using NCO 120 as the binder-free cathode, Li metal foils, and 1M LiTFSI in TEGDME as the electrolyte. LAB cells with NCO 180 and NCO150 cathodes were also constructed for comparison.

The cyclic voltammetric (CV) curves recorded for the LABs in the voltage window of 2.0-4.5 V at 0.2 mV s⁻¹ scan rate are presented in Figure 4.14 (a). The O₂ approaching the cathode-electrolyte interface will undergo a single electron reduction, forming superoxide radicals, and it will subsequently be coupled with Li-ion, forming LiO₂ as denoted in equation 4.1. The cathodic peak at ~ 2.2 V is associated with the mentioned reduction of O₂ forming LiO₂.

$$Li^{+}_{(s)} + O_{2(a)} + e \to LiO_{2(s)}$$
 (4.1)

The diffusivity of the LiO₂ into the electrolyte is determined by the properties of the cathode and the electrolyte, where the electrolytes with the high donor number (DN) have a higher solubility of LiO₂ in the electrolyte. In such scenarios, since LiO₂ is an unstable superoxide in the electrolyte with a small countercation, it is quickly disproportionate, producing lowsoluble insulating toroidal-shaped Li₂O₂ as presented in equation 4.2, which accommodates at the pores of the cathode. It requires higher charging overpotentials to decompose Li₂O₂ toroids upon charging since its crystalline nature, the weak coupling between the cathode surface, and the oxidation peak presented at and above 4.0V during the anodic scan is correlated with the decomposition of such bulk and dense Li₂O₂ [250].

$$2LiO_{2(sol)} \rightleftharpoons Li_2O_{2(s)} + O_{2(q)}$$
 (4.2)

The produced oxygen reduction intermediates as LiO_2 have a high tendency to stay in contact with the cathode surface on occasion at the cathode surface supporting high adsorption of O_2 and LiO_2 . In such scenarios, LiO_2 could undergo a second electrochemical reduction (see equation 4.3) in addition to the mentioned disproportionation-producing surface adsorbed amorphous Li_2O_2 . Further, the identified crystal defects/ oxygen vacancies could stabilise LiO_2 on the surface without further reduction. [244]

$$Li^{+} + LiO_{2(ads)} + e \rightarrow Li_2O_{2(ads)}$$

$$(4.3)$$

The presented additional anodic peaks at 3.19 V and 3.53 V related to NCO 120 cathode suggest the decomposition of the surface adsorbed LiO₂ and amorphous and non-stochiometric Li_{2-x}O₂ during the battery charging, which is significantly less for NCO 180 cathode. Even though NCO 180 exhibits good bifunctional catalytic activity, the NCO 120 cathode demonstrates superior performance with more positive ORR peak positions, less positive OER peak positions, and higher current densities. As was explained, it is noteworthy

to mention that the stochiometric changes engineering a favourable surface electronic structure with plentiful unsaturated e_g orbital coordinates could lead to the high adsorption in NCO 120, supporting the formation of well-adsorbed reaction intermediates allowing an easy decomposition of the discharged products which is possibly in weakly crystalline nature. The ability to decompose a higher portion of Li₂O₂ at a lower overpotential could suppress the amount of singlet oxygen (¹O₂) that could be generated during the decomposition of the discharged products at higher potentials, where the singlet oxygen was identified as the main culprit causing parasitic reactions during Li-O₂ battery cycling [84].



Figure 4.14: (a) CV analysis @0.2 mVs⁻¹ and (b) full discharge-charge @100 mA g⁻¹, and selected discharge-charge curves of (c) NCO120, (d) NCO 180 cathode-based LABs operated at 100 mAg⁻¹ for a limited capacity of 500 mAhg⁻¹, (e, f) Cycle life and performance analysis of LABs with NCO 120 and NCO 180 based cathodes with cut-off discharge capacity of 500 mAh g⁻¹ with 1M LiTFS1 dissolved in TEGDME electrolyte

The superior performance of the NCO 120 cathode is further investigated using the chargedischarge profiles of the LABs presented in Figure 4.14 (b). The discharge capacities of the batteries follow the order of NCO 120> NCO 180> NCO 150, following the same pattern observed during the aqueous medium. The initial discharge capacities of 5079 mAh g⁻¹ and 8431 mAh g⁻¹ showed by NCO 150 and NCO 180 based LABs, respectively is only 36.9 % and 61.3 % of the specific discharge capacity of 13759 mAh g⁻¹ achieved by the NCO 120 cathode-based battery. In addition to the remarkable catalytic activity displayed by NCO 120 owing to the abundant presence of surface catalytic sites featuring unsaturated eg orbitals as discovered through TEM and XPS studies, the high surface area and interconnected mesoporous microstructure, as evidenced by BET and SEM studies can also be considered as the main attributes of its superior charge-discharge performance. This is particularly evident in its ability to accommodate a substantial quantity of nanosized Li₂O₂ crystals and amorphous discharge products. The lowest observed charge voltage plateau of 3.89 V and the highest discharge voltage plateau of 2.80 V, along with the minimal charging overpotential of 1.09 V, are distinctive features of the NCO 120-based LAB, confirming the high affinity of it towards the rection intermediates. These characteristics further underscore its superior catalytic powers compared to the NCO 150 and NCO 180 microstructures, which exhibit significantly higher overpotentials of 1.46 V and 1.22 V, respectively, with limited support for OER and ORR.

The cyclability of NCO 120 and NC 180 cathode-based LABs was evaluated using the charging and discharging method at a current rate of 100 mA g⁻¹ with a limited discharge capacity of 500 mAhg⁻¹. Figure 4.14 (c)- (d) presents the resultant charge-discharge curves.

The LAB constructed with NCO 120 demonstrated the longest cycle life, successfully working up to 173 continuous cycles. In contrast, LAB with NCO 180 cathode only lasted for 84 cycles. The long cyclability exhibited the stability of the catalyst over a prolong period. The exhibited excellent cyclability of NCO 120-based LAB also surpasses the performances of many other NiCo₂O₄ and related-spinel cathode-based Li-Air and Li-O₂ batteries, as presented in Figure 4.16 (a) [251–255].

In addition to individual charge-discharge curves, the respective potentials at the end of each step were also recorded. As illustrated in Figure 4.14 (e), the charge potential remains mostly constant at around 3.85 V for the first 80 cycles before it starts to rise gradually. The observation validates the undiminished OER support, and the availability of catalyst cites to get attached for the reaction intermediates. The discharge potential, on the other hand, dropped steadily throughout the cyclic study until it reached the cut-off potential of 2.0 V during the 173rd cycle for NCO 120. In contrast, the relatively stable charge and discharge potentials rose and dropped sharply respectively by the 50th cycle during the cyclability analysis of NCO 180-based LAB, causing a sharp rise in the potential gap, as can be seen in Figure 4.14 (d) and (f). We believe, either the unfavourable physical properties of NCO 180 cathode where the attached 2D sheets could lose its contact with the surface of the cathode, or the fast-decaying catalytic properties is responsible for the reduced activity. Even though the NCO 180-based LAB performed marginally better in the first few cycles, the overall impressive, smooth, and steady operation was observed with the NCO 120-based Li-air battery system during the cyclability analysis, performing 173 cycles in the dry air medium for the span of 3460 hours by maintain a lower potential gap and the full cyclability. The high oxygen, LiO₂, and Li₂O₂ adsorption capabilities in NCO 120-based cathode attributed to its supportive surface electronic structure may contribute to long cyclability and low charge/discharge overpotential by providing high adsorption to the reaction intermediates.

Hence, a swift decomposition at lower charging overpotentials was achieved by forming a nano-crystalline layer of $Li_{2-x}O_2$ well-attached at the surface during discharge while suppressing the discharge product mitigating the electrolyte and the formation of a large toroid of Li_2O_2 .



Figure 4.15: Electrochemical performance analysis of NCO120 cathode-based LABs under different current densities: (a) full discharge-charge capacity, selected discharge-charge curves under a current density of (b) 100 mAg⁻¹, (c) 200 mAg⁻¹, and (d) 400 mAg⁻¹

Then the performance of the NCO 120 LAB was studied at higher current ratings. In principle, charging overpotential will increase faster under higher current densities. Hence, lower discharge capacities were expected at higher current densities since the discharge product is expected to form a thin layer at the cathode surface, ruling out further discharge by quickly covering all available sites for oxygen adsorption. Further, the decrease in oxygen diffusion depth contributes inversely to achieving higher discharge capacities at higher current densities [200]. As the current density increased to 200 mAg⁻¹, NCO120 LAB showed

an impressive discharge capacity of 10030 mAh g⁻¹ with a 93% coulombic efficiency, as indicated in Figure 4.15 (a). This achievement constitutes a noteworthy 72.7% of capacity retained compared to the discharge capacity obtained at a 100 mA g⁻¹ current rating. The discharge capacity decreased to 4,945 mAh g⁻¹ as the current density was further raised to 400 mAg⁻¹. This change was accompanied by a coulombic efficiency of 84.6% and a charge/discharge overpotential of 2.19 V, underscoring the challenges in maintaining full reversibility after full discharge, thus indicating reduced capacity. The cyclability of the NCO 120 LAB was impressively high at 200 mA g⁻¹ and 400 mA g⁻¹ current density, operating at nearly 100% coulombic efficiency for 96 and 59 respective cycles, as indicated in Figure 4.15 (b-d). In addition, the battery lasted for another 16 cycles of operation before decaying its performance <50% of charge retention as the cells cycled at the rate of 400 mA g⁻¹. Further, two voltage plateaus can be found in the studies related to fast charging. This is more likely to be associated with the decomposition of the surface grown nanocrystals of Li_{2-x}O₂ at a lower potential and the large toroid of Li₂O₂ needing a relatively high potential to get decomposed. The presence of the voltage plateaus in similar potential range as observed as peak positions during the cyclic voltametric studies further justifies the observations. In addition, a smooth charging step under 100 mAg⁻¹ rate of charge is noticeable, and it suggests that the formation of nanocrystalline/ amorphous product of Li_{2-x}O₂ is favourable during the discharging step. It is noteworthy to mention that the limiting factor for terminating the battery cycling occurred as the discharge process reached its cut-off conditions, unlike the typical scenario of the inability to complete recharge under the effective potential window. Therefore, it could suggest that the catalyst is exhibiting far greater OER performances over the ORR activity. Restrictions at oxygen diffusion with limited O₂ content in dry air and the changes in the cathode surface/ electrolyte during continuous cycling may trigger the reduction in the discharge potential.



Figure 4.16: (a) Literature comparison [251–255], (b) EIS analysis, (c) ex-situ Raman analysis on LAB cells with the free-standing NCO 120 cathode at various levels of discharge and charge

Figure 4.16 (a) presents a comparison between the NCO 120 electrode and other reported LAB cathodes in the literature. The figure demonstrates the stable and outperforming bifunctional catalytic activities of NCO 120. For instance, a slightly improved OER onset potential and ORR halfwave potential were achieved by Chang et al [255] with the aid of a hybridized carbonaceous structure, where their Co-Ni alloy was enclosed within N-doped graphene. However, this approach seems to have drawbacks. Specifically, it led to the system's deterioration, reducing the battery's lifespan, as it couldn't endure a significant number of charge/discharge cycles, possibly due to the electrochemical instability of the graphene at higher potentials. This prompted us to delve deeper into the associated reaction

mechanism and gain further insights into the exceptional bifunctional catalytic activity of the freestanding NCO cathode. Consequently, we conducted ex-situ analysis of discharge and charge products using Electrochemical Impedance Spectroscopy (EIS), SEM, and Raman spectroscopy.

Since a bottom-up growth approach has been used to grow the NCO catalysts on the Ni foam substrate, a superior interfacial bonding with good ohmic contact in between the catalyst sites and the substrate is expected. EIS analysis was conducted on LAB cells with the freestanding NCO 120 cathode at various levels of discharge, as presented in Figure 4.16 (b) as the battery discharged/charged at 100 mAh⁻¹ current density, using a sinusoidal signal with the amplitude of 5 mV_{pp} in the frequency domain of 0.01 -1000 Hz. In the Randles circuit fitted Nyquist plot obtained for LABs, the high-frequency interception of the semicircle with the real axis is related to the series ohmic resistance (R_s) , which is a sum of the lead resistance, contact resistance, and ionic resistance by the electrolyte and the separator, while the semicircle denotes the charge transfer resistance (R_{ct}) at low frequencies. The lowest Rs and Rct with respective values of 11.8 Ω and 168.3 Ω were found initially before the discharge. The ohmic resistance increased to 12.6 Ω , and 16.3 Ω , respectively after being discharged to 2000 mAhg⁻¹ depth and discharged fully, before decreasing to 12.2 Ω after being charged back. The charge transfer resistance also followed the same trend, where the respective values of 196.5 Ω , 362.7 Ω , and 177.4 Ω were recorded after the phases of limited discharge (2000 mAhg⁻¹), full discharge, and recharge. Irrespective of identified surface defects and favourable electronic structure, the overall insulative characteristics of metal-oxides may have contributed heavily to the initial resistance. An increase in the R_s and R_{ct} during the discharge is associated with the formation of the surface adsorbed Li₂O₂ insulating layer on the cathode, and the increased ionic resistance is also contributed as the Li-ion concentration reduced considerably while it participates in forming non-soluble Li₂O₂. It is noteworthy to

mention that the impedance increased only marginally after discharged to 2000 mAhg⁻¹, and more importantly, after the first charge, the R_s and R_{ct} reduced substantially, almost reaching the initial conditions, verifying the full decomposition of the discharged product, which further implies the excellent redox kinetics in NCO 120 freestanding cathode-based LAB. Further, the identified remarkable recoverability of the cell after being charged back may be pivotal in demonstrating excellent cycle performances of the NCO 120-based cells.

Raman analysis is a potent technique for analyzing the exiting phases on the air electrode, and it could identify the presence of a range of electrochemically and chemically generated Li species, which affects the cyclability and efficiency of the LAB. The conducted ex-situ Raman analysis on the battery cathode obtained at different stages of the discharge and charge is presented in Figure 4.16 (c). Apparently, the synthesized starting material is free of Li-related Raman peaks in the area of interest. Upon full discharge, two distinct peaks at 266 and 813 cm⁻¹ arose, which could be assigned to the desired discharge product of Li₂O₂ [225]. Almost full reversibility of the battery is demonstrated as the peaks disappear upon charging, where only a slight trace can be identified. Further, the Raman spectrum obtained for the NCO120 cathode after 50 cycles indicates residue Li_2O_2 left at the cathode surface. This explains the loss of capacity as more undecomposed discharge products accumulate at the cathode surface as the cycle number progresses. In addition to reversibility, the results further verify that none of the parasite products, like Li₂CO₃ or LiOH, were formed in the system in detectable quantities. High contributions from the self-standing cathode architecture and the high OER activity of the NCO 120 catalyst may pave the path towards a longer life span by minimizing the early degradation of cathode materials and electrolytes. The detection of strong peaks and the respective peak positioning further indicates the formation of amorphous layers of Li₂O₂ over crystalline toroidal-shaped particles since amorphous Li₂O₂ is easily detectable at relatively higher frequencies [252] (than crystalline Li₂O₂) due to its marginally uncoordinated defective nature and shorter O-O bond length.



Figure 4.17: Ex-situ SEM analysis of the free-standing NCO 120 cathode (a, d) initially before discharge, (b, e) fully discharged, and (c, f) recharged.

The conducted ex-situ SEM analysis of the NCO 120 cathode material at various stages of the discharge-charge process also provides further insight into the discharge mechanism, as presented in Figure 4.17. It was evident that the discharged product fully covered the cathode surface as the battery was fully discharged, as indicated in Figure 4.17 (b, e), compared to the cathode before discharge as in Figure 4.17 (a, d). The reversibility of the process is proven as the formed Li₂O₂ was decomposed upon charging, leaving the morphological features of the charged cathode (Figure 4.17 (c, f)) much similar to the initial NCO 120 cathode as indicated in Figure 4.17 (a, d). Further, it is noteworthy that the discharged product was deposited over the surface of the cathode as an amorphous coating without any crystalline shape, well distributed along the cathode surface. The observations made here validates the previous observations made during the cyclic voltammetry, galvanostatic charge-discharge, and Raman microscopic analysis, which favours the growth of nanocrystalline/ amorphous discharge

product over the growth of toroidal-shaped crystals of Li₂O₂, specially during the current rate of 100 mAg⁻¹. High abundancy of catalytic sites throughout the cathode surface, and the identified superior catalytic activity of the stoichiometrically modified Ni-Co oxide catalyst material with the vacant d-orbital sites with easy accessibility for the charge/ discharge intermediates are expected to be favouring the growth of easily decomposable surface-attached discharge product, promoting superior LAB performance.



Figure 4.18: Schematic illustration of the surface-adsorbed growth mechanism of Li₂O₂ on free-standing NCO 120 cathode during the LAB operation

Considering the observations made via EIS, ex-situ Raman, and ex-situ SEM studies, the following mechanism presented in Figure 4.18 seems to be well suited for describing the discharging-charging process of the studied NCO 120 cathode-based LABs. As the battery discharged, a thin layer of discharge product gradually covered the voids in proximity, and this layer largely dissipated as the battery underwent recharging. Despite earlier conjectures about the passivation of Li-air battery cathodes due to the formation of a thin layer of

discharge product on the surface, limiting the discharge capacity, our current study challenges this notion. We achieved a substantial discharge capacity while generating surface adsorbed LiO₂ and Li₂O₂. To attain such a substantial surface coating of the discharge product and to achieve long endurance during cycling, we postulate the following,

 The defect-rich cathode facets have a supportive electronic structure, promoting fast adsorption of reaction intermediates, which encourages discharge products to stay intact on the cathode surface even though a solvent with a high donor number (DN) was used. The reaction mechanism for the electrochemical reduction of O₂ occurred at the air-electrolyte-catalyst three-phase interface could be denoted as,

$$Li^{+}_{(s)} + O_{2(a)} + e \to LiO_{2(ads)}$$
 (4.4)

, where the formed superoxide radical (O_2^{-}) reacts with Li⁺ forming LiO₂. Since the produced Lithium superoxide stayed intact with the electrode surface, it could be assumed that the final discharged product of Li₂O₂ was mostly produced by the second electron transfer (as previously introduced) over the disproportionation of LiO₂.

$$Li^{+}_{(s)} + LiO_{2(ads)} + e \rightarrow Li_2O_{2(ads)}$$
 (4.3)

- 2. The coated discharged product is amorphous and is permeable to Li+ diffusion, allowing further discharge.
- 3. The catalyst exhibits high OER activity owing to the presence of unsaturated e_g orbital coordination sites, /and the Li₂O₂ is relatively conductive and easily decomposable, enabling a stable LAB operation over 170 cycles with a low charging overpotential.

- 4. Since the side products, such as Li₂CO₃, were not detected during the study in substantial quantities, it could be assumed that the reversible operation of LAB cells took place without many obstacles related to parasitic reactions due to the following.
 - a. As the reduced reactive oxygen species, LiO₂, and Li₂O₂, mostly stayed intact with the surface of the catalysts, it could be assumed that the electrolyte was less exposed to parasitic reactions during the discharging involving possible nucleophilic substitutions and H atom abstractions by the mentioned species.
 - b. Since Li₂O₂ stayed intact on the electrode surface as an amorphous coating and since it was fast decomposed upon charging, it could suppress the extensive singlet oxygen generation, protecting the electrolyte from prolonged exposure.
 - c. The self-standing NCO 120 cathode remained resistant to parasitic reactions, unlike carbon-based electrodes, which were reported to be susceptible.
 - d. The presence of a small CO₂ quantity (~0.04%) in dry air does not seriously affect the reversibility of LAB cells, and the number of parasitic reactions could occur in air medium via generating highly reactive protonated reduced oxygen species as HOO^{*}, HOO⁻, and HO^{*} were substantially reduced as the main proton source (moisture) was removed from the medium.

Only providing limited details on surface facets and their adsorption energies could be found as a limitation of the study, which could have a significant correlation with the battery performance, which is worth investing in the future. Even though we used Ni-Co oxides to demonstrate the effect of stoichiometry on catalytic performances, the concept can be expanded to other systems with greater effectiveness in the future. Since a more sensible pathway towards achieving a true Li-air battery through solid-electrolyte, separating Li metallic anode from the environment, it is particularly important to understand the effectiveness of derived solid electrocatalysts with solid electrolytes and the associated electrochemistry, where the solution-based redox mediators cannot expect to be compatible.

4.4. Conclusion

In summary, we developed a series of Ni and Co binary oxides with unique hierarchical 3D structures by controlling nucleation and growth during hydrothermal processes. The stoichiometry, electronic properties, morphology, and distortions in the crystal structure of the derived structures were found to depend on the parameters of the synthesis process, yielding three distinctive structures. The material analysis suggested that the NCO 120 has the most favourable catalytic structure with plentiful unsaturated eg orbital coordinates formed through substitutional disorders and a well-formed hierarchical network. This electrode demonstrated exceptional performance, achieving a discharge capacity of 13,759 mAhg⁻¹ at a current density of 100 mAg⁻¹. Moreover, the cell operated continuously for 3,460 hours, completing 173 charge/discharge cycles while maintaining a capacity of over 98% coulombic efficiency in a dry-air environment. This performance surpasses the performances of the constructed LABs with NCO 150 and NCO 180, and the performances of many other LABs reported with spinel oxides, indicating the significance of the study. Even though the study used the spinel structures of Ni-Co oxide, the discussed strategy could be extended for optimizing the stoichiometric ratios in other similar structures of oxides, sulfides, phosphides, etc. The introduced highly efficient cathode catalytic system could be coupled with a solid electrolyte to develop long-durable Li-air battery systems in future research by protecting the battery anode against contaminants.

Chapter 5: Hetero-nanostructured NiCoP/NiCo₂O₄ for sustainable Li-O₂ battery operation through optimised discharged product morphology

5.1. Preface

The limited charge storage capacity of current energy storage devices poses a challenge to the utilization of green energy. Due to their ultra-high theoretical energy density of 11.6 kWh kg⁻¹, Li-air batteries (LABs) are considered an ideal battery technology capable of delivering exceptional performance [256]. However, despite extensive research in the last few years, a viable LAB or a Li-O₂ (LOB) battery has yet to reach the commercial market. In such cells, difficulties in controlling the morphological and crystallographic properties of the discharge products often hinder their efficient decomposition, especially at high current densities, limiting the progress of LAB and LOB systems [25]. Presenting reasonable solutions to those challenges is a primary objective in this doctoral thesis.

Even noble metals and their derivatives like Au, Pt, PtPd, and RuO₂ effectively promote the kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER, the scrunty and high cost of such electrocatalysts limit their usage in commercial battery applications [257]. Despite the clear advantages of carbon nanostructures with highly diversified lightweight and conductive pore structure through accommodation of large amounts of discharged products [258], parasitic reactions due to the electrochemical instability of carbon materials at high charging overpotentials and average OER support wer found as major obstacles before utilizing carbon-based catalysts at the cathode of LOBs, leading to rapid decay in battery performance [25,257].

TMOs considered abundant, economical, stable, and suitable alternatives, and oxides of Ni, Co, V, Fe, and Mn were reported for such application with decent performance, where bimetallic oxides, engineered oxygen vacancies, and the derived binder-free self-standing cathode architectures provided a better support to enhanced performance of LOBs [253,259]. In the previous chapter, the utilisation of self-standing NiCo₂O₄ provided a long cycle stability of 173 cycles with a limited capacity of 500 mAhg⁻¹ and a high discharge capacity of 13759 mAhg⁻¹ at a current density of 100 mAg⁻¹. Nevertheless, the typical low electrical conductivity of TMOs often increases the charge transfer resistance, leading to high charging overpotentials, reducing energy efficiency and limiting the extended full cyclability only to low current densities in LOBs.

In contrast, as discussed during the literature review, transition metal phosphides (TMPs) are known for their high electrical conductivity and catalytic activity [260]. In particular, TMPs such as Ni₂P, CoP, FeP are currently acquiring sizable attention as efficient electrocatalysts in related fields, including water splitting [261], supercapacitor applications [262,263], Li-ion batteries [264–266], Li-S batteries [267], Zn-air batteries [268], and in general for catalysing individual ORR and OER kinetics[269-271]. Despite the potential suitability, studies concerning the utilization of TMPs in LOBs are still limited. Moreover, the performances of catalysts such as CoP [272] and MoP [205] in LOB applications were not satisfactory. Strategies such as modulating the surface electron structure [261,264,273] and promoting oxygen vacancies [274] can be effective ways of enhancing the electron and Li⁺ ion transport, hence the electrocatalytic performances of TMPs in LAB and LOB systems. Further, Dang et al. used the synergy of CNT and NiCoP to a better effect in LOBs. The cell was reported to survive for 150 cycles at a high current density of 500 mAhg⁻¹, indicating the high activity in bimetallic phosphides compared to mono-metallic counterparts.[275] As reported by Li et al., weakening the adsorption of LiO₂ on catalyst facets could lead towards superior Li-O₂ battery performances as it could help to reduce the surface passivation of the TMP catalysts by having a film-like growth of Li₂O₂. [276]

In the current research, we focus on improving LOB performance by controlling the morphology of the discharge product, where it's commonly reported as a thin layer covering the surface of the catalyst. As an efficient strategy, we report that optimising the catalytic activity of NiCoP is possible by hybridizing this phase with the NiCo₂O₄ phase. To this end, a unique hierarchical three-dimensional heterostructure of NiCo2O4/ NiCoP is directly anchored on the Ni foam to obtain desirable electrocatalytic activity, in comparison with those of individually grown NiCoP and NiCo₂O₄ with similar morphological features. The derived groundsel flower-like structure provides favourable morphological features, improving the electron transfer between heterogeneous NiCo₂O₄ (311) and NiCoP (111) surfaces, leading to a desirable catalytic activity that promotes both ORR and OER reaction kinetics. The unhindered durable operation of the heterogeneous catalyst is reported as key enabling the operation of the assembled LOB for >250 hours exceeding 400 cycles under a high current rate of 800 mAg⁻¹. In this system, the discharge product (Li_2O_2) is formed into thin sheets homogeneously spread over the surface of the cathode, well attached to the surface of the catalyst microstructure. The non-common morphology of the Li₂O₂ observed in this study and its areal distribution effectively support the early decomposition of the discharge product during the charging step as well as the swift diffusion of Li ions, allowing a long exposure of the cathode surface. The advanced features of the cathode structure and the discharge product morphology largely support the performance of the cathode at high rates, overcoming the inherent drawbacks of electrocatalysts based on metal oxide and metal phosphide compounds.

5.2. Experimental Section/ Methods

5.2.1. Synthesis of electrocatalyst-loaded electrodes

Catalytic cathode structures were prepared by following multiple synthesis steps. As the first step, a bottom-up hydrothermal synthesis technique was used to make the intermediate catalyst materials of Ni-Co-hydroxide microstructures directly anchored on nickel foam. Ni foams were well cleaned by degreasing the surface pollutants via ultrasonic cleaning in a water/ethanol mixture before removing the surface oxide layer by inserting the Ni foam into an acid solution (diluted mixture of HCl and HNO₃) for 3-4 h. Nutrition solution containing metal ion precursors was prepared by dissolving 2.5 mmol Ni (NO₃)₂· 6H₂O, 5 mmol of Co (NO₃)₂· 6H₂O, and 10 mmol of urea in 100 ml of deionised water through continuous stirring for 4 hours. In a typical synthesis, 70 ml of the nutrition solution was transferred into a 100 ml Teflon-lined stainless steel autoclave vessel, where freshly prepared 5× 2cm sized Ni foams were placed vertically. The autoclave vessel was heated at 5 °C min⁻¹ and maintained at 120 °C for 12 h, allowing sufficient time for the crystal growth before cooling down the system at the same rate. The hydrothermal product containing a pink-coloured coating attached to the Ni foam was collected and washed thoroughly with DI water before drying at 60⁰ for 12 h. For future reference, the product was labelled NC-OH/Ni.

The synthesised NC-OH/Ni structure was calcined for 4h at 400 $^{\circ}$ C under heating and cooling rates of 5 $^{\circ}$ C min⁻¹ to obtain the pre-catalyst material of NiCo₂O₄ anchored on the Ni foam labelled as NCO/Ni. The final catalyst compound was synthesised by partial phosphorisation, where the NCO/Ni precursor was placed downstream and excessive NaH₂PO₂.H₂O was placed upstream in a tube furnace heated to 300 $^{\circ}$ C for 2h. The final product, NCP@NCO/Ni, was collected as the furnace chamber cooled down.

For comparison, the catalytic cathode structure of NCP/Ni was prepared by the phosphorisation of the NC-OH/Ni product, following the previous procedure of phosphorisation.

5.2.2. Material Characterisation

X-ray powder diffraction (XRD, Siemens D5000) with Cu K_{α} radiation was used to analyse the crystalline phases of the as-synthesised catalytic compounds and the disassembled battery components. Scanning electron microscopy (SEM, HITACHI SU6600) images were used to analyse the morphological properties of the catalytic hierarchical microstructures grafted onto the Ni foam before inserting into the LOBs and after retrieving at different discharge/ charge process stages. Further evaluation of the morphological properties and surface crystallographic phases was conducted by transmission electron microscopy (TEM, JEOL JEM-2100 and JEOL JEM-1400) imaging combined with selected area electron diffraction (SAED) and further processing of high-resolution TEM images using GATAN DigitalMicrograph software. The surface chemical composition of the catalyst structures was studied using X-ray photoelectron Spectroscopy (XPS, ESCALB 250Xi spectrophotometer by Thermo Fisher, USA) using Al ka radiation with the spot size of 900 µm and with the monitored beam values of 14.4 kV (Anode HT), and 18.08 mA (Beam current). Constant analyser energy (CAE) mode was used for all the XPS measurements, and the samples were cleaned by exposing them to 2000 eV ion energy with the mid-range current for 30 seconds. The 3D cross-section of the catalysts was further analyzed with the small-angle X-ray scattering (SASX) technique. During the SASX analysis, radially averaged data were collected with a Xenocs nano-inXider instrument with a Cu K_{α} source using 1.2 mm diameter quartz capillaries for the samples.

5.2.3. Electrochemical Measurements

All electrochemical measurements were conducted using CR-2032-type meshed Li-O₂ battery coin cells which were assembled in an Ar-filled glove box. As synthesised catalyst-loaded Ni foams cut into disks with 13 mm diameter were used as battery cathodes, where the active material loading of individual cells was measured to vary 0.8- 1.0 mg cm⁻². A Li metal

foil and a celguard 2500 membrane were used as the battery anode and the separator, while 1 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) solution was used as the battery electrolyte. All electrochemical measurements were conducted after allowing the batteries to reach equilibrium conditions by keeping them in an oxygen-filled container for 12 hours, which was maintained at atmospheric pressure.

Cyclic voltammetry (CV) analysis for the assembled LOBs was conducted at 0.2 mVs^{-1} scan rate for a potential window of 2.0- 4.5 V Vs Li/Li⁺ using the IviumStat system. The same system was used for electrochemical impedance spectroscopy (EIS) analysis, where a sinusoidal signal with 5 mV amplitude was used in the frequency range of 1 MHz to 0.01 Hz for the study, and fitted equivalence circuits for the obtained results were used for further analysis. Galvanostatic discharge/ charge (GCD) analysis was conducted with the use of a Neware battery analyser to different depths of discharge and charge at a range of current densities from 100 mAg⁻¹ to 800 mAg⁻¹, and the amount of active material present in the cathode was used for the calculation of the corresponding specific capacities and current densities.

5.3. Results and Discussion

5.3.1. Material Analysis

The schematic diagram in Figure. 5.1 illustrates the typical experimental techniques used for synthesising NiCoP and NiCo₂O₄ /NiCoP hybrid catalysts. Ni and Co bimetallic hydroxide microstructures were first grown on the Ni foam via the hydrothermal method. The obtained groundsel flower-like microstructure network was calcined to obtain NiCo₂O₄ on the Ni foam. The final catalyst of NiCo₂O₄/NiCoP grafted on the Ni foam (NCP@NCO/Ni) was synthesised by the phosphorisation of the metal oxide precursor. The hydroxide precursor

was directly phosphorised for comparison, forming NiCoP on the Ni foam, denoted as NCP/Ni.



Figure 5.1: Schematic diagram of synthesis produces of catalytic structures

After the hydrothermal reaction, a pink-greyish coating appeared on the surface of the Ni foam. The magnified scanning electron microscopy (SEM) image (Figure 5.2) of the synthesised precursor presents a well-interconnected hierarchical network of groundsel flower-like microstructures with $\sim 4 \,\mu m$ in diameter, covering most parts of the Ni foam.



Figure 5.2: SEM image of the hydrothermal product

The obtained binary oxide precursor's SEM image (Fig. 5.3) verified that the microstructure is well-preserved during the calcination process. Notably, the Ni-Co oxide precursor has a surface Ni: Co stoichiometry of 1: 1.38, as found during the XPS survey scan (Fig. 5.4) conducted on the material. The final catalyst of NCP@NCO/Ni was formed by phosphating the binary oxide precursor, and the catalyst of NCP/Ni was also synthesised by the phosphorisation of the direct hydrothermal product for comparison. SEM images of the catalyst, as depicted in Fig. 5.5 (a-c), exhibit the core structure of the hydrothermally synthesised groundsel flower-like 3D hierarchical network was well preserved during the respective calcining and the phosphating steps, while the EDS elemental mapping (refer to Fig. 5.5 d) confirms the uniform presence of Ni, Co, P, and O within the synthesised NCP@NCO/Ni structure. Similar morphological details can be observed for the NCP/Ni (see Fig. 5.6 (a-c), where the hydrothermal product was directly phosphorised. The SEM image in

Fig. 5.5 (a) shows a substantial loading of catalyst microstructures, well-attached and welldistributed on the Ni foam. Further, Fig. 5.5 (c) suggests the surface of the Ni foam is also covered as a fuzzy coating of the catalyst material, providing an abundance presence of catalyst sites, which could allow it to reach high current densities during the LOB operation.



Figure 5.3: SEM image of the NiCo₂O₄ precursor



Figure 5.4: Survey Scan for NiCo₂O₄ (NCO), NiCoP (NCP), and NiCo₂O₄ and NiCoP (NCP@NCO) hybrid structure



Figure 5.5: SEM images structure (a-c), EDX elemental mapping (d), TEM images (e, f) of the NCP@NCO/Ni hybrid structure anchored on the Ni foam.

The individual catalyst micro-sized particle is an assembly of nanorods/ nanopetals with diameters of 30- 50 nm assembled into 4 μ m groundsel flower-like morphology as identified by the TEM in Fig. 5.5 (e). The TEM image in Fig. 5.5 (f) further reveals the catalyst material

is concentrated into an assembly of nanoclusters inside individual petals. Clear and abundant voids can be observed, possibly formed as the precursor decomposed during the calcination and phosphorisation steps. The developed morphology could help to enhance the OER and ORR kinetics by providing a high surface area and allowing O₂ to flow at the proximity of catalyst sites.



Figure 5.6: SEM images of NiCoP grafted on Ni foam (a-c)

The X-ray diffraction (XRD) pattern (Fig. 5.7 (a)) obtained for the as-synthesised material exhibits very low-intensity diffraction peaks for the metal hydroxide/ metal carbonate in comparison with the sharp Ni peaks (JCPDS No. 04-0850), verifying the amorphous nature of the product, which will be beneficial in accommodating high amounts of the discharge

product and to provide an enhanced catalytic activity via crystal defects. However, a distinct XRD diffraction pattern was obtained after calcining the material at 400 ^oC for 3 hours. The peak pattern of the calcined precursor is closely matched with the peak pattern of the NiCo₂O₄ (JCPDS 20-0781). For the hybrid catalyst of NCP@NCO/Ni, the diffraction peaks positioned at $2\Theta = 41.0, 47.5, 54.8, 76.3$ are assignable to (111), (210), (300)/(002), and (212) respective planes of the binary metallic phosphide (NiCoP), while the peaks located at 2Θ = 36.8, 42.8, 62.1 correspond to the diffraction peak pattern of NiCo₂O₄ (JCPDS No. 20-0781). The additional peaks present in the XRD spectrum at 2Θ = 44.3, 51.6, and 75.9 are for the Ni foam substrate. In comparison, the diffraction peaks related to NiCo₂O₄ are barely observable for the catalyst of NCP/Ni, produced by the phosphorisation of the direct hydrothermal product. Even though marginal shifts in peak positioning of NiCo₂O₄ are observed in the final catalyst due to disturbances to the spinel network during the phosphating process, the overall diffraction pattern of NCP@NCO/Ni structure implies the co-existence of the Ni-Co binary metal oxide and phosphide crystal structures within the bulk structure. Notably, all the diffraction patterns are diffused in nature, suggesting the low crystallinity/ nanocrystalline nature in the synthesised catalysts, which explains the morphological stability of the microstructures upon exposure to calcination and the phosphorisation steps. The absence of crystal phases related to nickel or cobalt phosphate further provides signs opposing the formation of metal phosphates during the phosphating process.



Figure 5.7: (a) XRD spectra of as synthesised catalytic microstructures on Ni foam, (b) HRTEM image, (c) corresponding SAED pattern, and (d) identified facets of NCP@NCO/Ni

The high-resolution TEM analysis realised that the phosphating process affects the surface crystallinity of the catalyst. The lattice fringes are randomly placed and more diffused in the NCP@NCO/Ni heterostructure, as presented in Figure 5.7 (b) and Figure 5.8 (b), compared to sharp fringes observed for the NCO precursor presented in Figure 5.8 (a), implying the surface of the NCP@NCO/Ni is populated by amorphous domains in addition to crystalline phases, providing further access to the reactive species. The observed diffraction rings associated with the selected area electron diffraction (SAED) attributed to the (311), (111), and (440) planes of NiCo₂O₄, and (111) and (212) planes of NiCoP presented in Figure 5.7

(c). This agrees with the previous results and indicates the presence of bimetallic oxide/ phosphide heterostructure, in addition to implying the polycrystalline nature of the material. Successful construction of the NiCoP/ NiCo₂O₄ heterostructure in the NCP@NCO/Ni catalyst is further verified by indexing the lattice fringes present on the catalyst surface. As indicated in Figure 5.7 (d), the identified lattice fringes with 0.22 nm and 0.25 nm correspond to the (111) characteristic plane of NiCoP and to the (311) facet of NiCo₂O₄, respectively, providing further evidence of the successful synthesis of the heterogeneous crystal structure.



Figure 5.8: HRTEM images of (a) NCO and, (b) NCP@NCO

Generally, phosphide phases are more conductive than the oxide phases [277], and a built-in electric field is created across the interface as two phases with dissimilar electric properties contact each other [278]. Hence, heterogeneous phases are in favour of modulating the electronic properties of the catalytic structure, where the charge-concentrated phase is capable of inducing the charge transfer across the boundary [279]. Previous literature suggests the coupling of heterogeneous phases is beneficial for accelerating oxygen kinetics by improving the adsorption of oxygen intermediates [280,281]. Further emphasizing, the electron-rich domain across the boundary acts as local nucleophilic regions favouring the fast adsorption reactive species promoting a fast ORR kinetics during the discharge, while the

electron-deficient domain favours the swift decomposition of discharged products by attracting them with inherent electrophilic properties [282]. In addition, the migration of the charge carriers across the interface improves the electrical conductivity of the material. Overall, the regulation of charge transfer through heterogeneous interfaces can be identified as an effective strategy to improve the oxygen kinetic in Li-O₂ batteries [283], and XPS studies were employed to further evaluate the effective modulation of the electronic structure in the synthesized heterogeneous catalyst. X-ray photoelectron spectroscopy (XPS) was used to identify the surface elemental composition, valent state composition, and chemical interactions between the components of the synthesized heterostructures. Mechanically detached catalyst particles were used for the study, and the conducted survey scan in Figure 5.4 identified the presence of Ni, Co, P, and O in NCP@NCO.


Figure 5.9: XPS analysis: (a) Ni 2p, (b) Co 2p spectra, (c) O 1s spectra, (d) P 2p spectra of assynthesized NiCoP@NiCo₂O₄ catalysts on Ni foam

The high-resolution photoelectron spectra of Ni 2p spectra depicted in Figure 5.9 (a), and all three samples of NCO, NCP, and NCP@NCO can be deconvoluted into well-fitted two spin-orbit doublets and shakeup satellites. For NiCo₂O₄, the peaks fitted at 853.9 and 871.3 eV corresponding to Ni²⁺ valance in Ni 2p $_{3/2}$ and Ni 2p $_{4/2}$ respective regions, while the peaks at

855.6 and 873.0 eV are assigned to Ni³⁺ [155,284]. In contrast, a significant shift of 1.0 eV towards lower binding energy is noticeable for the peaks corresponding to Ni²⁺ in NCP, and the peak positions of 870.2 eV (Ni 2p 1/2) and 852.9 (Ni 2p 3/2) confirm the presence of Ni-P bond [276]. The peak positioning of the Ni 2p spectra for the NCP@NCO catalyst is similar to the NCO precursor, except around 0.3 eV shift towards higher binding energy for Ni³⁺ in both $2p_{\frac{1}{2}}$ and $2p_{\frac{3}{2}}$ regions, and the corresponding shift was 0.5 eV and 0.6 eV respectively towards the same direction for the NCP catalyst. The positioning of the Ni³⁺ peak of the NCP@NCO catalyst in between the corresponding peaks of NCO and NCP structures suggests the presence of phases containing the bonds of Ni-O and Ni-P on the catalyst surface, which could lead to altered surface electrochemical properties as a result of induced charge distribution through the interaction between the identified chemical bonds [281,285]. Similar chemical modifications can be identified on the high-resolution Co 2p spectra presented in Figure 5.9 (b), which can also be fitted with two spin-orbit doubles and shakeup satellites. The peaks at 779.8 eV $(2p_{3/2})$ and 794.5 eV $(2p_{1/2})$ correspond to Co^{2+,} and the peaks positioned at 779.8 eV ($2p_{3/2}$) and 794.5 eV ($2p_{1/2}$) are attributed to Co³⁺ of NCO [155] The well-shifted peaks from NCO peak positions confirm the presence of the Co-P bond in the NCP catalyst with the presence peaks fitted for Co^{2+} valence at 778.6 and 796.7 eV for Co $2p_{3/2}$ and Co $2p_{1/2}$ respective regions [155], and the corresponding peaks for Co³⁺ in NCP@NCO were lightly shifted compared to NCP, closely following the trend observed on Ni 2p spectral analysis. Meanwhile, the O 1s spectra presented in Figure 5.9 (c) provide further evidence of chemical changes on the catalyst surface upon phosphorisation, where three common peaks can be identified in all three substances corresponding to lattice oxygen (O1), defect sites with low oxygen coordination, including P-O bond (O2), and surface adsorbed hydroxyl groups in water molecules (O3) [165]. An apparent reduction in the O1 peak strength with strength varies as NCO/Ni > NCP@NCO/Ni > NCP/Ni, and vice versa for

O2 and O3 peaks, providing strong evidence of the gradual reduction of metal-bonded oxides as a result of the insertion of P atoms. The observation is further justified by the shift of the O2 and O3 peaks towards the lower binding energy, consistent with the previous discussions on forming an interface between P and O atoms in two different phases of metal oxides and metal phosphides [283]. Further, the high-resolution photoelectron spectra of P 2p spectra of NCP/Ni and NCP@NCO/Ni depicted in Figure 5.9 (d) can be divided into two regions corresponding to metal-P (128.3 eV) and P-O bond (132.5 and 133.2 eV for P 2p 3/2 and P 2p $\frac{1}{2}$ respective regions)[286], where the later arisen due to unavoidable surface oxidation [286,287]. While the presence of a peak corresponds to Ni/Co-P bond confirms the successful phosphorisation in NCP/Ni and NCP@NCO/Ni catalysts, the peak shift of 0.6 eV to higher bonding energy for NCP@NCO/Ni compared to that of NCP/Ni suggests charge transfer between the atoms and strong electronic interactions in between the Ni/Co- oxide and Ni/Cophosphide heterogeneous interfaces. In summary, the observed shifts in binding energies indicate intense charge transfer between the electronic bonds and heterogeneous interfaces, which could result in reinforcing the catalytic performances of NCP@NCO/Ni through electronic structure modulation, promoting efficient adsorption and the desorption of oxygen intermediates, allowing a swift ORR/ OER operation and a longer lifespan.

5.3.2. Li-O₂ Battery Analysis

Following the material characterisation studies, the electrocatalytic performances of the derived NCP@NCO/Ni catalyst were studied as a binder-free cathode for Li-O₂ batteries. The aprotic Li-O₂ battery CR23032 coin cells were assembled using the synthesised catalyst-integrated Ni foam as the cathode, Li metal foil as the anode, and 1M LiTFSI in TEGDME as the electrolyte. In addition to the derived catalytic heterostructure of NCP@NCO/Ni, the pure catalysts of NCO/Ni and NCP/Ni-based cathodes were also studied for comparison. The corresponding support to OER and ORR was evaluated using the cyclic voltammetric (CV)

curves for constructed LOBs obtained at 0.2 mV s⁻¹ in the voltage region of 2.0- 4.5 V. As indicated in Figure 5.10 (a), the reduction peak at 2.48 V for the NCP@NCO/Ni cathode is attributed to the formation of the discharged product. The oxidation peaks at 3.46 V and 4.10 V detected correspond to the decomposition of the surface adsorbed non-stoichiometric/ amorphous Li_{2-x}O₂ and crystalline Li₂O₂, respectively, confirming the reversible operation. Even though the highest ORR (2.58 V) and lowest OER peak (4.05 V) positions with higher current densities were obtained for the NCP/Ni, indicating its superior catalytic activity, an improved catalytic activity was displayed by the NCP@NCO/Ni catalyst compared to its precursor of NCO/Ni, which recorded a much weaker catalytic activity with respective OER and ORR peak positions at 4.22 V and 2.23 V, and lower peak current densities. The electrochemical performance of the engineered self-standing cathodes was further studied using galvanostatic discharge/charge profiles, as shown in Figure 5.10 (b), which was conducted at a current density of 100 mA g⁻¹ in a limited voltage window of 2.0- 4.5 V. The OER and ORR onset potentials were the smallest for NCP/Ni, agreeing with the peak positions obtained during the CV study, implying the superior catalytic activity of NCP/Ni. Despite having a higher onset potential, the NCP@NCO/Ni shows the highest initial discharge/charge specific capacity of 15710/ 14632 mAh g⁻¹, exceeding the performances of NCP/Ni and NCO/Ni, which were only able to achieve 11840/ 11588 mAh g⁻¹ and 13760/ 13727 mAh g⁻¹, respectively. The lower overpotential in metal phosphide can be attributed to its high activity and high electrical conductivity compared to the metal oxide and the hybrid structure. But importantly, the high discharge/ charge capacity in the heterogeneous structure implies the superior surface charge distribution through the heterogeneous phases, which was identified during the XPS and HRTEM studies.



Figure 5.10: (a) Cyclic voltammetric (CV) curves for constructed LOBs obtained at 0.2 mV s⁻¹ in the voltage region of 2.0- 4.5 V, (b) galvanostatic discharge/charge profiles at a current density of 100 mA g⁻¹ (c) discharge capacity at different current densities, in a limited voltage window of 2.0- 4.5 V, cycle performance (d) potential vs. time profile, (f) terminal potential, and coulombic efficiency of the LOBs constructed with different cathodes at a current density of 800 mA g⁻¹ for a limited specific capacity of 500 mAg⁻¹, and (e) selected cycles of NCP@NCO/Ni cathode-based LOB.

As exhibited in Figure 5.10 (c) and Figure 5.11, the favourable rate capabilities in NCP@NCO/Ni cathode-based Li-O₂ batteries provide further evidence for the stable and fast activity in the hybrid catalyst, where the specific capacity decreases only by 10.2 % at the current rate as high as 600 mA g⁻¹, showing a specific discharge capacity of 14095 mAh g⁻¹. In contrast, a sharp decay in rate performances can be observed in NCP/Ni and NCO/Ni cathode-based Li-O₂ batteries, where the recorded respective specific discharge capacities of 4695 and 1285 mAh g⁻¹ at 600 mA g⁻¹ are only 39.0% and 9.4 % of the specific capacities achieved during initial discharge at a relatively a low current rate of 100 mA g⁻¹. The results exhibit a key pathway for overcoming the susceptibility in transition metal oxide catalysts in high current ratings through hybridising with metal phosphide phases without considerably altering the morphological properties. As mentioned previously, successful electron transfer from neighbouring phosphide phases could improve the catalytic activity of the oxide phases, while the presence of neighbouring oxide phases is expected to provide further stability to the phosphide phases, specifically in oxygen-rich environments like Li-O₂ batteries.

Figure 5.10 (d-g) presents the cycling performances of the LOBs constructed with different cathodes at a current density of 800 mA g⁻¹ for a limited specific capacity of 500 mAg⁻¹. The LOB with NCP@NCO/Ni cathode exhibits the most successful cycle performances by surviving over 250 hours of continuous operation (see Figure 5.10 (d)), as the catalysts placed in the cathode were able to support 409 cycles with almost 100% coulombic efficiency, as shown in Figure 5.10 (e, g). In comparison, the LOB with NCP/Ni cathode can sustain 226 hours of activity covering 362 cycles, while the LOB with the NCO/Ni failed almost immediately, continuing <10 cycles with the full cyclability, and the selected discharge/charge curves are presented in Figure 5.12. The NCP@NCO/Ni cathode exhibits a higher overpotential for OER and ORR for the first few cycles, following the trend observed during the conducted CV and galvanostatic discharge/charge studies. However, a noticeable

improvement in OER activity can be observed when the battery is cycled continuously, and a stable operation with steady terminal potentials until the 365th cycle, as depicted in Figure 5.10 (f) before the terminal voltages start to fluctuate, providing evidence of possible deterioration. In comparison, much early decay can be observed in the LOB with NCP/Ni cathode. The terminal voltages drift, increasing OER and ORR overpotentials by the 261st cycle, even though the cell lasted for 362 cycles before reaching the cut-off limits. These observations are further verified during the cyclic assessment by extending the discharge depth to 1000 mAh g⁻¹. The NCP@NCO/Ni catalyst-based LOB sustains its operation over 125 cycles during its successful 150 hours of continuous operation, as presented in Figure 5.13, despite the high overpotential compared to NCP/Ni cathode-based LOB. The NCP/Ni catalyst-based LOB can only survive 32 cycles, further exhibiting the long-term instability of the catalyst under the battery operation.



Figure 5.11: Rate Performance- Galvanostatic Discharge/Charge curves for (a) NCP@NCO/Ni, (b) NCP/Ni, and (c) NCO/Ni



Figure 5.12: Selected individual discharge/charge curves of a) NCP/Ni and b) NCO/Ni at 800 mAg⁻¹ with 500 mAh g⁻¹ limited capacity.



Figure 5.13: Cycle Performances of NCP@NCO/Ni and NCP/Ni cathode-based LOB at 800 mAg⁻¹ under limited capacity of 1000 mAhg⁻¹.

The early decay of the electrochemical performances of the NCP/Ni cathode is due to the poisoning of catalyst sites as the metal phosphide sites react with reduced oxygen intermediates and/or singlet oxygen (known to produce during the charging step of the Li- O_2 battery [288]) as presented in Equation 5.1, diminishing its catalytic activity over time.

$$NiCoP_{(s)} + 40^*_{(g)} \rightarrow NiCoPO_{4(s)} + 4e$$

$$(5.1)$$

Further understanding of the reaction mechanisms and the catalytic support from the derived catalysts on ORR/OER reaction kinetics were obtained by analysing the characteristic properties of the discharged and the charged cathode structures.

Good interfacial contact with lower ohmic resistance is expected as all catalysts are synthesised in situ on the Ni foam using a bottom-up growth technique. EIS analysis was conducted on LOBs containing the engineered free-standing cathodes of NCP/NCO@Ni and NCP@Ni at different discharge levels, and the charge is presented in Figure 5.14 (a). A sinusoidal signal with a 5 mV amplitude in the frequency range of 0.01- 1000 Hz was used for the analysis. The equivalent circuit (Randles circuit) fitted to the Nyquist plot was used to determine the series ohmic resistance (R_s) corresponds to the sum of resistive components arising from the lead wires, interfaces, and the ionic resistance (from the electrolyte and the separator), obtained from the real axis's high-frequency interception. In addition, the diameter of the semi-circle denotes the charge transfer resistance (R_{ct}) . For all systems under consideration, both R_s and R_{ct} are at the lowest initially before discharging, and NCP/Ni shows the smallest R_s of 10.87 Ω NiCoP provides higher electrical conductivity over the oxide counterpart and hybrid structure. Upon full discharge, the impedance of the cells considerably increases from the initial values. The recorded R_s is 29.3 Ω for the NCP/Ni cathode-based cell compared to the corresponding value of 18.5 Ω for NCP@NCO/Ni. After the full discharge, the charge transfer resistance (R_{ct}) increases to 415.5 Ω for the

NCP@NCO/Ni cell, still significantly lower than the NCP/Ni cell, which showed an extensive increase in the resistance to a value of 385.7Ω . High series resistance after discharge indicates the formation of a resistive layer on electrode surfaces, suggesting a surface-mediated growth of Li₂O₂ on the cathode surface. The observation of lower discharge capacity, lower charging overpotential, and reduced performances at higher current rates further coincides with the above suggestion, where such a growth of an insulating layer of discharge products is known to passivate the cathode surface and prohibit further reaction from taking place, limiting the discharge capacity. Since the discharge product is wellattached to the cathode surface, low charging overpotentials were observed, allowing for the fast decomposition of the discharged products. In comparison, the lower R_s (18.5 Ω) observed for the discharged NCP@NCO/Ni battery suggests a relatively solution-mediated ORR process took place during the battery discharge. The obtained relatively high discharge capacity and relatively high charging overpotential for NCP@NCO/Ni also align with the proposed mechanism and the recorded high charge transfer resistance (R_{ct}) upon full discharge due to the loss of many charge carriers in the electrolyte as the battery is discharged deeper than NCP/Ni cathode-based LOB. The inability to achieve a decent decomposition of the discharged product is the main challenge associated with the LOBs, as its operation deviated away from the surface-mediated mechanism where it's found difficult to decompose the large and crystalline toroid of Li₂O₂ formed in the electrolyte, disconnected from the cathode surface. A detailed explanation of this can be found in our recent review of bifunctional catalysts [25]. However, the experimental results indicate a decent decomposition of the discharged products in NCP@NCO/Ni cathode-based LOB, where the R_s and R_{ct} both return closer to their initial values after being charged. The XRD analysis conducted on discharged and charged cathodes further verified the reversibility of the NCP@NCO/Ni cathode. As indicated in Figure 5.14 (b), the XRD spectrum obtained from the discharged cathode provides evidence of nanocrystalline Li_2O_2 overlapping with the XRD peak pattern for the hexagonal structure of Li_2O_2 (JCPDS # 01-073-1640). Interestingly, the peak associated with Li_2O_2 disappeared upon charging, leaving the original material's peak pattern, implying the discharged product's successful decomposition. The morphological properties of the discharged cathodes were further evaluated with SEM imaging.

Figure 5.14 (c-e) presents the SEM images of the cathodes extracted from discharged LOBs. All batteries were run to 5000 mAhg⁻¹ depth of discharge at a current rate of 200 mAg⁻¹. As presented in Figure 5.14 (c), the discharge product tends to grow as a film covering the surface of the NCP/Ni catalyst. In contrast, Li₂O₂ grows as thick and large pellet/toroid-like particles on the catalytic surface of NCO, as presented in Figure 5.14 (e). Interestingly, a thin sheet-like product can be identified on the discharge cathode of NCP@NCO/Ni, closely attached to the surface of the catalyst but grown into the electrolyte, as can be observed in Figure 5.14 (d). Higher magnifications SEM and TEM micrographs of the discharged NCP@NCO/Ni cathode are depicted in Figure 5.15, verifying the mentioned observations. Figure 5.14 (f) provides graphical illustrations summarising the critical morphological differences observed during the SEM studies of the discharged product. The identified filmlike growth of Li₂O₂ in the discharged NCP/Ni cathode is closely associated with the previous results, suggesting that a surface-mediated mechanism could occur during the LOB operation.



Figure 5.14: Discharged/ charged product analysis via (a) EIS analysis, (b) XRD analysis, (ce) SEM analysis (f) graphical illustrations on LOB cells constructed with different catalytic cathodes of NCP@NCO/Ni, NCP/Ni, and NCO/Ni



Figure 5.15: (a) SEM, and (b) TEM images of discharged cathode of NCP@NCO/Ni

The high ORR activity, as observed during the CV analysis and GCD studies, strongly adsorbing the intermediate discharged product of LiO_2 as presented in equation 5.2, could

lead to the formation of the film-like growth of the discharged product, well-adsorbed into the surface of the cathode.

$$Li^{+}_{(s)} + O_{2(g)} + e \to LiO_{2(ads)}$$
 (5.2)

Further, the formation of the final discharged product of Li₂O₂ could also occur through a second electron transfer (see equation 5.3), skipping the well-stabilized disproportionation mechanism. Easy decomposition of the well surface-attached discharged product is the main advantage of the surface-adsorption mechanism as evidenced by the lower charging overpotentials in NCP/Ni cathode-based LOBs. The limited capacity and the fast passivation of the NCP/Ni catalyst sites are serious downsides due to the fast covering of the catalytic sites, hindering further activity and directly exposing the catalyst material at reactive intermediates and byproducts respectively.

$$Li^{+}_{(s)} + LiO_{2(ads)} + e \to Li_2O_{2(ads)}$$
 (5.3)

In contrast, poor catalytic activity and a highly solution-mediated reaction process are exhibited by the NCO/Ni cathode, where the formation of large pellets/toroid-like Li₂O₂ was identified during the discharge product analysis. According to previous studies, large particles of Li₂O₂ are produced due to the diffusion of LiO₂ intermediate structure into the electrolyte, which is produced at the tri-phase interface on the catalyst surface [289]. Since the diffused superoxide is unstable in the electrolyte as Li is a small countercation, LiO₂ will quickly disproportionate, producing the observed large pellet/toroid-like low soluble final product of Li₂O₂ following the reaction pathway as presented in equation 5.4. Usually, batteries find it difficult to achieve full reversibility and suffer from large coulombic losses, as observed in NCO/Ni-based LOBs, due to the challenge of decomposing the large crystals of discharged products.

$$2LiO_{2(sol)} \rightleftharpoons Li_2O_{2(s)} + O_{2(a)}$$
(5.4)

Understanding the operational mechanisms of NCP/Ni and NCO/Ni-based LOBs is important to recognise the superiority of the NCP@NCO/Ni catalytic system. During the LOB operations, it was evident that the batteries produced with NCP@NCO/Ni cathode have the following interesting features, highlighting the system's stability and durability.

- 1. Decent ORR and OER catalytic activity.
- 2. High discharge capacity only marginally faded as the current density increased, whereas the other two systems failed to be adapted.
- 3. High cyclability under a high current density, where the NCP/Ni system lags even after having a lower charging overpotential for the first 100 cycles, and the NCO/Ni system fails to operate over a few cycles.

We propose that the efficient charge transferring between the identified surface phases of NiCo₂O₄ and NiCoP phases (as identified during the XPS and HRTEM studies) promoted the balanced catalytic activity witnessed during the battery operation, which is ultimately observed during the discharged product analysis. We believe the presence of the individual nucleophilic and electrophilic domains in the heterostructure supporting the respective OER and ORR reactions as discussed previously, leads to the formation of the sheet-like discharge product morphology. On the contrary, the homogeneous catalytic cathodes always have a high tendency to form a film-like discharge product layer irrespective of the catalytic activity of the catalyst, as observed in NCP/Ni and NCO/Ni catalytic cathodes.

The formed sheet-like morphology of Li_2O_2 well attached to the electrode surface was the perfect structure that could overcome the drawbacks inherent with the film-like grown and large pellet/ toroid-like grown Li_2O_2 associated with the respective surface-mediated and solution-mediated operational processes. Further detailing, the growth of Li_2O_2 in parallel to

the catalyst's surface (see Figure 5.14 (d) and Figure 5.15) helped achieve a high discharge capacity since it allows a prompt Li ion diffusion towards the surface of the cathode, allowing further discharge. Critically, well-attached thin sheets of discharged product were found to be easily decomposable even at high current ratings, permitting the battery to cycle longer.

The catalytic microspheres could be hollow, enabling the LOBs to achieve high gravimetric capacities and fast reaction kinetics. However, only limited evidence was found during the study through SEM images of a rarely found broken sphere as presented in Figure 5.16, and Small-angle X-ray Scattering (SAXS) studies were found to be unsuccessful at probing the particles' structure (see Figure 5.17) as the size of the catalyst microstructures is beyond the range that can be probed with the technique. Nevertheless, our SAXS results confirmed that there are no further smaller spherical structures (in the range of 6 - 600 nm) beyond the catalytic microspheres observed with SEM. Future studies will also be focused on obtaining a further understanding of the 3D cross-section of such catalytic structures with suitable analytical techniques such as ultra-small angle scattering.





Figure 5.16: Hollow core on the broken sphere

Figure 5.17: Unsuccessful core-shell spherical structure model fitting for SAXS confirming the absence of spherical structures in the size range of 6 - 600 nm.

Overall, the study provides superior battery performances compared to recent literature in Table 5.1, bringing Li-air battery technology a step toward commercialisation. While this study provides experimental proof of the efficiency of transition metal oxide-transition metal phosphide heterostructure towards promoting durable and swift Li-air battery operation, we invite theoretical material science experts to shed more light on unraveling the mechanism at the atomic/ molecular level with relevant theoretical studies discovering further knowledge on the modifications occurred in the band structure enabling the balanced catalytic activity as discussed by the Sabatier principle.

Catalyst	Shape	Dis. Cap $(mA h a^{-1})$	Rate $(mA g^{-1})$	Cycle Numb er	Rate $(mA g^{-1})$	Over Pote ntial	Li ₂ O ₂ shape
MoP	nanoflakes	<u>g</u>) 5187.5	125	400	125	0.81	Toroidal [205]
СоР	microspheres	2994	100	80	100	1.43	Film-like[207]
CoFeP	nanodots	11969	100	141	100	1.35	Flake-like [210]
CoP/Co ₂ P	Polyhedral	14632	200	161	200	1.19	Porous box [260]
NiCoP/CNT	Tubular	9320	100	150	500	0.87	Film-like [275]
This work	Spiky microsphere s	15710/ 14092	100/ 600	409	800	1.07	Nanosheets

Table 5.1: Comparison of performances of LOBs with TMP cathodes

5.4. Conclusion

In summary, we developed a high-performing and stable heterostructured catalytic through partial phosphorisation of binary metal oxide precursors. Hierarchically distributed groundsel flower-shaped NiCoP@NiCo2O4 in-situ grafted on Ni foam substrate (NCP@NCO/Ni) exhibited favourable electrical, chemical, and morphological properties, promoting the electron transfer through heterogeneous phases present on the catalytic cathode surface. Such heterogeneous nanocrystalline catalyst was able to provide the desired catalytic activity, supporting both ORR and OER kinetics, leading to achieving superior Li-O₂ battery performances outperforming cells prepared using pure oxide and phosphide phases with similar morphological properties. Sustainable battery operation under high current densities was the main advantage of the assembled NCP@NCO/Ni cathode-based batteries, where the assembled LOBs provided a lifespan above 250 hours of continuous operation exceeding 400 cycles under a high current rate of 800 mAg⁻¹. In addition, the highest discharge/ charge capacities of 15710/ 14632 mAh g⁻¹ was achieved at 100 mAg⁻¹, which was only reduced by 10% to 14092 mAh g⁻¹ at the great current density of 600 mAg⁻¹. In contrast, the capacity of cells utilising pure metal phosphide and metal oxide cathodes faded substantially. We believe the optimised catalytic structure proposed in this study promotes the growth of the sheet-like discharge product (Li₂O₂), crucial to obtain the fully reversible LOB battery operation under high current ratings. These characteristics are attributed to the desirable morphology of the discharge product allowing its facile decomposition due to the swift diffusion of charge carriers through the electrocatalyst overcoming the drawbacks of the traditional Li_2O_2 morphologies formed during the LOB operation.

Chapter 6: Tri-phase heterogeneous electrocatalysts of Ni and Co for highperforming Li-O₂ batteries

6.1. Preface

The evolution of high-performing secondary batteries is a necessity for achieving sustainable goals such as electrifying transportation [290]. Uprising of metal-sulfur [291] and metal-air batteries [25] with superior capacity retention capabilities have the potential to make these goals more realistic. Amongst, Li-air (or Li-O₂) batteries received significant attention due to their extraordinary theoretical energy density of 11.6 kWh kg⁻¹ [256]. Nevertheless, the researchers are struggling to achieve the theoretical capacity due to certain complexities, despite years of promising research. Sluggish oxygen kinetics at the battery cathode and the parasitic reactions were identified as the major culprits hindering the performance of Li-O2 batteries (LOBs) [292].

As discussed in detail in previous chapters, solid electrocatalysts integrated cathodes with high affinity to intermediate discharge products are known to support the surface-mediated mechanism, allowing the film-like growth of Li₂O₂, covering the surface of the cathode [293]. Such systems suffer from limited discharge capacity as the film-like growth of Li₂O₂ is fast passivating the cathode surface [294]. On the contrary, LOBs operating under solution-mediated processes are commonly suffocating with higher charging overpotentials and extended exposure to singlet oxygen upon charging as Li₂O₂ toroid are loosely in contact with the cathode, reducing the lifespan of the batteries [295]. Hence, recent studies were focused to identify strategies that could control the structural and morphological properties of the Li₂O₂, enabling faster and prolonged oxygen kinetics, and facilitating the achievement of high discharge capacity as well as extended cyclability.

Including the work presented in chapter 4, special efforts were made to optimize the d-orbital electron occupancy of transition metal compounds promoting the adsorption of O₂ and intermediate discharge products on the catalyst surface facilitating faster oxygen kinetics. Synthesis of binary multivalent compounds with optimized stoichiometry [165], heteroatom doping [164], alloying [296], high-index facet growth [83,297], and hybrid structures [283] are some of the recently studied techniques for altering the electronic structure of catalysts, resulting in improved LOB performances. Synthesis of hybrid catalysts with heterogeneous phases is identified as an effective strategy in redistributing the surface electron structure in electrocatalysts, well-backed by the DFT calculations-based theoretical studies [298]. Studies conducted by Peng et al. [299] and Liang et al. [300] with dual-phase heterogeneous catalysts already benefited from the optimized electronic properties yield discharged capacities of 10 050 mAh g^{-1} at 200 mA g^{-1} and 3530 mAh g^{-1} at 600 mA g^{-1} , respectively. The study by Yan et al with NiO and NiP phases on Ni foam further solidified the theoretical understanding of the working mechanism of the electrocatalyst with heterogeneous phases, while delivering decent battery performances [283]. Our previous study in chapter 5 found the interfaces of heterogeneous phases of binary transition metallic compounds are more efficient in promoting durable faster kinetics in LOBs, while Wu et al. [301] and Hu et al. [302] also find this strategy useful in enhancing LOB performances.

Advancing from dual-phase heterogeneous catalytic compounds, we synthesized a tri-phase heterogeneous electrocatalytic structure comprising binary phases of oxide, sulfide, and phosphide of Ni and Co. The conducted XPS studies confirmed that redistribution of the electronic structure of the material with electron transfers in between the heterogeneous phases of NiCo₂O₄, NiCoP, and NiCo₂S₄. The modified catalytic structure provides a suitable environment to promote the growth of sheet-like discharge products, growing into the electrolyte while well attached to the surface of the cathode. The morphology and orientation

of Li₂O₂ helped the battery to achieve an impressive initial specific discharge capacity of 25 162 mAh g^{-1} at 400 mA g^{-1} , allowing a continuous diffusion of Li⁺ ions on the catalytic surface through the vertically growing pillars of Li₂O₂ during the discharge. In addition to suitable catalytic properties, the direct contact between Li₂O₂ and the catalytic sites was able to swiftly decompose the discharge products achieving extended cycle durability with 270 cycles at 400 mAg⁻¹ under a limited discharge depth of 1000 mAhg⁻¹, exceeding 1350 hours of continuous operation. The hollow micro-spherical structure of the catalytic particles was also beneficial towards achieving superior gravimetric capacities, Further, the bottom-up grown self-assembled hierarchical network of catalytic structures on the Ni foam was supportive in achieving lower ohmic resistances as well as protecting the cathode from potential nucleophile attacks, allowing a highly efficient and durable operation of the assembled LOBs.

6.2. Experimental

6.2.1. Synthesis of Catalytic Structures

Intermediate catalysts were synthesized via hydrothermal method by heating the well-sealed semi-filled Teflon-lined autoclave vessel to achieve the in-situ growth of catalytic microstructures on the inserted Ni foam. Ni foam was cleaned thoroughly with a DI water/ ethanol mixture to remove the surface pollutants using an ultrasonic bath cleaner (Elmasonic Easy 10 H, 37 kHz), followed by etching out of the surface oxide layer by dipping in a diluted HCl/ HNO₃ for 3-4 hours, before rinsing with DI water. The nutrient solution for the hydrothermal reaction was prepared by adding metal salts of 2.5 mmol Ni (NO₃)₂·6H₂O and 5 mmol of Co (NO₃)₂·6H₂O with 10 mmol of urea into 100 ml DI water and continuously stirring the mixture for 4 hours until the dispersed salts are fully dissolved in water. In a typical synthesis, 70 ml of the nutrient solution was added along with a vertically placed Ni foam in the autoclave chamber, and the hydrothermal vessel was heated to 120 0 C at a 5

⁰C/min rate. After enabling the crystal growth for 12 hours at 120 ⁰C, the vessel was cooled down at the same rate, and pink-grey coloured hydrothermal product coated on the Ni foam was collected once the vessel reached room temperature. The loosely attached particles on the intermediate catalyst-coated Ni foams were removed by placing them in the ultrasonic bath for several minutes. The foams were further washed with DI water and dried overnight at 120 ⁰C before further processing, and the intermediate catalytic product is labelled as NC-OH@Ni for future reference.

The intermediate catalytic structures were placed downstream in a horizontal tube furnace (CARBOLITE CTF 12) with equally weighted NaH₂PO₂.H₂0 and thiourea placed upstream. The partial phosphorization and sulfurization were achieved by heating the furnace to 400 ^oC for 3 hours while maintaining a steady Ar flow. A constant temperature gradient of 5 ^oC/min was maintained during both the heating and cooling phases of the calcination process, and the final catalyst (NCP/NCS/NCO@Ni) was collected and kept under inert conditions. For comparison, NCS@Ni and NCP@Ni catalytic cathodes were prepared by replacing the upstream material with excessive amounts of thiourea and NaH₂PO₂.H₂0 respectively, while NCO@Ni was prepared by opening the chamber to air without any upstream precursor while keeping the other process conditions same. Figure 6.1 presents a graphical illustration of the synthesis process.

Material Characterization

Morphological and dimensional properties of the in-situ synthesized catalytic microstructures were analyzed using a scanning electron microscope (SEM, HITACHI SU6600). The same technique was later used during the discharge/charge product analysis. The crystalline phases present in the synthesized catalytic structures and the discharged products were analyzed using an X-ray diffraction microscope (XRD, Siemens D5000 with Cu Kα). Brunauer–

Emmett–Teller (BET) surface area was measured using N₂ adsorption/desorption at 77.3 K on an Autosorb iQ Station 1 after the samples were degassed at 150 0 C for 12 h under vacuum before physisorption measurements. The X-ray photoelectron Spectroscopy (XPS, ESCALB 250Xi Thermo Fisher, USA) was used to understand the surface chemical composition and to determine the redistribution of the surface electronic structure as a result of forming the heterostructure. The analysis was carried out in the constant analyzer energy (CAE) mode by exposing the samples to a 2000 eV ion beam (sourced from an Al K α target) for 30 seconds with a 900 µm spot size. Further analysis of the nanocrystalline catalytic structures was carried out using a transmission electron microscope (TEM, JEOL JEM-2100), and the high-resolution TEM images were further processed by GATAN DigitalMicrograph software to determine the reveal the crystallographic phases present in the catalytic heterostructures.

6.2.2. Electrochemical Studies

Electrochemical measurements were conducted using the assembled meshed CR2032-type Li-O₂ battery cells. All batteries were assembled inside an Ar-filled glove box and during the assembly, Li metal chip, celguard 2500 membrane, and 13mm diameter-sized disks of synthesized catalytic Ni foam were used as the anode, separator, and cathode of the battery, respectively, while 1M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME) was used as the battery electrolyte. Active material mass-loading in the catalytic cathodes was varied from 0.8-1.1 mg/cm⁻², and all freshly assembled LOBs were allowed to reach their equilibrium conditions before conducting any electrochemical analysis by keeping them in an O_2 -filled sealed container for 12 hours under atmospheric pressure.

Catalytic performances of the as-synthesized catalysts integrated cathode structures were analyzed using cyclic voltammetry (CV) studies, which were conducted in a potential window of 2.0- 4.5 V vs Li/Li⁺ at a scan rate of 0.2 mV/s, using IviumStat system. A 5mV sinusoidal signal in the frequency range of 1 MHz – 0.01 Hz was used for the electrochemical

impedance spectroscopy (EIS) analysis and the resultant spectrums were fitted for an equivalent electrical circuit representing the referred electrochemical system. Galvanostatic charge/ discharge (GCD) analysis was used to determine the discharge/ charge capacity, cycle stability, and rate performances of the assembled LOB cells. Neware battery analyzer was used for all GCD studies, and current densities ranging from 100 mAg⁻¹ to 800 mAg⁻¹ were used during the analysis, and the amount of active materials present at the individual cathodes was considered while determining the corresponding current densities and the specific capacities.



Figure 6.1: Schematic diagram of synthesis produces of catalytic structures

6.3. Results and discussion

The study was conducted with the focus of developing heterogeneous crystal facets to achieve control over the morphology and the orientation of the discharged product in order to achieve faster and more durable LOB operation. As illustrated in Figure 6.1, hydrothermal synthesis was used as the first step of catalytical particle synthesis. In-situ phosphorisation and sulphurisation were conducted in parallel during the second step to achieve both sulfide and phosphide phases in the final catalytic product of NCP/NCS/NCO@Ni, and the full

conversion to either phosphide or sulfide phases was avoided by using a limited quantity of the phosphorous and sulfur sources in the upstream during the calcination.



Figure 6.2: (a-c) SEM images, (d) graphical illustration of the hollow core, (e) EDX elemental mapping of the NCP/NCS/NCO@Ni catalyst structure

6.3.1. Material analysis

During the hydrothermal synthesis, unidirectional crystal growth was noticed, where the formed individual nanoneedles assembled into groundsel flower-like microspheres. Further, the individual microspheres were self-assembled hierarchically on the Ni foam as presented previously on Figure 5.2. The particle shapes and the morphological features remain similar in the final catalyst as well, where the hierarchically grafted catalytic structures with 3-5 µm diameter were observed in the final catalyst of NCP/NCS/NCO@Ni as depicted in Figure 6.2 (a, b). It's noteworthy to mention that the catalytic microstructures were found to be hollow (see Figure 6.2 (c)), and Figure 6.2 (d) provides a graphical overview of the 3D cross-section of an individual catalyst particle. Unlike Li-ion batteries, a hollow core is beneficial for Li-O₂ batteries in obtaining high specific capacities, since only the catalytic sites present at the surface of the cathode partake in the reaction process. Surface morphology of the catalytic cathode is also pivotal in achieving higher discharge capacities, since the mesoporous surface structure with a high surface area could provide a well-suited space to accumulate large quantities of the discharge products, and the NCP/NCS/NCO catalytic particles with 71.18 m2/g BET surface area representing the type IV isotherm and H3 hysteresis characteristic behaviour, consist with adequate surface properties (Figure 6.3) promoting higher discharge capacities. The energy-dispersive X-ray (EDX) mapping of the catalyst surface confirms the presence of Ni, Co, P, S, and O elements on the surface, and the study further verified the uniform distribution of the elements over the surface of the synthesized microstructures as depicted in Figure 6.2 (e).



Figure 6.3 BET analysis of NC-OH precursor and the NCP/NCS/NCO@Ni catalyst

The catalytic structures provided weak X-ray diffraction signals due to their nanocrystalline nature. Hence the catalyst particles detached from the Ni foam substrate were used using the X-ray diffractometry (XRD) analysis to obtain a higher clarity. The XRD analysis presented in Figure 6.4 (a) indicates the existence of multiple heterogeneous crystal phases in the final catalyst. The peak positions of $2\Theta = 40.25$, 45.02, 47.57, 54.42, 66.45, and 72.92 are closely overlapped with the peak structure in JCPDS# 071-2336 which are assignable to (111), (201), (210), (002)/ (300), (310), and (212) phases of NiCoP, while the peaks found at $2\Theta = 26.79$, 34.23, 37.85, 51.18, 56.63, 62.63, and 78.39 provide evidence of the presence of the binary cubic spinel structure of NiCo₂S₄ (JCPDS# 020-0782). Overlapping of the remaining peaks of the XRD spectra at $2\Theta = 35.75$, 38.79, 45.02, 60.36, and 77.47 with the peak structure.



Figure 6.4: (a) XRD spectra, (b) TEM image, (c) identified 311 facet of NiCo2O4, (d) HRTEM image, (e) identified 311 facet of NiCo2S4, and (f) identified 111 facet of NiCoP of the heterogeneous catalyst of NCP/NCS/NCO@Ni

The TEM image in Figure 6.4 (b) shows the assembly of nanoclusters forming into petal-like nanoneedles which are further assembled into hierarchical hollow spheres. High-resolution TEM (HRTEM) studies helped to realize that individual nanoclusters were comprised of phosphide, sulfide, and oxide facets of Ni and Co as depicted in Figure 6.4 (d). The identified lattice fringes with an interlayer distance of 0.21 nm correspond with the (111) characteristic facet of NiCoP [270]. Similarly, the crystal facets with 0.25 nm and 0.30 nm are assignable to the (311) phases of NiCo₂O₄ [155] and NiCo₂S₄ [303], respectively. The realization of the co-existence of three heterogeneous phases (typically with different binding energies to O₂ and intermediate discharge products) is critical in understanding the discharging and charging mechanisms of the LOB. Placing a limited quantity of NaH₂PO₂.H₂O and thiourea upstream during the calcination is pivotal in achieving partial phosphorisation and partial sulphurisation, and the remaining portions of the material were converted to metal oxide phases as observed during both XRD and HRTEM studies. Interactions between the identified heterogeneous domains were analyzed by the XPS studies.

XPS studies presented in Figure 6.5 were used to identify the elemental composition and the interaction between the different elements in the synthesized heterogeneous microstructure of NCP/NCS/NCO@Ni, and the XPS spectra of synthesized microstructures of individual transition metal binary derivatives of NCO/Ni and NCP/Ni were also studied for comprehensive understanding. Mechanically separated catalyst particles were used during the experiment and the survey spectra depicted in Figure 6.5 (a) identify the presence of Ni, Co, O, S, and P elements in the surface of the heterogeneous catalyst of NCP/NCS/NCO. The spectra detect the presence of C, which could be sourced from the contaminations or adventurous carbon.



Figure 6.5: XPS (a) survey spectra of NCP/NCS/NCO@Ni, and narrow spectra of (b) Ni 2p, (c) Co 2p, (d) P 2p, (e) O 1s, and (f) S 2p

The deconvoluted Ni 2p high-resolution narrow band spectra of NCP/NCS/NCO@Ni and NCO@Ni are shown in Figure 6.5 (b), and both samples are well-fitted into spin doublets with shake-up satellite peaks. Ni^{2+} and Ni^{3+} valances related to Ni 2p $_{3/2}$ were positioned at

853.7 and 855.2 eV respectively in NCO/Ni[165]. However, a significant shift in the binding energies was observed with Ni²⁺ red shifting by 1.0 eV to 852.7 eV, while Ni³⁺ was blue shifted by 1.2 eV to 856.4 eV in the heterogenous catalyst of NCP/NCS/NCO@Ni. Considerable shifts in binding energies indicate the presence of other Ni-involved chemical phases and possible interactions between the phases. Similar observations were during Co 2p spectra analysis. Co 2p spectra can also be deconvoluted into well-fitted spin doublets and related shakeup peaks. The Co²⁺ valance of Co 2p _{3/2}, originally placed at 779.7 eV for NCO@Ni, was moved by 0.4 eV towards higher binding energies in the NCP/NCS/NCO@Ni (see Figure 6.5 (c)), supplementing the observations made on Ni 2p spectra. The presence of P was identified in the heterogeneous catalyst during the P 2p spectral analysis (see Figure 6.5 (d)), and as commonly observed during XPS analysis of metal phosphides, surface phosphide phases were oxidized in contact with atmospheric air [304]. Further, it was noticed that the phosphate peak was shifted towards higher binding energies (133.2 eV) in the heterostructure compared to the peak position of the pure phosphide phase (132.8 eV), also suggesting an electron transfer between neighbouring heterogeneous phases [260]. Figure 6.5 (e) presents O 1s spectra, and three peaks O1, O2, and O3 represent lattice oxygen, low oxygen coordination sites/ P-O bond or S-O bond, and surface adsorbed hydroxyl groups in water molecules, respectively [260]. The figure provides strong evidence of chemical modification on the catalytic surface structure upon the conducted in-situ phosphorization and sulfurization. Compared to the pure oxide phase, the O1/O2 peak ratio is substantially reduced in the heterogeneous structure of NCP/NCS/NCO@Ni suggesting, significantly fewer lattice-oxygen bonds of metal oxide domains are presented in the heterogeneous structure implying the successful phosphorization [305] and sulfurization [306]. Moreover, the binding energy of the lattice-oxygen bond shifted by 0.4 eV towards a lower value of 529.3 eV (compared to its position on the pure metal oxide phase), providing further evidence

of interactions of Ni-Co oxide phases with neighbouring Ni-Co sulfide and Ni-Co phosphide phases. Overall, the XPS studies confirm the presence of Ni-Co oxide, Ni-Co sulfide, and Ni-Co phosphide heterogeneous phases in the synthesized catalytic microstructure. Further, shifts in binding energies of certain chemical bonds indicate strong interactions and charge transfer between the identified heterogeneous phases effectively modulating the electronic structure of the NCP/NCS/NCO@Ni.

6.3.2. Electrochemical analysis

All electrochemical analyses for the derived catalytic structures were conducted using assembled CR2032-type meshed Li-O₂ battery coin cells. The disks cut into 13 mm diameter of the NCP/NCS/NCO integrated catalyst heterostructure on the Ni foam were used as the binder-free cathode, while Li foil, celgard 2400 membrane, and 1M LiTFS1 in TEGDME were used as the anode, separator, and the electrolyte of the battery, respectively. LOBs assembled with NCO@Ni, NCS@Ni, and NCP@Ni were used for the comparative analysis.

As presented in Figure 6.6 (a), cyclic voltammetry (CV) studies were employed to analyze the electrocatalytic activity of the catalytic cathodes, which were conducted at a rate of 0.2 mV s⁻¹ within the voltage window of 2.0 – 4.5 V. All catalytic cathodes indicate ORR and OER activities during the respective cathodic and anodic cycles. CV studies reveal possibly the most conductive phases of all, the phosphide phases are highly electrochemically active, where the respective reduction and oxidation peaks of NCP@Ni presented at 2.23 V and 4.05 V were found to be least shifted from the equilibrium of 2.96 V. Overall, the weakest activity was provided by the NCO@Ni, and the peak positioning and the current density of NCS@Ni was marginally better, compared to NCO@Ni. The heterogeneous cathode provided improved catalytic activity compared to pure oxide and sulfide counterparts, and its peak current densities and peak positioning were only second to the NCP@Ni. The oxidation peak present at 3.47 V, in addition to the peak at 4.24 V in NCP/NCS/NCO@Ni, indicates the

early-decomposition of amorphously form Li_{2-x}O₂ [165], which could be beneficial during the LOB operation to achieve lower charging overpotential under a limited discharge depth.

The low contact and interfacial resistance are essential for efficient and durable battery operation. The bottom-up crystal growth approach is known for engineering catalytic cathodes with superior interfacial properties compared to the tape-casted electrodes with non-conductive binders [163]. Hence, as anticipated, all the derived self-standing catalytic electrodes exhibited a small series ohmic resistance during the electrochemical impedance spectroscopy (EIS) analysis conducted with 5 mV sinusoidal signals for a frequency range of 0.01- 1000 Hz. The well-fitted equivalent circuits for the Nyquist plots provided in Figure 6.6 (b) confirm the lowest series ohmic resistance (R_s) of 10.87 Ω is provided by the NCP@Ni cathode-based LOB, while the hybrid, oxide, and sulfide cathodes provide respectively lower conductivities with the highest R_s of 12. 19 Ω was reported by the NCS@Ni-based system. Alike R_s , the charge transfer resistance (R_{ct}), which were calculated by the diameter of the semi-circle, were also found to be quite analogous to each other. The observations suggest the initial conditions of the LOBs are mostly alike, which is justifiable given expected changes in certain chemical properties of the cathode material, all other parameters are identical.



Figure 6.6: Electrochemical performances of different catalytic cathodes in the assembled LOBs: (a) cyclic voltammetry study conducted at scan rate 0.2 mV s⁻¹ in between 2.0- 4.5 V,
(b) EIS analysis of LOBs prior operation, (c) specific discharge/ charge capacity at 400 mAg⁻¹, (d) specific discharge/ charge capacity of NCP/NCS/NCO@Ni cathode-based LOB under different current densities

As illustrated in Figure 6.6 (c), galvanostatic charge-discharge profiles (GCD) of the assembled batteries with different self-standing catalytic cathodes were analyzed to reveal the depth of maximum discharge and the decomposition capabilities at 400 mAg⁻¹ under the voltage window of 2.0 - 4.5 V. During the study, exceptionally good initial specific discharge capacity was shown by the LOB assembled with the hybrid cathode of NCP/NCS/NCO@Ni, showing 25162 mAhg⁻¹ discharge capacity. The battery was able to well compose the discharge product by achieving a specific charging capacity of 22590
mAhg⁻¹, which is roughly 90% of the discharge capacity. In comparison, the LOBs with NCP@Ni, NCS@Ni, and NCO@Ni were only able to achieve the respective specific discharge/ charge capacities of 8030/ 7916, 4910/ 4892, 5068/2493 mAhg⁻¹. The highest capacities achieved by the catalysts with homogeneous phases were less than a $1/3^{rd}$ of the initial capacities achieved by the heterogeneous catalyst system, showcasing the superiority of the NCP/NCS/NCO@Ni cathode-based LOBs operating under high current densities as 400 mAg⁻¹. The measured charging overpotential of 1.05 V in NCP/NCS/NCO@Ni cathodebased LOB is also the lowest, which is 0.21 V lower than the next best-performing cathode of NCP@Ni, verifying the stable catalytic performances in the heterogeneous catalyst. We reveal the morphology and the orientation of the discharge product is responsible for the greater charge storage performances, and the contribution of its surface charge distribution for the advantages of discharge product properties will be discussed in the following sections. The heterogeneous catalyst produced healthy discharge/charge capacities even as the current rate increased considerably as depicted in Figure 6.6 (d), showcasing the capabilities of the heterogeneous catalyst to adapt at faster reaction kinetics. The specific discharge/charge capacities were reported as 16730/ 14085, 7510/ 6376, 3128/ 2819 mAhg⁻¹ at respective current rates of 600, 800, and 1000 mAg⁻¹, indicating the heterogeneous catalyst can deliver similar capacitive depths at twice higher current rates, compared to the second-best performing catalyst of NCP@Ni.

Further delving into the electrocatalytic activities, the cycle performance of the assembled LOBs with the heterogeneous and the individual catalyst phases were studied under a current density of 400 mAg⁻¹ with a limited discharge capacity of 1000 mAhg⁻¹.



Fig 6.7: (a) Votage vs. Time profile of different catalytic cathodes, selected cycles of (b) NCS@Ni, (c) NCP@Ni, (d) NCP/NCS/NCO@Ni cathode-based LOBs, (e) Coulombic efficiency during the cycling process conducted at a rate of 400 mAg⁻¹ under a limited discharge depth of 1000 mAhg⁻¹ (f) Voltage vs. time profile of heterogeneous and NCP@Ni cathode-based LOBs cycled at 800 mAg⁻¹ under a limited discharge depth of 1000 mAhg⁻¹

Figure 6.7 (a) depicts overlapped voltage-time profiles of the studied LOBs. Which, by far the longest cycle stability was provided by the NCP/NCS/NCO@Ni heterogeneous cathode-based LOB, surviving over 1350 hours of continuous operation. The heterogeneous LOB

system provides a steady performance with a small overpotential of around 0.7 V and 100% coulombic efficiency throughout its operation of 270 cycles, without any noticeable signs of degradation, where Figure 6.7 (d) and Figure 6.7 (e) provide information on the selected discharge/charge cycles during NCP/NCS/NCO@Ni catalyst-based LOB operation and the energy efficiency during the LOB operation, respectively. Following the trend observed during the deep-discharge studies, the LOB assembled with bimetallic phosphide cathode delivered the second-best cycle performances. The NCP@Ni cathode-based LOB was active for a continuous 675 hours operation, completing 137 cycles, before reaching the threshold conditions. The battery performances started to deteriorate after the first 200 hours (40 cycles) of steady operation as indicated in Figure 6.7 (b), which is verified as the charging overpotential of 0.95 V observed after 50 cycles jumped to 1.15V by the 100th cycle, as observed in Figure 6.7 (c). These observations imply that even the best-performing individual catalyst of NiCoP is struggling to reach the designated discharge depths and the decomposition of the discharge products without considerable overpotential rises over 50 cycles. Comparatively, weak catalyst phases of NiCo₂S₄ and NiCo₂O₄ identified during the cyclic voltammetry studies, were only able to survive 32 and 17 cycles, respectively with the full energy efficiency. Inherent low conductivity in the transition metal oxide and sulfide phases [260] could also account for the sluggish kinetics display by the NCO@Ni and the NCS@Ni (see Figure 6.7 (b)), as those catalysts failed to deliver under a current density as high as 400 mAg⁻¹. The superior cyclic performance of the heterogenous phases-based cathode was verified again as the cyclic capabilities of the LOBs were assessed under an increased current density (800 mAg⁻¹). As exhibited in Figure 6.7 (e), the NCP/NCS/NCO@Ni cathode-based LOB survived for 213 hours completing 85 cycles with a 100% coulombic efficiency, while the NCP@Ni cathode-based LOB was only able to last 28 cycles operating for 71 hours.

Over the years, most of the arguments were against the suitability of cathodic solid electrocatalysts, citing the catalysts will become inaccessible and useless as a film-like discharge product grows on top of the cathode surface, covering the catalytic sites [228,293]. However, the electrochemical performances of the heterogenous tri-phase catalyst have shown considerably improved outcomes, overcoming the key limitations identified with the single-structure catalysts. We believe the swift charge transfers between the heterogeneous phases as identified during the XPS studies, are playing a pivotal role in the enhanced catalytic performances, and its impact on the discharge product morphology and orientation is discussed using the SEM images of the dissembled LOB cathode as presented in Figure 6.8, obtained once the batteries were fully discharged at 400 mAg⁻¹.

The SEM images of the disassembled battery cathodes obtained after the full discharge provide invaluable information on the battery discharging mechanism. During the LOB discharge, initially, O₂ gas diffusing into the battery will electrochemically reduce at the surface of the cathode forming an unstable discharge product of LiO₂, as presented in the following equation [25].

$$Li^{+}{}_{(s)} + O_{2(g)} + e \to LiO_{2(ads)}$$
 (6.1)

The solid electrocatalysts tend to keep the intermediate discharge product and the final discharge product of Li₂O₂ to the surface of the cathode, irrespective of the formation mechanism of Li₂O₂, either through the more common reaction pathway of disproportionation (see equation 6.2) or through a second electrochemical reduction as indicated in equation 6.3[25].

$$2LiO_{2(sol)} \rightleftharpoons Li_2O_{2(s)} + O_{2(g)}$$
(6.2)

$$Li^{+}_{(s)} + LiO_{2(ads)} + e \to Li_2O_{2(ads)}$$
 (6.3)

. . . .



Figure 6.8: SEM images of discharged LOB cathodes and relevant graphical representations of (a, b) NCO@Ni, (c, d) NCS@Ni, (e, f) NCP@Ni, and (g, h) heterogeneous cathode of NCP/NCS/NCO@Ni

Once the produced Li₂O₂ stays well-attached to the surface, it grows as a surface coating covering the surface of the cathode. Previous studies concluded that porosity and the electrical conductivity of the cathode reduce as the thickness of the Li₂O₂ layer increases, and the cathode surface becomes mostly passivated once the Li₂O₂ layer becomes 9 nm thick, terminating the further discharge [307]. In such scenarios, the volumetric discharge capacities achieved are rather limited, even though the LOBs could charge with relatively lower overpotentials compared to the ones using redox mediators since the discharge product is kept well intact with the surface of the cathode. Hence, irrespective of the catalytic activity, the discharge depths that could be achieved by a solid electrocatalyst were limited, which makes an indistinct future for solid electrocatalysts in LOBs. In addition to the previously discussed cycle stability and discharge capacity studies, the observation made during the SEM studies mostly followed up with the above-mentioned rationale. Since the catalytic particles provide a similar catalytic activity throughout the catalytic microstructure, NCO@Ni supports the growth of a film-like discharge product morphology forming a coating covering the surface of the cathode, as depicted in Figure 6.8 (a, b), including a graphical representation of surface coating of Li₂O₂ (black) covering the catalytic particles, represents in red colour. Unsurprisingly, similar morphological features were presented by the discharge cathode of NCS@Ni, which also confirms the growth of a film-like Li₂O₂ as presented in Figure 6.8 (c, d). Even though the NCP@Ni cathode acquired a thicker coverage of Li₂O₂ upon discharge, mostly due to better conductivity and better catalytic activity, the growth mechanism of the discharge product was still the same as displayed in Figure 6.8 (e, However, a different discharge product morphology was observed in the f). NCP/NCS/NCO@Ni discharge battery cathode, which is a slightly curved sheet-like structure, grown parallel to the surface of the cathode as presented in Figure 6.8 (g, h) with relevant graphical illustrations. Unlike a similar catalytic activity observed throughout the

microstructure in homogeneous catalytic phases, the identified heterogeneous phases of NiCo₂S₄, and NiCo₂O₄ have produced a different catalytic activity in individual domains, producing a non-homogenous catalytic activity within the heterogeneous catalyst microstructures, which continues throughout the hierarchical network. Herein, certain high conductive and electron-rich domains such as NiCoP could provide additional support for oxygen reduction by acting as local nucleophilic domains, while the inherently low conductive metal oxide domains as NiCo₂O₄ could promote the decomposition of the Li₂O₂ by acting as local electrophilic domains, as previous reports suggest [298,301]. Hence, the growth of the discharge product was not uniform throughout the catalytic surface, and the induced local electric fields from the local charge concentrated domains towards the local charge deficient domains could ensure a fast charge transport while modulating the surface electron structure as observed during the XPS studies.

The SEM observations made during the SEM study of the discharged cathode of NCP/NCS/NCO@Ni heterogeneous cathode further justified the observations made during the electrochemical studies. Unlike a film-like layer, the parallelly grown sheet-like morphology of the discharge product will not block the Li-ion diffusion into the cathode or passivate the catalyst sites, in favour of achieving a higher discharge depth as reported, more than 3 times over the studied homogeneous catalyst phases. Further, the presence of heterogeneous phases overcomes the reaction kinetic limitations that could occur in the systems with individual phases, allowing the LOBs to perform well in higher current densities. Essentially, since the produced Li₂O₂ deposited in contact with the battery cathode, significantly low charging overpotentials were reported, allowing the constructed LOB system to outperform well-above than homogeneously distributed single catalyst systems reported in recent years (see Table 6.1).

Catalyst	Shape	Dis.	Rate	Cycle	Rate	Over	Li ₂ O ₂
		Cap	(mA	Numb	(mA	Pote	shape
		(mA h	g^{-1})	er	g^{-1})	ntial	
		<u>g</u> ⁻¹)				(V)	
MoP	nanoflakes	5187.5	125	400	125	0.81	Toroidal [205]
СоР	microspheres	2994	100	80	100	1.43	Film-like[207]
CoFeP	nanodots	11969	100	141	100	1.35	Flake-like
							[210]
CoP/Co ₂ P	Polyhedral	14632	200	161	200	1.19	Porous box
	-						[260]
NiCoP/CNT	Tubular	9320	100	150	500	0.87	Film-like
							[275]
This work	Hollow	25162	400	270	400	1.05	Nanosheets
	microsphere						
	S						

Table 6.1: Comparison of Li-O2 battery performances

6.4. Conclusion

In summary, we have synthesised and integrated a tri-phase heterogeneous catalytic microstructure as the O₂ cathode in Li-O₂ batteries. The catalyst material comprises the domains of binary oxide, sulfide, and phosphide phases of NiCoP, NiCo₂S₄, and NiCo₂O₄ within on the hollow microstructures, which are assembled in a hierarchical order on a Ni foam. While the hollow core benefits in achieving higher gravimetric performances, the major contribution was made by the heterogeneous phases towards the superior LOB performances, by modulating the discharge product morphology and the orientation. The phases with different electronic properties were found to be promoting the growth of sheet-like Li₂O₂, assembled vertically on the cathode surface. The mechanism advocates fast reaction kinetics, higher discharge depths, and longer cyclability, where the heterogeneous catalytic cathode-based LOB achieved 25162 mAhg⁻¹ of first discharge capacity at 400 mAg⁻¹, and 270 cycles at 400 mAg⁻¹ under a limited discharge depth of 1000 mAhg⁻¹, exceeding

1350 hours of continuous operation. In comparison, the NiCoP-used cathode-based LOB performed best among the individual catalytic structures explored on the heterogeneous catalytic system. However, the performances of NiC_oP are less than one-third and half of the produced respective specific capacity and cyclability by the heterogeneous catalyst-based LOBs, exhibiting the effectiveness in the explored strategy.

Chapter 7

Conclusion and perspectives

7.1. Conclusion

Several types of electrocatalyst materials and cathode architectures were explored during the doctoral studies, searching for better-performing electrocatalytic cathodic structures, which could promote faster oxygen kinetics in Li-O₂ and Li-air batteries. All the synthesized materials were thoroughly examined with various physicochemical, structural, and microscopic analytical tools, and the capacity retention capabilities and the cyclability of the assembled batteries were systematically analyzed with several electrochemical techniques. The synthesized self-standing cathodic structures of three-dimensional hierarchical networks of NiCo₂O₄ / NiCoP produced standout performances with high discharge capacities, long cyclability, and low overpotential, suggesting their better suitability in catalysing oxygen kinetic in Li-air/ Li-O₂ batteries. The recognition of the ability of heterogeneous catalysts to control the discharge product orientation and the morphology is one of the key findings made during the study, which led to achieving a higher discharge depth and a longer cyclability, overcoming the bottlenecks experienced with traditional homogenous catalyst structures. A summary of notable findings in the individual studies is provided in the following paragraphs.

A series of Ni and Co binary oxides with unique hierarchical 3D structures were synthesized by controlling nucleation and growth during hydrothermal processes. The stoichiometry, electronic properties, morphology, and distortions in the crystal structure of the derived structures were found to depend on the parameters of the synthesis process, yielding three distinctive structures. The material analysis suggested that the NCO 120, groundsel flowerlike hierarchical network which was synthesized at 120 $^{\circ}$ C for 12 hours, has the most favourable catalytic structure with plentiful unsaturated e_g orbital coordinates formed through substitutional disorders and a well-formed hierarchical network. This material exhibited superior performance compared to the Li-air battery cathodes of NCO 150 and NCO 180 synthesized at 150 °C and 180 °C, achieving a discharge capacity of 13,759 mAhg⁻¹ at a current density of 100 mAg⁻¹. Moreover, the cell operated continuously for 3,460 hours, completing 173 charge/discharge cycles while maintaining a capacity of over 98% coulombic efficiency in a dry-air environment. This performance surpasses the performances of many other LABs reported with spinel oxides, indicating the significance of the study.

Advancing from the initial study, a high-performing and stable heterostructured catalytic cathode through partial phosphorisation of binary metal oxide precursors was synthesized. During the study, hierarchically distributed groundsel flower-shaped NiCoP@NiCo₂O₄ in-situ grafted on Ni foam substrate (NCP@NCO/Ni) exhibited favourable electrical, chemical, and morphological properties, promoting the electron transfer through heterogeneous phases present on the catalytic cathode surface. The heterogeneous nanocrystalline catalyst was able to provide the desired catalytic activity, supporting both ORR and OER kinetics, leading to achieving superior Li-O₂ battery performances outperforming the cells prepared using pure oxide and phosphide phases with similar morphological properties. Sustainable battery operation under high current densities was the main advantage of the assembled NCP@NCO/Ni cathode-based batteries, where the assembled LOBs provided a lifespan above 250 hours of continuous operation exceeding 400 cycles under a high current rate of 800 mAg⁻¹. In addition, the highest discharge/ charge capacities of 15710/ 14632 mAh g⁻¹ was achieved at 100 mAg⁻¹, which was only reduced by 10% to 14092 mAh g⁻¹ at the great current density of 600 mAg⁻¹. In contrast, the capacity of cells utilising pure metal phosphide and metal oxide cathodes faded substantially. We believe the optimised catalytic structure proposed in this study promotes the growth of the sheet-like discharge product (Li₂O₂), crucial to obtain the fully reversible LOB battery operation under high current ratings. These

characteristics are attributed to the desirable morphology of the discharge product allowing its facile decomposition due to the swift diffusion of charge carriers through the electrocatalyst overcoming the drawbacks of the traditional Li_2O_2 morphologies formed during the LOB operation.

As the final study, a more sophisticated tri-phase heterogeneous catalytic microstructure was synthesised and integrated as the O₂ cathode in Li-O₂ batteries. The catalyst material comprises the domains of binary oxide, sulfide, and phosphide phases of NiCoP, NiCo₂S₄, and NiCo₂O₄ within the hollow microstructures, which are assembled in a hierarchical order on Ni foam. While the hollow core benefits in achieving higher gravimetric performances, the major contribution was made by the heterogeneous phases towards the superior LOB performances, by modulating the discharge product morphology and the orientation. The phases with different electronic properties were found to be promoting the growth of sheetlike Li₂O₂, assembled vertically on the cathode surface. The mechanism advocates fast reaction kinetics, higher discharge depths, and longer cyclability, where the heterogeneous catalytic cathode-based LOB achieved 25162 mAhg⁻¹ of first discharge capacity at 400 mAg⁻ ¹, and 270 cycles at 400 mAg⁻¹ under a limited discharge depth of 1000 mAhg⁻¹, exceeding 1350 hours of continuous operation. In comparison, the NiCoP-used cathode-based LOB performed best among the individual catalytic structures explored on the heterogeneous catalytic system. However, the performances of NiCoP are less than one-third and half of the produced respective specific capacity and cyclability by the heterogeneous catalyst-based LOBs, exhibiting the effectiveness in the explored strategy.

7.2. Perspectives

The study investigated different strategies to improve the catalytic performances in Li-air and Li-O₂ batteries, which were largely found to be successful in enhancing the cathodic electrocatalytic activity, leading to obtain increased discharge/ charge capacities and cyclability.

Even though significant improvements were achieved regarding the charge storage capacities and the cyclability, compared to the Li-ion battery technology, the charging overpotential remains considerably high with a lower round-trip efficiency. A well-distributed catalytic microparticle growth was achieved on the Ni foam during the conducted small-scale hydrothermal reactions. However, the relatively high weight in the Ni foam reduced the overall gravimetric performances of the cathode. Hence, it will be essential to research lowcost and lightweight porous conductive gas diffusion membranes, and their capabilities in supporting large-scale in-situ catalyst growth need to be carefully investigated as the technology moves towards commercialization.

The successful research strategies implemented in the current study can be further investigated to achieve better outcomes. For example, improved Li-air battery performances were achieved by increasing the presence of Ni³⁺ with half-filled e_g orbital occupation via optimising the stoichiometry in Ni-Co binary oxide compounds as discussed in the 4th chapter. The study can be extended to other metal oxide combinations, and into more conductive derivatives such as phosphides, sulfides, and nitrides to further validate the concept as well as to identify better-functioning catalysts. The study presented in Chapter 5 introduced the heterogeneous catalytic network of NiCo₂O₄/ NiCoP as a superior electrocatalyst for Li-O₂ batteries, and the more sophisticated heterogeneous electrocatalyst of NiCo₂O₄/ NiCo2S₄/NiCoP introduced in chapter 6 was able to produce much-improved Li-O₂ battery performances than both catalysts discussed previously. The key strategy discussed

in both the 5th and 6th chapters is the ability of heterogeneous catalysts to modulate the charge transportation within the catalytic structure, allowing morphological and structural changes in the discharge product. The strategy was found to be useful in achieving high discharge capacities compared to the batteries assembled with homogeneous cathodic electrocatalysts, and improved cycle life was also achieved. The findings are crucial in avoiding the film-like growth of Li₂O₂ discharge products, which limits the usability of solid electrocatalysts in Li-O₂ batteries. Hence, more focused theoretical and experimental studies on the topic with more precise control over the phosphorisation and sulfurization processes may provide a better understanding of the mechanism as well as information on the way forward. Such understanding will be critical, specially with the rapid developments in solid-state electrolytes and the incompatibility of the currently well-performing redox mediators to support the oxygen kinetics in a solid-state electrolyte environment. Furthermore, the techniques discussed here may not limited to the use in Li-O₂ batteries, and the strategies may also be effective in Na-O₂, K-O₂, and Zn-air like other related battery technologies, and in any environments where electrocatalysts are being used.

Despite the precautions taken, the current study lacks a comprehensive health and safety assessment of Li-air battery technology, which presents significant risks due to its high energy storage capacity. The use of Li metal anodes poses a considerable short-circuiting hazard through dendrite growth, potentially leading to thermal runaway, fire, and the release of toxic gases from electrolyte decomposition. Future research should prioritize incorporating non-flammable electrolyte additives, transitioning to solid-state electrolytes, and enhancing Li anode stability with protective coatings (as discussed in Section 2.2.3) to mitigate dendrite formation and improve overall battery safety.

To date, the limited lifespan and low recycling rate (~5%) of LIBs have led to the accumulation of vast quantities of spent batteries, contributing to resource scarcity,

environmental pollution, safety hazards, and rising costs. With the rapid expansion of electric vehicle adoption, these challenges are expected to intensify in the coming years. Additionally, the release of carcinogenic heavy metals and toxic electrolytes from discarded LIBs poses severe threats to human health and ecosystems. Therefore, accelerating the development of efficient secondary battery recycling technologies is crucial. Advances in LIB regeneration techniques could provide valuable insights for establishing effective recycling strategies for Li-air and Li-O₂ batteries, ensuring a more sustainable energy storage future.

I hope the current and future researchers will find my doctoral studies interesting and inspiring to achieve further developments in Li-O₂/Li-air batteries and related technologies.

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