Development of Efficient Electrocatalysts for Lithium Oxygen Batteries

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Development of Efficient Electrocatalysts for Lithium Oxygen Batteries

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I, Lili Liu, declare that this thesis is submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting & Electronic Materials (ISEM), Faculty of Engineering, University of Wollongong, NSW, Australia. This thesis is wholly my own work unless otherwise referenced or acknowledged. All the experimental data in this thesis is original. This thesis has never been submitted for qualifications at any other academic institutions.

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Rechargeable nonaqueous Li-O₂ batteries are considered and are expected to be the most promising energy storage and conversion candidate for future electric vehicle applications due to their ultra-high theoretical energy density. Bright prospects can be easily imagined, but critical challenges remain. High overpotentials, low capacity, low rate capability, and short cycle life, which are mainly caused by the sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) dynamics on the cathode, seriously hinder further development of this battery technology. The oxygen-breathing cathode, therefore, has been identified as a key factor influencing the overall performances of a nonaqueous Li-O₂ battery. Searching for an efficient cathode catalyst combined with an optimum architecture should be the ideal pathway to address the current challenges. In this thesis, three-dimensional (3D) foam-like NiCo₂O₄, nanofibrous Co₃O₄/polypyrrole (PPy) composite, three-dimensional (3D) hierarchical porous Co₃O₄ nanotube (Co₃O₄ HPNT) networks, and Ag nanocrystals encapsulated in nitrogen-doped carbon fiber (NCF) have been synthesized and studied as cathode catalysts for Li-O₂ batteries.

A self-assembled three-dimensional (3D) foam-like NiCo₂O₄ catalyst has been synthesized via a simple and environmentally friendly approach, wherein environmentally friendly starch acts as the template to form the unique 3D architecture. Interestingly, when employed as cathode for lithium oxygen batteries, it demonstrated superior bi-functional electrocatalytic activities towards both the oxygen reduction reaction and the oxygen evolution reaction, with a relatively high round-trip efficiency of 70% and high discharge capacity of 10137 mAh g⁻¹ at a current density of 200 mA
g\textsuperscript{-1}, which is much higher than those in previously reported results. Meanwhile, rotating disk electrode measurements in both aqueous and non-aqueous electrolyte were also employed to confirm the electrocatalytic activity for the first time. This excellent performance is attributed to the synergistic benefits of the unique 3D foam-like structure and the intrinsically high catalytic activity of NiCo\textsubscript{2}O\textsubscript{4}.

A novel nanofibrous Co\textsubscript{3}O\textsubscript{4}/PPy composite with a three-dimensional (3D) nanoweb structure was synthesized by in-situ growth of Co\textsubscript{3}O\textsubscript{4} nanocrystals on PPy nanofibers via a rapid hydrothermal method, and the resultant nanofibrous composite and pristine PPy were studied as catalysts in nonaqueous Li-O\textsubscript{2} batteries. With the uniform growth of Co\textsubscript{3}O\textsubscript{4} nanoparticles on the PPy nanofibers, improved oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) performances were achieved. Enlarged initial discharge and charge capacity were obtained to be 3585.2 mAh g\textsuperscript{-1} and 2783.6 mAh g\textsuperscript{-1}, respectively, at a current density of 100 mAg\textsuperscript{-1}. It also showed lower charge overpotential as well as better rate capability. Rotating disk electrode (RDE) measurements and electrocatalytic testing, as well as characterizations after cycling, showed that pristine PPy could act as good support and ORR catalyst, but only a poor OER catalyst, with Li\textsubscript{2}O\textsubscript{2} and Li\textsubscript{2}CO\textsubscript{3} as its main discharge products, while nanofibrous Co\textsubscript{3}O\textsubscript{4}/PPy composite could catalyse reversible Li\textsubscript{2}O\textsubscript{2} formation and decomposition in Li-O\textsubscript{2} batteries. The improved performance is attributed to the synergistic effects from the PPy matrix with its highly conductive nanoweb structure and the Co\textsubscript{3}O\textsubscript{4} nanoparticles with intrinsically high catalytic activity.

An approach to the synthesis of three-dimensional (3D) hierarchical porous Co\textsubscript{3}O\textsubscript{4} nanotube (Co\textsubscript{3}O\textsubscript{4} HPNT) networks has been proposed. Polypyrrole nanofiber (PPyNF)
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A facile synthesis of Ag nanocrystals encapsulated in nitrogen-doped carbon fiber (NCF) has been proposed, based on the simultaneous reaction of pyrrole and Ag$^+$ ions in an aqueous medium followed by a heat treatment. The as prepared Ag/NCF demonstrated a much reduced discharge/charge gap of 0.89 V compared with 1.38 V for NCF cathode under fixed capacity in lithium oxygen batteries, indicating that the introduction of Ag crystals into NCF facilitates the ORR/OER kinetics. X-ray diffraction analysis coupled with Raman spectroscopy confirmed the reversible formation and decomposition of Li$_2$O$_2$ on the Ag/NCF cathode. The as-acquired favourable electrocatalytic results probably benefit from the perfect synergistic effects.
between the NCF matrix and the encapsulated Ag nanocrystals, in which the former acts as a highly electrically conductive web to facilitate efficient electron transfer, while the latter offer highly catalytic sites.
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<th>Abbreviation</th>
<th>Full name</th>
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<tbody>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>APS</td>
<td>Ammonium peroxydisulfate</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>CNFs</td>
<td>Carbon nanofibers</td>
</tr>
<tr>
<td>CNTs</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EV</td>
<td>Electric vehicle</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy carbon</td>
</tr>
<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>LOBs</td>
<td>Lithium-oxygen batteries</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammograms</td>
</tr>
<tr>
<td>M</td>
<td>Metal element</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly(tetrafluoroethylene)</td>
</tr>
<tr>
<td>Py</td>
<td>Pyrrole</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disk electrode</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
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<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscope</td>
</tr>
<tr>
<td>TEGDME</td>
<td>Tetraethylene glycol dimethyl ether</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>DC</td>
<td>Discharge</td>
</tr>
<tr>
<td>RC</td>
<td>Recharge</td>
</tr>
<tr>
<td>NCF</td>
<td>N-doped carbon fiber</td>
</tr>
<tr>
<td>EMD</td>
<td>Electrolytic manganese dioxide</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>LITFSI</td>
<td>Lithium bis(trifluoromethylsulphonyl)imide</td>
</tr>
<tr>
<td>LiCF$_3$SO$_3$</td>
<td>Lithium trifluoromethanesulfonate</td>
</tr>
<tr>
<td>RM</td>
<td>Redox mediator</td>
</tr>
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# LIST OF SYMBOLS

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<thead>
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<th>Symbol</th>
<th>Name</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
<td>kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$2\theta$</td>
<td>Detection angle in XRD</td>
<td>Degree</td>
</tr>
<tr>
<td>C-rate</td>
<td>Charge or discharge rate</td>
<td>mA g$^{-1}$</td>
</tr>
<tr>
<td>$d$</td>
<td>Lattice spacing</td>
<td>nm</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant = 96485</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
<td>A</td>
</tr>
<tr>
<td>$N$</td>
<td>Avogadro's number = 6.022 × 10$^{23}$</td>
<td>mol$^{-1}$</td>
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<tr>
<td>°C</td>
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<td>-</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>Pa</td>
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<tr>
<td>$P_0$</td>
<td>Saturation pressure</td>
<td>Pa</td>
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<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K or °C</td>
</tr>
<tr>
<td>$i$</td>
<td>Time</td>
<td>h or s</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
<td>V</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percent</td>
<td>-</td>
</tr>
<tr>
<td>$\eta_e$</td>
<td>Coulombic efficiency</td>
<td>%</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
<td>Å</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Ionic conductivity</td>
<td>S cm$^{-1}$</td>
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## LIST OF ORGANIZATIONS

<table>
<thead>
<tr>
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<tr>
<td>ISEM</td>
<td>Institute for Superconducting and Electronic Materials</td>
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<td>UOW</td>
<td>University of Wollongong</td>
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1.1 General background

Nowadays, more than 85% of energy demand around the world depends on the supply of fossil fuels\cite{1}. As a consequence, serious global climate issues have emerged due to emissions of large quantities of greenhouse gases (GHG), e.g. CO$_2$ and CH$_4$, into the atmosphere, as a result of worldwide fossil fuel burning. The energy crisis and climate problem have motivated researchers worldwide to search for sustainable energy sources that can offer more effective energy saving and low emissions. Fortunately, researchers have estimated that an all-electric vehicle will generate 25% less GHG emissions than a conventional gasoline-powered vehicle on a well-to-wheel basis\cite{2,3}. Therefore, it would greatly benefit the world to develop an electrical energy storage system that can integrate the renewable energy into the grid smoothly and effectively. Among the various energy storage systems, the lithium secondary battery is considered as one of the most promising candidates due to its high energy conversion efficiency. Nevertheless, the state-of-the-art Li-ion batteries are still far from meeting the energy storage needs of future generations, despite the spectacular success that they have already achieved\cite{4}. It is therefore worthwhile to devote intensive research to alternatives that can go beyond the limits of the current Li ion battery.

The lithium-air (Li-O$_2$) battery, which uses O$_2$ derived from air, would provide a theoretical specific energy (energy per unit mass) of 3623 Wh/kg when discharged to the lithium peroxide composition (Li$_2$O$_2$), which is almost ten times that of Li-ion batteries \cite{5,6}. Whether it would be capable of practical energy storage is uncertain, as many factors are unknown, but values are predicted in the range of 500 to 1,000 Wh
kg$^{-1}$. This is sufficient to deliver significantly in excess of a 500 km driving range if the Li-O$_2$ battery is employed as an electric vehicle battery$^{[7]}$. The full development of the Li-O$_2$ battery is therefore expected to make a significant contribution to solving the energy crisis worldwide.

Currently, four types of Li-O$_2$ batteries are under development. They are designated by the type of electrolyte employed$^{[8,9]}$: nonaqueous (aprotic), aqueous, solid-state, and hybrid. Nonaqueous electrolyte has been verified to be more feasible than the usual aqueous electrolyte for alleviating parasitic corrosion on the Li anode. Coupled with higher energy density than the other systems, the nonaqueous Li-O$_2$ battery has attracted the most attention worldwide$^{[10]}$. Therefore, this doctoral thesis is focused on research on nonaqueous Li-O$_2$ batteries, and the term “Li-O$_2$” is referring to the “nonaqueous Li-O$_2$” in this thesis except when otherwise indicated.

### 1.2 Challenges for Li-O$_2$ batteries

Exciting progress on the Li-O$_2$ battery has been made over the past few years, although critical challenges remain that are opposing its practical realization. High discharge-charge over-potential, low energy efficiency, poor rate capability, and especially short cycle life result from the sluggish kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER)$^{[11]}$. Unlike O$_2$ reduction in fuel cells, which produces H$_2$O, the product at the cathode in the Li-O$_2$ battery is the insulating solid Li$_2$O$_2$, which has a profound impact on various characteristics of the battery, e.g. discharge capacity, discharge and charge overpotential, and reversibility. It has been demonstrated that the performance of Li-O$_2$ batteries is strongly determined by
both the materials and the architecture of the oxygen electrodes, which contribute most of the voltage gap and cycling capability of such batteries\cite{8}. Based on the existing challenges, most current efforts devoted to constructing advanced Li-O\textsubscript{2} batteries involve cathode material exploration. This involves formation of a favourable cathode structures for the traditional electrocatalysts, exploration of novel cathode materials or utilization of composite materials, e.g. doping with elements, novel technology to deposit efficient catalysts on a high conductivity matrix, etc. In this thesis work, most efforts have mainly been devoted to developing efficient cathode catalyst materials for the nonaqueous Li-O\textsubscript{2} battery and to further understanding how the structure and morphology of the cathode affect the oxygen reaction process.

1.3 The goals of this work

In this doctoral work, the main goal is to explore and design efficient cathode materials for nonaqueous Li-O\textsubscript{2} batteries. The nanostructured transition metal oxide materials NiCo\textsubscript{2}O\textsubscript{4} and Co\textsubscript{3}O\textsubscript{4} with high specific surface area were selected as my first research subjects due to their high electrocatalytic activities toward the ORR and OER, long cycling capability, and low cost. To further mitigate the discharge and charge voltage gap, silver nanocrystals were embedded into nitrogen-doped carbon fibers to create a bifunctional cathode material. Through the introduction of these electrocatalysts with optimum structure, the performances of Li-O\textsubscript{2} batteries could be greatly enhanced. Moreover, technologies such as ex-situ X-ray diffraction (XRD), ex-situ X-ray photoelectron spectroscopy (XPS), ex-situ transmission electron microscopy (TEM), and in-situ XRD were implemented to investigate the characteristics and catalytic properties of the candidate cathode materials. Figure 1.1 provides a clear association illustrating the challenges of lithium oxygen batteries and research goals of this thesis.
1.4 Outlines of the thesis

The scope of this doctoral work is briefly summarized as follows:

Chapter 1 concisely introduces the general background, main challenges, some strategies for improving the electrochemical performance of Li-O₂ batteries, and the outline of this study.

Chapter 2 contains a literature review on Li-O₂ batteries, which includes the general background, a brief history, general principles, basic concepts, and the current research status related to Li-O₂ batteries.

Chapter 3 presents the list of chemicals and methods applied for the synthesis of cathode materials in this thesis, and the physical and electrochemical characterization methods used in this study are also briefly introduced.
Chapter 4 introduces a simple and environmentally friendly approach to the synthesis of self-assembled three-dimensional (3D) foam-like NiCo$_2$O$_4$ catalyst, wherein starch acts as the template to form the unique 3D architecture. Superior bi-functional electrocatalytic performance towards both the oxygen reduction reaction and the oxygen evolution reaction is also demonstrated. A relatively high round-trip efficiency of 70% and high discharge capacity of 10137 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$ was achieved.

A novel nanofibrous Co$_3$O$_4$/polypyrrole (PPy) composite with a three-dimensional (3D) nanoweb structure is presented in Chapter 5. Co$_3$O$_4$ nanocrystals are grown on the PPy nanofibers via a rapid hydrothermal method. The as prepared nanofibrous Co$_3$O$_4$/PPy can act as efficient bifunctional catalyst in Li-O$_2$ batteries, which is attributed to the synergistic effects from the PPy matrix with a highly conductive nanoweb structure and the Co$_3$O$_4$ nanoparticles with intrinsically high catalytic activity.

Chapter 6 is devoted to the synthesis of 3D hierarchical porous Co$_3$O$_4$ nanotube (Co$_3$O$_4$ HPNT) networks with polypyrrole nanofiber (PPyNF) as the sacrificial template. The present technique may offer a new strategy for the design and synthesis of 3D structured porous nanotubular materials. The 3D Co$_3$O$_4$ HPNT network demonstrated superior bi-functional electrocatalytic activities towards both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), with a rather low charge overpotential of 99 mV and high discharge/charge capacity of 4164 mAh g$^{-1}$/4299 mAh g$^{-1}$, respectively.
Chapter 7 discusses the facile synthesis of Ag nanocrystals encapsulated in nitrogen-doped carbon fiber (NCF). The synthesis involves the simultaneous reaction of pyrrole and Ag$^+$ ions in an aqueous medium followed by a heat treatment. The as-prepared Ag/NCF features a much reduced discharge/charge gap of 0.89 V compared with 1.38 V for NCF cathode under fixed capacity in lithium oxygen batteries. X-ray diffraction analysis coupled with Raman spectroscopy confirmed the reversible formation and decomposition of Li$_2$O$_2$ on the Ag/NCF cathode.

Chapter 8 covers the main conclusions and achievements of this thesis. A brief outlook based on this study is also provided for researchers, followed by the lists of references and publications during the period of this study.
CHAPTER 2 LITERATURE REVIEW

2.1 Development history of the Li-O₂ batteries

The dream of electric vehicles (EVs) has a long history, dating back to the 18th century, as shown in Figure 2.1. Strictly speaking, the Li-air battery stems from metal-O₂ batteries, which could generate electricity by redox reactions between the metal and the oxygen in air. In 1979, Blurton and Sammells reviewed detailed information on primary metal-O₂ batteries. During that period of time, however, more attention was paid to Zn-O₂ batteries because of their practical vehicle applications, instead of the Li-O₂ battery. Surprisingly, they found that a high theoretical gravimetric energy density of 11140 Wh kg⁻¹ with 3 V open-circuit voltage could be achieved for the Li-O₂ battery, if
the discharge product reached Li₂O. In 1996, Abraham and Jiang first reported a successful rechargeable Li-O₂ battery, which consisted of a Li metal anode, an organic polymer electrolyte, and a porous carbon air cathode. In the next two decades, however, the Li-O₂ battery failed to draw worldwide attention due to its poor cycle life. In 2006, Bruce and his coworkers again demonstrated the rechargeability of the Li₂O₂ electrode by replaced the polymer electrolyte with an organic electrolyte, using Li₂O₂ embedded int carbon and MnO₂ as a cathode. Since then, numerous studies have focused on the rechargeability of this technology, and the Li-O₂ battery has quickly appeared over the research horizon. This is because it could provide significantly enhanced energy storage capability that would be sufficient to drive electric vehicles of more than 300 miles (per charge), which is comparable to the performance of gasoline vehicles, as shown in Figure 2.2.

![Figure 2.2 Gravimetric energy densities (Wh kg⁻¹) for various types of rechargeable batteries](image)

Figure 2.2 Gravimetric energy densities (Wh kg⁻¹) for various types of rechargeable batteries.
With the rapid development of the Li-O₂ battery, electrolytes, from early unstable carbonate-based to later dimethyl sulfoxide (DMSO) and ether based solvents, have gradually evolved to stabilize battery cycling⁵, 21-23. Multiple kinds of catalysts, e.g., metal oxides²⁴, ²⁵, novel metals (alloys)²⁶, and carbon-based²⁷-²⁹, and carbon-free³⁰, ³¹ materials, have been widely investigated to reduce the overpotential and improve reversibility.³⁶, ²⁶, ³²-³⁴ In recent years, mediators (also denoted as soluble catalysts) such as LiI and 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) have been adopted to enlarge the discharge/charge capacity and prolong the cycling capability.³⁵-³⁷ Experiments combined with theoretical calculations for understanding the mechanisms of Li₂O₂ formation/decomposition, regardless of whether via solid surface pathways or solution-mediated, have also been proposed, carried out, and well-reviewed by many groups⁴, ³⁸, ³⁹

### 2.2 General principles and working mechanism

As discussed above, Li-O₂ batteries of different types have been developed and classified according to the electrolytes used, such as aqueous, nonaqueous (aprotic), hybrid, and solid state electrolytes. The nonaqueous Li-O₂ battery possesses a relatively simple structure and has the highest energy density of all the Li-O₂ batteries. A typical design for nonaqueous Li-O₂ batteries is shown in Figure 2.3(a). Unlike most other batteries that must incorporate both the anode and cathode inside a storage system, nonaqueous Li-O₂ batteries are unique, in that the cathode material (oxygen) is not stored in the battery. Instead, oxygen can be absorbed from the environment and reduced by catalytic surfaces inside the air cathode⁴⁰. The battery contains a metallic lithium anode, an electrolyte comprising a dissolved lithium salt in an aprotic solvent,
and a porous O₂-breathing cathode composed of large-surface-area carbon particles and catalyst particles, both bound to a metal mesh using a binder.\textsuperscript{[41]}

Figure 2.3 Schematic illustration of the four different architectures for the Li-air battery\textsuperscript{[42]}. 

The chemistry proposed for the nonaqueous Li-O₂ batteries differs from those of other batteries since oxygen is supplied as a reactant during the battery cycling. During electrochemical discharge, the Li anode is oxidized by releasing an electron to the external circuit to produce Li ions in the electrolyte, whereas the oxygen is reduced at the catalytic air electrode surface to form lithium peroxide (and possibly Li₂O) (Figure 2.4a)\textsuperscript{[43]}. Based on this principle, theoretical voltages are calculated using the Nernst equation for possible Li-O₂ battery reactions\textsuperscript{[44]} as shown in Eqs. (2.1, 2.2)

\[ 2\text{Li} + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2, \Delta G^0 = -571.0 \text{ kJ mol}^{-1} \quad (E^0 = 2.96 \text{ V}) \] (2.1)
\[ 4\text{Li} + \text{O}_2 \rightarrow 2\text{Li}_2\text{O}, \Delta G^0 = -562.1 \text{ kJ mol}^{-1}, \quad (E^0 = 2.91 \text{ V}) \quad (2.2) \]

The process in Equation (2.1) is expected to be reversed on electrochemical charge in the nonaqueous system, making the battery rechargeable. The cathode functions as an oxygen reduction reaction (ORR) catalyst during discharge and hopefully works as an oxygen evolution reaction (OER) catalyst during charge\[^{[45]}\].

![Diagram of battery operation](image)

Figure 2.4 (a) Schematic illustration of operation of nonaqueous battery, and (b) typical measured discharge-charge cycle (based on Super P carbon) for the rechargeable nonaqueous Li-O\(_2\) batteries\[^{[43]}\].
A typical plot of voltage vs. capacity during the discharge-charge cycle of a Li-O₂ battery is shown in Figure 2.4b. The deviations from the thermodynamic potential (open circuit potential) on discharge and charge (overpotentials) are the result of reactions at the cathode. The cathode should have a large surface area to offer sufficient active sites for the ORR and OER. Meanwhile, a large pore volume is desirable to store the discharge product Li₂O₂, which significantly determines the discharge capacity of a Li-O₂ battery\(^{[19]}\).

The O₂ reduction mechanism is reported to be significantly influenced by the current density, the solvent, the lithium salt, and whether the LiO₂ intermediate is dissolved in solution or adsorbed on the electrode surface. The two kinds of O₂ reduction mechanisms are summarized in Figure 2.5.
Figure 2.5 Reduction mechanisms in a Li-O_2 cell at low overpotentials. Where LiO_2 is soluble (for example, due to use of a high donor number solvent that strongly solvates Li^+), Li_2O_2 grows as particles from solution. Where LiO_2 is insoluble (for example, due to use of a low donor number solvent that weakly solvates Li^+), Li_2O_2 grows on the electrode surface. The reactions above refer to those occurring during discharge via the solution mechanism and the surface mechanism\[46\].

### 2.3 Basic Concepts

Some basic concepts are illustrated below in order to properly describe the Li-O_2 battery system and evaluate the battery performance:
**Potential**: In fact, each electrochemical reaction relates to a standard electrode potential ($E^0$). It could be calculated from the Gibbs free energy ($\Delta G^0$) from Equation (2.3):

$$\Delta G^o = W = -nFE^o$$  \hspace{1cm} (2.3)

Where $F$ is the Faraday constant. If all the Gibbs free energy was completely transformed to electrical energy, the electrode potential ($E^o$) could be calculated from Equation (2.4) as follows:

$$E^o = -\Delta G^o/nF$$  \hspace{1cm} (2.4)

Where $\Delta G$ is the Gibbs free energy, $F$ is the Faraday constant (96485 C), $n$ is the number of electrons involved in a stoichiometric reaction, and $E^0$ is the electrode potential.

**Onset potential**: This refers to the electrical potential difference between the cathode and the anode of a battery when there is no current flow in the battery.

**Overpotential**: This refers to the potential difference between the practical reduction potential in a redox reaction and its thermodynamic potential. The existence of overpotential means that more energy than thermodynamically expected is needed to drive a reaction.

**Capacity**: This refers the total charge that the cathode or anode delivers in the redox reaction during the discharge/charge process in a battery. It can be calculated by Equation (2.5):

$$Q = \int_{t_1}^{t_2} I(t)dt = nzF$$  \hspace{1cm} (2.5)
Where \( I(t) \) is the current, \( t \) is the time, \( n \) is the number of the ions (mol), \( z \) is the valence of the ions, and \( F \) is the Faraday constant (96485 C mol\(^{-1}\)).

**Specific discharge/charge capacity**: This refers to the amount of capacity calculated based on the per unit weight of the active material during the discharge or charge process. The units are usually in mAh g\(^{-1}\).

**Round-trip efficiency**: This refers to the ratio between the discharge voltage and the charge voltage. It is mostly determined by the properties of the catalyst in the battery.

### 2.4 Cathode materials

Among the various issues influencing Li-O\(_2\) battery performance, the cathode has been identified as the dominant factor\(^{[20]}\). O\(_2\) from the atmosphere is supposed to be reduced to Li\(_2\)O\(_2\) during the discharge process, whereas the desired discharge product is expected to oxidize to O\(_2\) reversibly during the charge process. It is the sluggish kinetics of the ORR and OER that results in the high discharge/charge overpotential and irreversibility of the Li-O\(_2\) battery. Meanwhile, the high charging overpotential readily causes the oxidation and decomposition of electrolyte, which leads to the formation and accumulation of insoluble side products, and thus blocks the oxygen diffusion channels and results in the death of cells\(^{[47]}\).

To date, numerous efforts have been devoted to developing cathode materials that can significantly reduce the overpotential and improve the battery performance. Among them, a conductive porous structure to store discharge products and provide channels
for oxygen diffusion is essential \[48, 49\]. The morphology should facilitate electrolyte wettability to afford ionic transfer during discharge/charge processes. The pore volume, in particular, also is a critical factor. Further studies have since revealed that the volume of the pores in the range of 2–50 nm rather than the surface area of the air electrode material appears to be the limiting factor that determines the discharge capacity of the battery\[50, 51\]. Besides a favourable structure, a bifunctional catalyst which has a high ability to accelerate the kinetics of both the ORR and OER is in urgent demand. Only with an optimum structure coupled with an efficient catalyst can the Li-O\(_2\) battery deliver satisfactory performance. Moreover, as the ideal discharge product in the non-aqueous Li-O\(_2\) battery, the morphology and properties of Li\(_2\)O\(_2\) plays a critical role in affecting the kinetics of the OER during the charge process\[52, 53\]. Therefore, the cathode structure and the catalyst type, as well as the operation conditions, have been investigated to determine the Li\(_2\)O\(_2\) growth process in the cathode \[54, 55\]. Figure 2.6 provides a detailed summary on how the cathode e.g. catalyst, structure affect the performance of a Li-O\(_2\) battery\[42\]. In the current state of the Li-O\(_2\) battery, there have been a huge number of studies related to cathode material exploration, including some already successfully applied in fuel cells and metal-air batteries. Generally, these are classified into the following five main groups: carbon cathode materials, carbon-free cathode materials, metal oxides, metals (alloys) and their composites, and soluble catalysts.
Figure 2.6 Approaches to the fabrication of an ideal cathode for the non-aqueous Li-air battery.[42]

2.4.1 Carbon cathode materials

Carbon materials have been widely employed in energy-storage systems because of their low cost, excellent electrical conductivity, light weight, and large surface area. They are now also extensively used as catalysts or as catalyst support materials in Li-O2 batteries.[4] Various carbon materials, such as commercial carbon,[51, 56-58], graphene nanosheet (GNS)[59, 60], carbon nanotubes (CNT)[61, 62], carbon nanofibers (NCF)[63], 3D porous carbon[64], carbon nanocages[65], and nitrogen-doped carbon[66-70] have been studied so far.
Table 2.1 Reported capacities of commercial carbon materials in non-aqueous Li-O₂
batteries\cite{8}.

<table>
<thead>
<tr>
<th>Carbon materials</th>
<th>Capacity (mA h g⁻¹)</th>
<th>Current density (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Super P</td>
<td>2120</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>1800</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>~ 1000</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>3400</td>
<td>70 mA g⁻¹</td>
</tr>
<tr>
<td>KB EC600JD</td>
<td>2700</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>3374.4</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>3000</td>
<td>0.2</td>
</tr>
<tr>
<td>Vulcan XC-72</td>
<td>1200</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>762</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>1053</td>
<td>75 mA g⁻¹</td>
</tr>
<tr>
<td>Super S</td>
<td>1000</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>70</td>
</tr>
<tr>
<td>Black Pearls 2000</td>
<td>50</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>1909.1</td>
<td>75 mA g⁻¹</td>
</tr>
<tr>
<td>KB EC300JD</td>
<td>2200</td>
<td>0.1</td>
</tr>
<tr>
<td>Graphite</td>
<td>560</td>
<td>0.1</td>
</tr>
<tr>
<td>Darco G-60</td>
<td>250</td>
<td>0.1</td>
</tr>
<tr>
<td>Norit carbon black</td>
<td>4400</td>
<td>70 mA g⁻¹</td>
</tr>
<tr>
<td>Calgon activated black</td>
<td>80</td>
<td>0.05</td>
</tr>
<tr>
<td>Ensaco 250G</td>
<td>550</td>
<td>0.1</td>
</tr>
</tbody>
</table>
The reported discharge capacity of various commercial carbon materials, e.g. Super P, Ketjen Black, and Vulcan carbon, are summarized in Table 2. These materials, however, were verified to deliver sufficient ORR but limited OER activities. Xia et al. designed three-dimensional ordered mesoporous/macroporous carbon sphere arrays (MMCSAs) as cathode material for the Li-O₂ battery, in which the ordered mesoporous channels and hierarchical mesoporous/macroporous structure of the MMCSAs facilitated electrolyte immersion and Li⁺ diffusion, and provided effective space for O₂ diffusion and O₂/Li₂O₂ conversion. Cathodes based on porous graphene with different pore sizes exhibited remarkably higher discharge capacities than nonporous graphene for Li-O₂ batteries, and the graphene with pore diameter around 250 nm exhibited the highest discharge capacity of 29,375 mA h/g. Schmidt et al. developed a kind of ultra-polar carbon (UPC) as the cathode substrate for the Li-O₂ battery. The porous carbon with ultra-polar surface served as an efficient support for dispersion of catalyst nanoparticles, suggesting that such ultra-polar hierarchical carbon-based composites can be appealing materials for rechargeable Li-O₂ batteries. Although the above carbon cathodes showed high discharge capacity, the also high charge overpotential limits their further use as efficient OER catalysts. Therefore, in most recent studies, commercial carbon materials are usually used as conductive agents and/or for catalyst support rather than for reaction sites in the cathode of Li-O₂ batteries.
As an alternative, introducing defects or vacancies into the carbon structure has been verified as a robust strategy to dramatically mitigate the overpotential during the OER process. Among them, CNT, CNF, and their derivatives have been considered for use in lithium/air batteries, due to their unique structures, high surface areas, and greater number of defects/vacancies compared to the bulk counterpart\cite{74}. A pure CNT cathode was reported to deliver a discharge capacity of about 800 mAh g\(^{-1}\) at the current density of 0.4 mA cm\(^{-2}\)\cite{75}, whereas a pure CNTs sponge cathode exhibited a discharge voltage and specific capacity of 2.45 V and 6424 mAh g\(^{-1}\), respectively, at a current density of 0.05 mA cm\(^{-2}\)\cite{76}. Superior rate capability was exhibited by a free-standing CNT-based cathode; when the discharge rate was increased to 0.2 and 0.5 mA cm\(^{-2}\), discharge capacity of about 8000 mA h g\(_{\text{carbon}}^{-1}\) and 2000 mA h g\(_{\text{carbon}}^{-1}\) could be achieved, respectively\cite{77}. Lim et al.\cite{78} prepared a hierarchical CNT fibril cathode for the Li-O\(_2\) battery. Owing to the tuned porosity in its woven structure, the CNT fibril cathode could effectively promote the reversible uniform formation and decomposition of Li\(_2\)O\(_2\) that was deposited among the fibrils.

Nitrogen-doped carbon represents another series of carbon materials that are loaded with defects or vacancies. The doped heteroatom N can change the chemical and electronic nature of carbon-based materials leading to the formation of defects and functional groups, so that the N-doped carbon exhibits higher electrocatalytic properties than unmodified carbon materials\cite{79,80}. Shui et al. \cite{81} reported a vertically aligned nitrogen-doped coral-like carbon nanofiber (VANCCF) array cathode (Figure 2.7a-b). The Li-O\(_2\) battery with this cathode presented an ultra-narrow voltage gap of 0.3 V between discharge and charge at a current density of 100 mA g\(^{-1}\) (Figure 2.7c).
Figure 2.7 (a) TEM image of an individual VA-NCCF. (b) Schematic illustration of Li$_2$O$_2$ grown on a coral-like carbon fiber, which has the advantage of tightly holding the Li$_2$O$_2$ deposited on its rugged surface, (c) Rate performance of the VANCCF electrode under current densities of 100, 600, and 1000 mA g$^{-1}$ [81]. (d) SEM image of highly porous N-HGr electrode made from dimethyl formamide (DMF), (e) discharge/charge voltage profiles of dense and porous N-HGr electrodes. The current density was 40 mA/g [82].

Recently, the same group successfully introduced N into holey graphene (N-HGr) for Li-O$_2$ battery cathodes (Figure 2.7d) [82]. Besides a remarkably reduced charge overpotential, they also found that the porous structure was the key factor influencing the charge overpotential (Figure 2.7e). A high round-trip efficiency (85%) and a long cycling life (> 100 cycles) under controlled discharge/charge depths were also obtained, which made N-HGr superior to most other carbonaceous materials. Mi et al. found that the application of nitrogen-doped CNTs on the substrate increased the capacity in both carbonate-based and ether-based electrolytes beyond that of untreated CNTs [83]. Density
functional theory (DFT) investigations showed that N-doping could not only enhance the adsorption of oxygen atoms but also decrease the energy barrier for \( \text{O}_2 \) dissociation from 2.39 eV to 1.20 eV, leading to better catalytic activity in the \( \text{O}_2 \) dissociation reaction \(^{[84]}\). A nitrogen-enriched mesoporous carbon was reported to increase the discharge voltage plateau by 100 mV and deliver 1.73 times higher discharge capacity than commercial carbon (BP 2000), at a current density of 30 mA \( \text{g}_{\text{carbon}}^{-1} \). \(^{[85]}\)

### 2.4.2 Carbon-free cathode materials

Although carbon-based support materials exhibited outstanding prospects for Li-O\(_2\) batteries, their low polarity and highly hydrophobic nature are identified as the major drawbacks that limit the rate performance of the carbon-supported cells. Actually, in early 2011, P.G. Bruce\(^{[86]}\) found that carbon was unstable beyond 3.5 V \((\text{vs. Li}^+/\text{Li})\) on discharge or charge, oxidatively decomposing to form \( \text{Li}_2\text{CO}_3 \), especially in the case of hydrophobic carbon. Direct chemical reaction of carbon promotes electrolyte decomposition during discharge and charge in a Li-O\(_2\) cell, giving rise to \( \text{Li}_2\text{CO}_3 \) and Li carboxylates (in dimethyl sulfoxide (DMSO) and tetraglyme electrolytes). Therefore, developing carbon-free cathode materials is a promising strategy for mitigating the side reactions associated with carbon instability in Li-O\(_2\) batteries. Liu et al.\(^{[87]}\) proposed a possible solution for a carbon-free cathode in a Li-O\(_2\) battery (Figure 2.8), which avoids \( \text{Li}_2\text{O}_2 \) on the surface of the cathodes and possible carbon corrosion under a high potential. For proper use, the carbon-free cathode should possess the follow features \(^{[88]}\): (1) chemical stability, (1) high electrochemical conductivity for facilitating charge transport at the interface, (3) high specific surface area for electrochemical redox reactions, (4) optimized structure and porosity for accommodating the discharge product,
and (5) low cost. Currently, several groups of carbon-free materials, such as polypyrrole (PPy), metal nitrides, and tin/titanium-based materials have shown their feasibility as potential cathode support materials for Li-O₂ batteries.

Figure 2.8 Possible reactions in the interfaces between the cathode and electrolyte in Li-O₂ batteries with carbon based and carbon-free cathodes [87].

2.4.2.1 Polypyrrole (PPy)

Polypyrrole (PPy), a very attractive polymer, has many advantages, such as high electric conductivity, high chemical and electrochemical stability, a stable three-dimensional structure, ease of synthesis, good adhesion, and especially, higher polarity than the carbon materials, expressed as a higher hydrophilic property [47]. Cui and co-workers first reported a tubular structured conducting polymer, tubular polypyrrole (TPPy), as an alternate support material for the air cathode of Li-O₂ batteries. The discharge voltage of the TPPy electrode was consistently higher than that of a granular PPy (GPPy) electrode
by about 100 mV and higher than that of an acetylene carbon black (AB) electrode by about 300 mV, while its charge voltage was substantially lower than that of GPPy by 100 mV and AB by 600 mV, respectively, at a current density of 0.1 mA cm$^{-2}$ (Figure 2.9)\textsuperscript{47}. The enhanced performance was ascribed to the abundant gas diffusion channels and reaction sites of the TPPy. Composites of PPy grown uniformly on reduced graphene oxide were also studied by Munichandraiah and co-workers as catalysts for Li-O$_2$ batteries, and a discharge capacity of 3353 mAh g$^{-1}$ was delivered. PPy/graphene oxide (GO) composite\textsuperscript{89} and PPy doped with Cl$^{-}$\textsuperscript{90} were also investigated as cathode materials for Li-O$_2$ batteries. Zhang et al. \textsuperscript{91} found that PPy could exhibit both higher capacity and better cycling performance than carbon materials owing to its high catalytic activity towards the ORR as well as the OER. The electrochemical performance of PPy could be significantly influenced by the dopants, and the PPy doped with Cl$^{-}$ exhibited higher capacity and more stable cyclability than that doped with ClO$_4^{-}$\textsuperscript{42}. 
Figure 2.9 SEM image of the as-prepared TPy supported air electrodes (a); Contact angles of the non-aqueous electrolyte on AB (inset) and PPy, with the electrolyte lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,2-dimethoxyethane (DME) (b); First discharge-charge curves of the AB, GPy and TPy supported Li-O₂ cells at 0.5 mA cm⁻² (c), and specific capacities per gram of the supports (d)\(^{[92]}\).

2.4.2.2 Others

In addition to the above support materials reported, indium tin oxide (ITO) and Sb-doped tin oxide (STO) could also act as support materials for Li-O₂ batteries. Zhou’s group\(^{[93]}\) first introduced a stable conductive ITO electrode embedded with Ru nanoparticles as a carbon-free cathode in Li-O₂ batteries, which exhibited excellent cycling performance. ITO is heavy, however, which leads to a low specific capacity per
unit mass. Later, they again reported that STO, ~ 6 nm in size, supporting Ru nanoparticles (Ru/STO) could be applied as a carbon-free cathode for Li-O₂ batteries with a large specific capacity of 750 mAh g⁻¹; and low discharge and charge overpotentials have been obtained[94]. Most recently, nanocrystalline TiC has been demonstrated by Thiotyl et al. to be an efficient gas diffusion cathode [95, 96]. Nazar et al. [96] reported surface-passivated Mo₂C nanofibers with low charging potentials (~3.2 V vs. Li⁺/Li) as a carbon-free cathode. Later, the same group synthesized a metallic Magneli phase Ti₄O₇ with a crystallite size between 10-20 nm. The material exhibited greatly reduced overpotential compared to carbon. Oxidation of lithium peroxide on charge started just above 3 V, comparable to gold and TiC, and the majority (65%) of oxygen release occurred in the 3-3.5 V window vs. Li⁺/Li [97].

2.4.3 Metal oxides

2.4.3.1 Metal oxides (MOs)

![Figure 2.10 Charge curves of prepacked Li₂O₂ electrode with various metal oxide electrocatalysts](image)

Figure 2.10 Charge curves of prepacked Li₂O₂ electrode with various metal oxide electrocatalysts [43].
Bruce and co-workers\textsuperscript{[98]} were the first to study the catalytic activities of different transition metal oxides, including MnO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, Fe$_2$O$_3$, NiO, and CuO for Li-O$_2$ batteries, and the results is shown in Figure 2.10. Thapa et al. then investigated the performance of various metal oxides, including MnO$_2$, Co$_3$O$_4$, NiO, Fe$_2$O$_3$, CuO, V$_2$O$_5$, MoO$_3$, and Y$_2$O$_3$ as cathode catalysts for Li-O$_2$ batteries\textsuperscript{[99]}. They found that most of the metal oxides displayed improved discharge capacity after five cycles, as is listed in Table 2.1.

Among these transition metal oxides\textsuperscript{Co$_3$O$_4$} in particular has been widely studied as a cathode catalyst for Li-O$_2$ batteries \textsuperscript{[100-106]. Kim et al. \textsuperscript{[107]} investigated the performance of cube-type, flower-type, and villiform-type Co$_3$O$_4$ nanoparticles, while Riaz et al.\textsuperscript{[108]} synthesized Co$_3$O$_4$-only electrodes with morphologies of nanosheets, nanoneedles, and nanoflowers. They both claimed that the performances of Li-O$_2$ batteries were strongly dependent on the architecture of the Co$_3$O$_4$ cathode. The electrochemical performances of Co$_3$O$_4$ cathodes with nanoscale morphologies significantly outperformed the commercial ones when used for Li-O$_2$ batteries. Among the three catalysts, the nanoneedles Co$_3$O$_4$ electrode had the best long-term cyclability, with a discharge voltage of about 2.75 V (vs. Li$^+/\text{Li}$) and charge voltage as low as 3.85 V (vs. Li$^+/\text{Li}$)\textsuperscript{[108]}. The dense hollow Co$_3$O$_4$ cathode reported by Ming et al.\textsuperscript{[109]} showed improved performance compared with mesoporous and nanoparticle Co$_3$O$_4$. It sustained good cyclability, greater than 100 cycles, with a fixed capacity of 2000 mA h g$_{\text{catalyst}}^{-1}$ at 200 mA g$_{\text{catalyst}}^{-1}$. Through a recent investigation on single crystalline Co$_3$O$_4$ nanocrystals with different crystal planes exposed, Su et al.\textsuperscript{[110]} discovered correlations between different Co$_3$O$_4$ crystal planes and their effects towards reducing charge-discharge over-potential. In addition, some researchers found that Co$_3$O$_4$ could offer high ORR
and OER activities when attached on a highly conductive support due to the synergistic coupling effect\cite{8a,9}. A Li-O\textsubscript{2} battery with ultrathin Co\textsubscript{3}O\textsubscript{4} nanosheets grown on reduced graphene oxide (Co\textsubscript{3}O\textsubscript{4}/rGO) as the cathode showed high initial capacity of 10,528 mAh g\textsuperscript{-1} along with a high coulombic efficiency (84.4\%) and stability for 113 cycles when the cut-off discharge voltage remained above 2.5 V. This exciting performance benefited from the synergistic effects between Co\textsubscript{3}O\textsubscript{4} and rGO\cite{111}. Very recently, by employing a combination of electrochemical and gas spectrometry measurements, Bethune et al.\cite{112} investigated the effect of transition metal oxides (TMOs) on the charge potentials and oxygen evolution efficiency in aprotic Li-O\textsubscript{2} batteries, in which Ketjenblack (KB) and KB mixed with MnO\textsubscript{x}, Co\textsubscript{3}O\textsubscript{4}, and RuO\textsubscript{2} served as cathodes. Results showed that the TMO-based cathodes all could decrease the overpotential during charge (Figure 2.11a). RuO\textsubscript{2}, in particular, gave the lowest overpotential, best oxygen evolution efficiency, and best cyclability among them (Figure 2.11b).
Figure 2.11 (a) Galvanostatic voltage profiles for the first cycle of Li-O₂ batteries with TMO-based electrodes with KB and pure KB (KB tested at 0.380 mA cm⁻² (black solid line) and 0.129 mA cm⁻² (black dashed line)); (b) cycle life of TMO cathodes with KB tested at 400 mA g⁻¹ carbon under 1.5 atm of O₂ with 1 M LiTFSI/DME electrolyte [¹¹²]. (c) TEM images of Ru or RuO₂·0.64H₂O-rGO hybrid, and (d) voltage profiles for the 5th cycle and selected following cycles of RuO₂·0.64H₂O-rGO hybrid [¹¹³].

Table 2.2 Discharge capacity of cycles 1 and 5 for various metal oxide catalysts [⁹⁹].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Capacity (mAh g⁻¹) 1st cycle</th>
<th>Capacity (mAh g⁻¹) 5th cycle</th>
<th>Capacity retention per cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>262</td>
<td>653</td>
<td>248</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>199</td>
<td>304</td>
<td>152</td>
</tr>
<tr>
<td>NiO</td>
<td>298</td>
<td>362</td>
<td>121</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>264</td>
<td>285</td>
<td>108</td>
</tr>
<tr>
<td>CuO</td>
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<tr>
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<td>829</td>
<td>383</td>
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<tr>
<td>MoO₃</td>
<td>152</td>
<td>152</td>
<td>100</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>238</td>
<td>213</td>
<td>89</td>
</tr>
</tbody>
</table>

Some precious metal oxides, e.g. RuO₂ [³², ¹¹⁴] and Ir₂O₃ [¹¹⁵], have been explored to efficiently catalyse ORR and OER processes in Li-O₂ batteries. Thapa et al. [⁹⁹] reported that Li-O₂ batteries based on RuO₂ and Ir₂O₃ cathodes could deliver the initial discharge capacities of 317 and 345 mA h gₑlectrode⁻¹, respectively, at a current density of 0.025 mA cm⁻². Jian et al. [³²] designed a core/shell-structured CNT@RuO₂ composite as a cathode
for the Li-O_2 battery, in which the RuO_2 shell showed good catalytic activities towards the ORR and OER without sacrificing the high electronic conductivity of CNT. Remarkably reduced charge potentials, as well as excellent cyclability (> 100 cycles) at a high current density of 500 mA g\text{total}^{-1}, were observed in comparison with the CNT-only cathode. Lee and co-workers\textsuperscript{[113]} reported that RuO_2·0.64H_2O-rGO hybrids significantly reduced the average charge potential to ~3.7 V as well as offering high reversibility at the high current density of 500 mA g\textsuperscript{-1} in a Li-O_2 battery (Figure 2.10). The use of precious metals in this type of catalyst, however, will significantly increase the cost of Li-O_2 batteries, which limits their wide application.

\textbf{2.4.3.2 Ternary metal oxides}

Besides pure metal oxides, several researchers have proposed M\textsubscript{x}N\textsubscript{y}O (M, N = Fe, Co, Mn, Ni, Zn)\textsuperscript{[116-119]} as efficient catalysts for Li-O_2 batteries. In the early studies, Mn\textsubscript{0.5}Co\textsubscript{2.5}O\textsubscript{4}, MnCo\textsubscript{2}O\textsubscript{4}, and Mn\textsubscript{1.5}Co\textsubscript{1.5}O\textsubscript{4} catalysts were used as cathodes for the Li-O_2 battery by substituting Mn for Co in Co\textsubscript{3}O\textsubscript{4}. Their recharge overpotential was apparently larger than for the Co\textsubscript{3}O\textsubscript{4} catalyst, although they presented almost the same discharge voltage and slightly lower discharge capacities\textsuperscript{[120]}. To improve this, NiCo\textsubscript{2}O\textsubscript{4} (NCO), a typical ternary spinel nickel cobalt oxide, with the advantages of low cost, natural abundance, and higher electronic conductivity than Co\textsubscript{3}O\textsubscript{4} and NiO, aroused much interest for use as an electrocatalyst for Li-O_2 batteries\textsuperscript{[118, 121-125]}. With two solid-state redox couple (Co\textsuperscript{3+/2+} and Ni\textsuperscript{3+/2+}) units in its structure, it was enabled to exhibit remarkable catalytic activity towards the ORR and OER in Li-O_2 batteries\textsuperscript{[118]}. Wang et al. synthesized mesoporous NiCo\textsubscript{2}O\textsubscript{4} nanosheets via a hydrothermal method (Figure 2.12a-b), and reversible Li\textsubscript{2}O\textsubscript{2} formation and decomposition were clearly observed.
Li et al. synthesized some ordered mesoporous NiCo$_2$O$_4$ cathodes using KIT-6 as the hard template, and comparatively studied the effects of the amount of NiCo$_2$O$_4$ on the discharge capacity and voltage plateau. Mesoporous NiCo$_2$O$_4$ nanoflake was reported to exhibit a much higher ORR onset potential, larger discharge capacity, and much lower recharge overpotential than the pure carbon cathode. Enhanced rate capability was achieved by a hierarchical NiCo$_2$O$_4$ nanorod-based cathode, which delivered discharge capacity of 5700 mA h g$_{\text{carbon}}^{-1}$ at a high current density of 1000 mA g$_{\text{carbon}}^{-1}$. Gong et al. firmly anchored NiCo$_2$O$_4$ nanoparticles (NCO NPs) on the surface of N-doped reduced graphene oxide (N-rGO) by the hydrothermal method. Owing to the special architecture and intrinsic properties of NCO, the cathode presented excellent cycling stability for 112 cycles with cut-off capacity of 1000 mAh g$^{-1}$ (Figure 2.12e). Very recently, Lee et al. reported spinel-NiCo$_2$O$_4$-deposited CNT (carbon nanotube) bulky paper as a cathode for Li-O$_2$ batteries. The oxide-deposited cathode showed high specific capacity and remarkably reduced charge potentials (in comparison with a carbon-only cathode) as well as excellent cyclability.
Figure 2.12 SEM (a) and TEM (b) images of NCO nanosheet, (c) SEM image NCO electrode after the 1st discharge \cite{18}. (d) SEM image of the NCO@N-rGO composite, and (e) Cycling performance of the NCO@N-rGO cathode at the current density of 200 mA g\(^{-1}\)\cite{129}.

Following a similar idea, CoMoO\(_4\) \cite{131,132} and ZnCo\(_2\)O\(_4\) \cite{133} nanostructured materials have also been investigated as cathodes for the Li-O\(_2\) battery, with much better performance than the Super P-based ones.

### 2.4.3.3 Perovskite-related oxides

Perovskite oxides, which present the archetypal formulas ABO\(_3\) or AA'BB'O\(_3\), have been considered as promising low-cost candidate to serve as cathode catalysts for the Li-O\(_2\) battery, due to their tunable physical and chemical properties and their ability to catalyze both the ORR and the OER\cite{134}. Typically studied perovskite oxides are La\(_{0.75}\)Sr\(_{0.25}\)MnO\(_3\) \cite{135}, LaNiO\(_3\) \cite{136}, and LaNi\(_{1-x}\)Fe\(_x\)O\(_3\) \cite{137}. Nanosized g-La\(_{0.88}\)Sr\(_{0.2}\)MnO\(_3\)
demonstrated a discharge capacity of 1900 mA h g\text{carbon}^{-1} at a current density of 0.1 mA cm\textsuperscript{-2} as a cathode for the Li-O\textsubscript{2} battery \textsuperscript{138}. Later, perovskite-based porous La\textsubscript{0.75}Sr\textsubscript{0.25}MnO\textsubscript{3} (PNT-LSM) nanotubes were reported to significantly mitigate the ORR and OER overpotential\textsuperscript{139}. La\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{2.91} perovskite with a hierarchical mesoporous nanowires morphology that was synthesized by Zhao et al. displayed a capacity of 11059 mAh g\textsubscript{catalyst+carbon}^{-1} at a current density of 50 mA g\textsubscript{catalyst+carbon}^{-1}\textsuperscript{140}. Kalubarne and co-workers claimed that LaNi\textsubscript{0.25}Co\textsubscript{0.75}O\textsubscript{3} exhibited the best performance in terms of lowest charge voltage and highest discharge capacity among the LaNi\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{3} (x = 0, 0.25, 0.5, 0.75 and 1) catalysts that were studied \textsuperscript{141}. Han et al. proposed that CaMnO\textsubscript{3} could be used as a cathode catalyst for Li-O\textsubscript{2} batteries, and stable cyclability over 80 cycles with a discharge plateau higher than 2.35 V was achieved with this perovskite material \textsuperscript{142}.

### 2.4.4 Metals and metal alloys

Some non-precious-metal electrocatalysts that were originally developed for fuel cells have now also been studied in nonaqueous Li-O\textsubscript{2} batteries. Liu et al.\textsuperscript{143} reported that a Li-O\textsubscript{2} cell with Fe/N/C as the cathode catalyst showed lower overpotentials than α-MnO\textsubscript{2}/carbon catalyst and carbon-only material, and a lifespan of 50 discharge-charge cycles was achieved. Wu et al.\textsuperscript{144} recently designed a graphene/graphene-tube-rich N-Fe-MOF catalyst, and their results verified that this highly active precious-metal-free catalyst exhibited superior ORR activity and improved cathode performance in Li-O\textsubscript{2} batteries (Figure 2.13). Meanwhile, some Co- and Ni-based non-precious metal catalysts were studied for high performance Li-O\textsubscript{2} batteries \textsuperscript{59, 66}. 


Figure 2.13 (a) Initial discharge performance for various catalysts at a current density of 50 mA g\text{cat}^{-1} in Li-O\textsubscript{2} battery tests. (b) Cycling test of the N-Fe-MOF catalyst at a current density of 400 mA g\text{cat}^{-1} with voltage cut-offs at 2.5 V (discharge) and 4.1 V (charge)\textsuperscript{[144]}.

Some precious metal, e.g. Pt, Au, Ru, Pd, and Ag, have been investigated as catalysts for Li-O\textsubscript{2} batteries. The results demonstrated that these metals have a remarkable ability to decrease the ORR and OER overpotentials for Li-O\textsubscript{2} batteries\textsuperscript{[145-149]}. Through investigation of the activities of typical precious metals, Lu et al.\textsuperscript{[150]} claimed that the ORR activities drop in the order: Pd > Pt > Ru ≈ Au > glassy carbon, which is closely related to the oxygen adsorption energy on their surfaces (Figure 2.14).
Figure 2.14 Non-aqueous Li-ORR potential at 2 μA cm\(^{-2}\) as a function of the calculated oxygen adsorption energy, $\Delta E^0$ (per oxygen atom relative to an atom in the gas phase), relative to that of Pt\(^{[150]}\).

Silver crystal, as a less precious catalyst compared with Pt, Pd, or Ru-based catalyst, has been one promising alternative for the Li-O\(_2\) battery cathode in recent years.\(^{[151-153]}\) The effect of the size of silver nanoclusters was reported to have a surprising influence on the morphology of the discharge product of the Li-O\(_2\) battery due to a different ORR mechanism\(^{[152]}\). Sun et al. then deposited Ag particles from few microns to 50 μm in size on a gas diffusion layer (GDL). The Ag cathode with 50 μm particles showed a very low polarization, corresponding to a charge potential of 3.6 V during cycling (Figure 2.15)\(^{[153]}\). Later, the same group\(^{[151]}\) deeply investigated the influence of the morphology of Ag based cathodes on the battery performances. Ag nanowires presented much lower charge overpotential (3.2 V vs. Li\(^+\)/Li) than silver nanoparticles (Ag NP).
Figure 2.15 SEM images of the pristine Ag/GDL cathodes with a deposition time of (a) 3, (b) 10, (c) 30, and (d) 300 s at an electrodeposition voltage of -0.25 V. Voltage profiles of the Li-O_2 cells containing cathodes deposited for (e) 3, (f) 10, (g) 30, and (h) 300 s under the 10 h time-controlled mode at a current density of 0.032 mA cm^{-2} [153].

Furthermore, some metal alloy cathodes such as PtCo\textsuperscript{[154]}, AuPt\textsuperscript{[155]}, Pd\textsubscript{3}Fe\textsuperscript{[156]}, and PdCu\textsuperscript{[157]} have been reported to present superior electrocatalytic performance compared to those of the single metal cathodes. Yin et al.\textsuperscript{[158]} observed that the fully and partially alloyed PtAu/C catalysts showed higher discharge capacity, limited overpotentials, and higher round-trip efficiency compared with Au/C and Pt/C cathodes.

### 2.4.5 Soluble catalyst

Soluble catalyst is also called solution-phase catalyst. It mainly refers to soluble redox mediators (RM). These are molecules dissolved in the electrolyte that are oxidized at a potential slightly above the equilibrium potential for Li_2O_2 formation. Once oxidized at the electrode surface, they diffuse to and oxidize Li_2O_2 particles. Since the discharge
product Li$_2$O$_2$ in the Li-O$_2$ battery is in the solid state, it will accumulate at the catalyst surface and hence block the electrode reactions during the discharge process. Meanwhile, it is difficult for a solid catalyst to achieve good contact with the Li$_2$O$_2$ \cite{159, 160}. Therefore, a soluble catalyst could be used to alleviate the above-mentioned problem. To act as effective soluble catalyst, it should meet the following criteria: a high diffusion coefficient, fast charge transfer kinetics (particularly the charge transfer associated with Li$_2$O$_2$ oxidation) at voltages approaching the Li$_2$O$_2$ formation potential, and high stability.

So far, there is a wide range of soluble catalysts which succeed in reducing the oxidation over-potential, including iron phthalocyanine (FePc)\cite{161}, tetrathiafulvalene (TFF)\cite{162}, lithium iodide (LiI)\cite{163, 164}, lithium bromide (LiBr), 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO)\cite{165}, tris[4-(diethylamino)phenyl]amine (TDPA)\cite{166}, indium tri-iodide (InI$_3$)\cite{167}, and 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ)\cite{168}. These redox mediators effectively decrease the charge potential from 4.3-4.5 V \textit{vs.} Li$^+/\text{Li}$ (all potentials hereinafter referenced to Li$^+/\text{Li}$) to 3.3-3.6 V. Even so, solution-phase catalysis is still an unexplored field, which requires more research attention.

### 2.5 Anode Materials

Metallic lithium is the current choice of anode material for Li-O$_2$ batteries. It is expected to achieve the highest energy density, since lithium itself has an extremely high specific energy (3860 mAh g$^{-1}$) and a low negative potential (-3.04 V \textit{vs.} standard hydrogen electrode (SHE)) \cite{20, 169}. Nevertheless, Li dendrite formation and low
coulombic efficiency are two chief issues facing the lithium electrode and have been long-standing problems remaining to be addressed \cite{9, 170, 171}. In addition, Li anode is prone to be attacked by moisture, and oxygen which cross over from the cathode to the anode and results in the formation of LiOH and Li$_2$CO$_3$ \cite{172, 173}.

So far, extensive investigations have been made to address the challenging issues related to the cathode and electrolyte, but only a handful of researchers have conducted work on the anode component. Among them, gel-polymer electrolytes (GPE) have been proposed as an alternative to suppress the formation of Li dendrites \cite{174, 175}. Meanwhile, researchers found that by coating a protective layer, the stability of Li anode could be greatly enhanced. For example, with an Al$_2$O$_3$/polyvinylidenefluoride-hexafluoropropylene (PVdF-HFP) protective layer on Li anode, the Li-O$_2$ battery presented a charge overpotential of 0.71 V and 91.3% capacity retention, along with 98.4% coulombic efficiency at the 60$^{th}$ cycle (Figure 2.1) \cite{174, 175}. Zhang and co-worker \cite{173} proposed the formation of a composite protective film on Li anode, which could effectively suppress the parasitic reaction on the Li anode/electrolyte interfaces. Visco et al. \cite{176} demonstrated that a protected lithium electrode (PLE) sold by the PolyPlus Battery Company afforded an elegant solution for isolating the lithium core from the reaction with moisture in ambient air. Although there are a wide variety of protective films described above that
Figure 2.16 Charge/discharge profiles at the first, third, fifth, and tenth cycles of (a) CPL-coated Li electrodes (cell B). (b) Cycling stabilities of both cells at a discharge depth of 1000 mA h g\(^{-1}\)\(_{\text{carbon}}\) and a current density of 0.2 mA cm\(^{-2}\) (250 mA g\(^{-1}\)\(_{\text{carbon}}\)) [174, 175].

significantly hinder corrosion by moisture and oxygen cross-over on Li metal to some extent, they introduce some unwanted additional issues, e.g. high interface resistance of the battery causing power loss\(^{[74]}\). Walker et al. \(^{[177]}\) verified that a stable protective solid-electrolyte-interphase (SEI) film can help Li anode resist the crossing over of O\(_2\) from the cathode. Lithium nitritate (LiNO\(_3\)) is such a lithium salt which favors the production of a stable SEI in the presence of the solvent. A Li-O\(_2\) cell containing this
electrolyte composition was shown to cycle for more than 2000 h (> 80 cycles) at a current density of 0.1 mA cm\(^{-2}\). Recently, several researchers proposed to replace the Li metal anode with a lithiated silicon/tin-carbon composite to stabilize the system.\(^{[178-181]}\) The principle relies on the fact that the SEI film deposited on the silicon/tin surface can function as a barrier, effectively suppressing crossover-related side reactions on the anode. The first report was by Hassoun and coworker, who substituted a lithiated silicon-carbon composite for Li metal. The energy density of the Li\(_x\)Si-O\(_2\) battery was estimated as equal to 980 Wh kg\(^{-1}\). Later, Hassoun et al. introduced fluoroethylene carbonate (FEC) to optimize the SEI film, resulting in a small potential gap of only 0.40 V, while impressive discharge-charge capability was delivered based on commercial silicon particles as a substitute for Li metal as anode (Figure 2.17)\(^{[181]}\). In addition, Li\(_x\)Al-C composite electrode was also reported as an alternative anode for Li-air batteries\(^{[182]}\).

Figure 2.17 (a) Voltage profile of the first galvanostatic cycle of the lithiated-silicon/carbon-oxygen cell. (b) Selected discharge-charge profiles of Li ion O\(_2\)
batteries with F-L-Si anodes. (c) SEI film evolution of lithium Si (L-Si) and fluorine L-Si (F-L-Si) anodes in Li ion O₂ batteries during a discharge-charge cycle and their resistance against the O₂ crossover effect on the Si anode. In the case of the L-Si anodes, the SEI film is not strong enough to sustain the large volume changes and will crack during cycling, resulting in poor resistance against O₂ crossover and increased thickness, along with large electrochemical impedance. For the F-L-Si anodes, the unique durable SEI film can remain intact during cycling and efficiently prohibit O₂ crossover, providing long life to the Li ion O₂ batteries with F-L-Si anodes[181].

2.6 Non-aqueous electrolyte

Similar to Li-ion batteries, electrolyte in nonaqueous Li-O₂ batteries plays a critical role in determining the overall electrochemical performance. Unlike in Li-ion batteries, however, the electrolyte for Li-O₂ batteries is exposed to the open system environment and oxygen-rich atmosphere, which is much more aggressive and requires higher stability of the electrolyte. During the oxygen reduction reaction process, the electrolyte will suffer attack and mediate oxidation from nucleophilic oxygen species such as O₂⁻, and O₂⁻⁻[183]. A suitable nonaqueous electrolyte for a Li-O₂ battery must support the formation of highly pure Li₂O₂ at the cathode on discharge and also support its reversible decomposition on charge, with this process being sustained during cycling[184]. To date, however, the challenge of developing a compatible and stable electrolyte is still a great obstacle to the practical introduction of rechargeable aprotic Li-O₂ batteries. Besides the consideration of stability towards its reduced species, a suitable electrolyte in a rechargeable aprotic Li-O₂ battery should meet the following requirements, which are typical for Li-ion batteries[185-187]: (1) high chemical and
electrochemical stability toward lithium metal; (2) high boiling point and low volatility to minimize the evaporation of the solvent due to the open cell system; (3) high oxygen solubility and diffusivity to facilitate the oxygen reduction and oxygen evolution reactions on the air electrode; and (4) low viscosity to improve the rate performance of the oxygen electrode. The organic liquid electrolyte includes organic solvent(s), a lithium salt, and the additives. Addressing the specific criteria for each part and each kind of electrolyte may help solve the problems related to electrolyte.

2.6.1 Organic carbonate solvent

Traditional organic carbonate-based solvents, such as propylene carbonate (PC), dimethyl carbonate (DMC), and ethylene carbonate (EC) were widely used in early-stage nonaqueous Li-O_2 batteries, because they showed some stability in Li-ion batteries. These carbonate based solvents possess evident advantages\(^{[20, 21, 187]}\): wide electrochemical window, low volatility, a wide liquid-temperature range, etc. Such solvents, however, are unstable toward the oxygen radicals generated during discharge, leading to the formation of lithium carbonate and other lithium alkyl carbonates, rather than the ideal discharge product Li_2O_2 \(^{[184]}\). Similarly, Bruce et al. provided further evidence for this unwanted phenomenon and detected alkyl carbonates such as Li_2CO_3, C_3H_6(OCO_2Li)_2, HCO_2Li, and CH_3CO_2Li during the discharge process\(^{[21]}\). Other researchers have also confirmed this conclusion\(^{[187, 188]}\). With the accumulation of such irreversible alkyl carbonate in the cathode during cycling, the capacity fades, and the battery consumes the electrolyte and goes into failure. Organic carbonate-based solvents, therefore, were abandoned in the development of Li-O_2 batteries and were not
applied anymore. As a result, it is very important to investigate other solvents in the search for a suitable electrolyte.

### 2.6.2 Ether based solvent

Ether-based solvents became key examples of aprotic solvents for Li-O$_2$ batteries after organic carbonates were confirmed to be highly susceptible to attack by oxygen radicals. Ethers are attractive for the Li-O$_2$ battery because they are one of the few solvents that combine the following attributes $^5$: capable of operating with a lithium metal anode, stable to oxidation potentials in excess of 4.5 V (vs. Li$^+/\text{Li}$), safe, and low-cost. To date, the most widely studied ether-based solvents are mainly 1,2-dimethoxyethane (DME), triethylene glycol dimethyl ether (G3), tetraethylene glycol dimethyl ether (TEGDME or G4), tetrahydrofuran (THF), and polyethylene glycol dimethyl ether (PEGDME).

In fact, Read first proposed an ether-based solvent for Li-O$_2$ batteries in 2006, much earlier than researchers understood the instability of carbonate-based solvents$^{57}$. Although his attempt showed both good stability and excellent rate capability of the ether solvent, it failed to show any evidence of the formation of Li$_2$O$_2$. Later, numerous groups have identified Li$_2$O$_2$ as the predominant discharge product in Li-O$_2$ cells with ether-based electrolytes through various spectroscopic/analytical techniques$^{189, 190}$.

Among the ether based solvents, dimethoxyethane (DME) was proved to show the highest stability in Li-O$_2$ batteries by McCloskey et al $^{191}$. Afterwards, DME was employed for a long time to evaluate the performance of the catalyst and other factors in Li-O$_2$ batteries due to its stability towards O$_2$ radicals $^{95, 192}$. Unfortunately, with more
intensive research on ether solvents, they were found not to be ideal solvent candidates for nonaqueous Li-O_2 batteries. For example, McCloskey et al. demonstrated that DME-based electrolytes produced principally Li_2O_2 on discharge and O_2 on charge. Nevertheless, XPS and isotope labelling, coupled with differential electrochemical mass spectrometry (DEMS) of conduction on the cathode during discharge, provide strong evidence that ether solvent reacts with Li_2O_2 to form a certain amount of Li_2CO_3[^191]. Similarly, Bruce et al.[^5] showed strong evidence from Raman spectroscopy and XRD that tetraglyme-based electrolyte decomposes with the formation of Li_2O_2 during the first discharge process, giving a mixture of Li_2CO_3, HCO_2Li, CH_3CO_2Li, polyethers/esters, CO_2, and H_2O. After only 5 cycles there is little or no evidence of Li_2O_2 from powder X-ray diffraction (Figure 2.18).

![Figure 2.18](image)

Figure 2.18 (a) Powder X-ray diffraction patterns of the composite cathode (Super P/Kynar) cycled in 1m LiPF_6 in tetraglyme under 1 atm O_2 between 2 and 4.6 V versus Li^+/Li, rate = 70 mA g\(^{-1}\). (b) Load curves for the same cell[^5].

### 2.6.3 Dimethyl sulfoxide (DMSO) solvent
Dimethyl sulfoxide (DMSO) is another prevalent solvent that was the object of particular interest for nonaqueous Li-O\textsubscript{2} batteries. Besides a high donor number (DN), DMSO possesses several attributes that could help it to serve as a suitable solvent, e.g., low volatility and viscosity, good oxygen diffusion capability, and high conductivity\textsuperscript{[187].} Actually, DMSO was first investigated as a possible aprotic solvent for the Li-air battery in 2010 by Laoire et al., who demonstrated increased stability of the oxygen reduction species\textsuperscript{[193].} In 2012, Li-O\textsubscript{2} batteries based on a DMSO/LiClO\textsubscript{4} electrolyte and a porous gold cathode sustained 100 cycles with 95\% capacity retention (Figure 2.19a-b\textsuperscript{[95]}. Even on the 100\textsuperscript{th} cycle, 99\% pure Li\textsubscript{2}O\textsubscript{2} formed, with complete oxidation on charge (Figure 2.19c-d). Afterwards, Bruce et al. observed the formation of O\textsubscript{2} species on the electrode surface via in-situ electrochemical surface enhanced Raman spectroscopy (SERS) at high potentials and short times, providing direct evidence that the mechanism of the ORR in DMSO based electrolyte is in accordance with a solution model\textsuperscript{[194].} Very recently, Peng et al. further confirmed the solution-mediated disproportionation mechanism of Li\textsubscript{2}O\textsubscript{2} formation in DMSO-based electrolyte at low overpotentials ($> 2 \text{V vs. Li}^+$/Li) by spectroscopic identification of the reaction intermediates coupled with density functional theory (DFT) calculations\textsuperscript{[195].}

Despite the stable cycling performances of DMSO-based electrolyte presented by number of researchers on DMSO, some parasitic reactions during the Li-O\textsubscript{2} battery cycling occurred with further investigation of DMSO\textsuperscript{[187, 196].} Several degradation mechanisms of DMSO were proposed. For example, DMSO was found to be oxidized to dimethyl sulfone (DMSO\textsubscript{2}) in the presence of superoxide anions\textsuperscript{[197, 198].} Recently, a theoretical model by Noked predicted that DMSO will suffer attack by superoxide or peroxide, whereas experimental evidence showed that DMSO supported superior
stability toward a Pt@CNT cathode in a potential window of 2.65-4 V, under 4 months of continuous cycling. The same group performed X-ray photoelectron spectroscopy (XPS) studies on the Li anode surface for DMSO-based Li-O₂ Ru-catalyzed batteries, and they provided pioneering evidence that a stable cathode/DMSO electrolyte interface depends on the operation conditions, e.g., appropriate cycling capacity and potential limitations.

Figure 2.19 Charge/discharge curves (a) and cycling profile (b) for a Li-O₂ cell with a 0.1 M LiClO₄-DMSO electrolyte and a nanoporous gold (NPG) cathode, at a current density of 500 mAg⁻¹ (based on the mass of Au). Because the capacities are given per gram of Au, which is ~10-fold heavier (more dense) than carbon, 300 mAh g⁻¹ (based
on the mass of Au) would, for the same porous electrode, but formed from carbon, correspond to ~3000 mAh g\(^{-1}\) (based on the mass of carbon). Vibrational spectra of an NPG cathode at the end of discharge and charge in 0.1 M LiClO\(_4\)-DMSO: (c) FTIR and (d) SERS spectra\(^{[95]}\).

In general, the advantages exhibited by DMSO-based electrolyte outweigh its parasitic reactions if optimum operational conditions are chosen. Nevertheless, further investigations on solvents should be conducted in the long run to achieve the commercialization of Li-O\(_2\) batteries.

### 2.6.4 Other solvents

Besides the above-mentioned prevailing solvents, some other types of solvents such as amide and acetonitrile have been proposed as promising alternative electrolytes in nonaqueous Li-O\(_2\) batteries. Some of them have been highlighted as stable solvents, such as dimethylformamide (DMF), dimethylacetamide (DMA)\(^{[201]}\), and N-methyl-2-pyrrolidone (NMP)\(^{[184]}\). The amide-based solvents possess several advantages: high nucleophilic stability, low C-H acidity, and reasonable autoxidative stability against O\(_2\) and O\(_2\) reduction products in the O\(_2\) electrode.

### 2.6.5 Lithium salt

Besides a stable organic solvent, lithium salt is also an indispensable component of the electrolyte. The decomposition of lithium salt during cycling could initiate side reactions, which will affect the whole performance of a battery. To enhance the
electrochemical features, it is critical to identify stable solvents and Li salts that will promote the formation of Li$_2$O$_2$ and mitigate the decomposition of electrolyte. Generally, an ideal lithium salt for aprotic Li-O$_2$ batteries must meet the following prerequisites$^{186, 202}$: (1) the salt should have high enough solubility in the solvent and reach a certain concentration to support fast ion transport; (2) anions must be stable under the required potentials and especially in the presence of Li$_2$O$_2$ and O$_2$- radicals; and (3) the anion of the salt should be inert to the solvent and other cell components, such as current collectors and separators.

To date, Li salts such as lithium hexafluorophosphate (LiPF$_6$), lithium perchlorate (LiClO$_4$), tetrafluoroborate (LiBF$_4$), lithium triflate (LiCF$_3$SO$_3$), lithium bis(trifluoromethanesulphonyl)imide (LiTFSI), lithium bromide (LiBr), lithium iodide (LiI), and lithium imides, such as (LiN(SO$_2$CF$_3$)$_2$), LiN(SO$_2$C$_2$F$_5$)$_2$, etc., have been widely studied in Li-O$_2$ batteries.

Figure 2.20 (a) Cycling performances of different lithium salts, and (b) major products of different lithium salts$^{203}$. 

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Zhang et al.\textsuperscript{[203]} performed a systematic investigation on the influence of lithium salts on the performance of Li-O\textsubscript{2} batteries and the stability of salt anions in the O\textsubscript{2} atmosphere during discharge/charge processes, and the results are shown in Figure 2.20a. They provide strong evidence that lithium tetrafluoroborate (LiBF\textsubscript{4}) and lithium bis(oxalato)borate (LiBOB) decomposed and formed LiF and lithium oxalate, respectively, as well as lithium borates during discharge of Li-O\textsubscript{2} batteries (Figure 2.20b. The discharge products of Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium trifluoromethanesulfonate (LiTf), lithium hexafluorophosphate (LiPF\textsubscript{6}), lithium perchlorate (LiClO\textsubscript{4}), and lithium bromide (LiBr) mainly consisted of Li\textsubscript{2}O\textsubscript{2} and carbonates, with minor signs of decomposition of LiTFSI, LiTf, and LiPF\textsubscript{6}. LiBr and LiClO\textsubscript{4} showed the best stability during the discharge process, while LiTf and LiTFSI presented the best cycling performance among the studied salts. LiClO\textsubscript{4} appears to be the least reactive Li salt.
CHAPTER 3 EXPERIMENTAL

Figure 3.1 shows an overview of the experimental procedures in this doctoral work. The cathode materials 3D foam-like NiCo$_2$O$_4$, nanofibrous Co$_3$O$_4$/PPy, nanoporous tubular Co$_3$O$_4$, and Ag/nitrogen-doped carbon fibers were prepared through various synthesis methods and then characterized by a series of physical techniques. Finally, these prepared materials were used to prepare cathodes and electrochemical measurements, including RDE tests, were conducted. The structure and morphology of the materials after electrochemical cycling were also investigated.

3.1 Materials and Chemicals

The list of materials and chemicals used in this study are summarized in Table 3.1.

Table 3.1 Description of chemicals and materials used in this doctoral work.
<table>
<thead>
<tr>
<th>Materials/Chemicals</th>
<th>Formula</th>
<th>Purity</th>
<th>Supplier</th>
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<tr>
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<td>(NH$_4$)$_2$S$_2$O$_8$</td>
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<td>Sigma-Aldrich</td>
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<tr>
<td>Ammonia solution</td>
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<tr>
<td>Cobalt acetate</td>
<td>(CH$_3$COO)$_2$Co · 4H$_2$O</td>
<td>98%+</td>
<td>Sigma-Aldrich</td>
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<tr>
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<td>C</td>
<td>Super P</td>
<td>Timcal Belgium</td>
</tr>
<tr>
<td>Cetyltrimethylammonium bromide</td>
<td>C$<em>{19}$H$</em>{42}$BrN</td>
<td>99%+</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
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<td>Reagent</td>
<td>Q-Store Australia</td>
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<tr>
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<td>Sigma-Aldrich</td>
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<td>Iron(III) chloride</td>
<td>FeCl$_3$</td>
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<td>Sigma-Aldrich</td>
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<tr>
<td>Silver Nitrate</td>
<td>AgNO$_3$</td>
<td>99.9%+</td>
<td>Sigma-Aldrich</td>
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<tr>
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</table>
3.2 Materials Preparation

3.2.1 Sol-gel reaction

The sol-gel approach has emerged as a robust method for the preparation of oxide materials in recent years. This method consists of simultaneous hydrolysis and condensation reactions, starting with alkoxide precursors, to form glassy polymer networks, which typically exhibit a micro- or nanoporous character.\textsuperscript{[204]} The sol-gel method can be used under extraordinarily mild conditions, and it is possible to obtain products of various sizes, shapes, and morphologies (e.g. fibers, films, and porous and nanosized particles)\textsuperscript{[205]} In the sol-gel process, the precursors (starting compounds) for synthesis of a colloid consist of a metal or metalloid element surrounded by various ligands. Metal alkoxides are members of the family of metalorganic compounds, which have an organic ligand attached to a metal or metalloid atom\textsuperscript{[206]} Silicon tetraethoxide (TEOS) is one widely investigated example of such a compound. Soluble starch has also been applied as a complexing agent for the preparation of a series of metal oxides. As a natural polysaccharide polymer with abundant hydroxyl groups, starch could facilitate supramolecular associations by inter- and intramolecular hydrogen bonding. Co$^{2+}$ and Ni$^{2+}$ cations, formed by the dissolution of nickel acetate and cobalt acetate in water, can thus favourably bind with the -OH containing groups on starch molecules when they are mixed together.

In Chapter 4, the sol-gel method was used to synthesize the 3D foam-like NiCo$_2$O$_4$ from a precursor solution containing soluble starch, Co(CH$_3$COO)$_2$·4H$_2$O and Ni(CH$_3$COO)$_2$·4H$_2$O. In this process, starch acts as not only as a template, but also as a
passivating reagent. So, the resultant NiCo$_2$O$_4$ features a 3D foam-like framework with continuous walls that consist of closely packed nanoparticles.

### 3.2.2 Polymerization reaction

Polymerization is a chemical reaction that induces monomer molecules to form polymer chains or three-dimensional networks\textsuperscript{\textsuperscript{[207]}}. Various reaction mechanisms for polymerization exist because of the functional groups present in the reacting compounds and their inherent steric effects. In some straightforward polymerization, relatively stable alkenes with $\sigma$ bonding between carbon atoms form polymers by relatively simple radical reactions; on the other hand, more complex reactions such as those that include substitution at the carbonyl group require more complex synthesis due to the way in which reacting molecules polymerize\textsuperscript{\textsuperscript{[208, 209]}}.

In general, at least 100 monomer molecules should be involved in order to form a polymer that can present some remarkable physical properties e.g. high tensile strength, elasticity, or the ability to form fibers. There are a variety of polymerization routes involving different reactions. Typically, there are two kinds of polymers: homopolymers and copolymers. Polymers that consist of repeated long chains or structures of the same monomer unit are referred to “homopolymers” (Equation 3.1), whereas those consist of more than one kind of monomer are referred to as “copolymers” (Equation 3.2)\textsuperscript{\textsuperscript{[210]}}:

\begin{align*}
\text{Homopolymers:} & \quad A + A + A… \rightarrow AAA… \quad \text{(3.1)} \\
\text{Copolymers:} & \quad A + B + A… \rightarrow ABA \quad \text{(3.2)}
\end{align*}
In Chapter 5 and Chapter 6, polypyrrole (PPy) nanofibers were synthesized via the chemical polymerization route. Cetyltrimethylammonium bromide (CTAB) was employed as the surfactant, and ammonium peroxydisulfate (APS) was served as the initiating agent. The polymerization precursor solution was allowed to react for 24 h, and polypyrrole (PPy) nanofibers were obtained. In Chapter 7, methyl orange (MO) was used as the surfactant and silver nitrate. An Ag/PPy composite was finally obtained through the simultaneous reaction of pyrrole and Ag⁺ ions in an aqueous.

### 3.2.3 Hydrothermal Method

The hydrothermal method is a widely used wet-chemical process to gradually crystallize substances from high-temperature aqueous solutions at high vapour pressures. Efficient crystal growth and nanomaterials can be achieved by using such technology. It can be of benefit for the preparation of novel phases, stabilization of new complexes, and synthesis of various material morphologies for specific applications. The composition, morphology, and crystal structure of the final products are generally affected by the solvent, the concentration of the precursor solution, the temperature, the pH value, and the use of surfactant.

Figure 3.2 shows the device used in this doctoral work (4748 Acid Digestion Bombs with 125 ml capacity from the Parr Instrument Company). It contains a polytetrafluoroethylene (PTFE) vessel on the inside along with a stainless steel protector on the outside. Usually, 2/3 of the volume of the PTFE vessel is the precursor volume limit to ensure safety. The maximum working temperature is 250 °C.
In Chapter 5 and Chapter 6, the hydrothermal reaction was used to fabricate the nanofibrous Co$_3$O$_4$/PPy. Small Co$_3$O$_4$ nanoparticles with a size distribution of 5-6 nm are tightly and homogeneously anchored on the surfaces of the PPy nanofibers.

Figure 3.2 Hydrothermal autoclave (Acid Digestion Bombs 4748) from Parr Instruments (left) with a cross-sectional view (right).

### 3.3 Structural and physical characterization

#### 3.3.1 X-ray diffraction

X-ray diffraction (XRD) is a basic and robust technique to identify an unknown crystallographic structure, the crystallite size (grain size), and the preferred orientation in polycrystalline or powdered solid samples. Figure 3.3 illustrates the principle of XRD.

When X-rays strike crystals, they will be scattered by each set of lattice planes at a unique angle, which is called elastic scattering. Since every crystal features a set of
unique \(d\)-spacings, the pattern has a functional relationship with the crystal structure, which is described by Bragg’s law (Equation 3.3):

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

(3.3)

Where \(n\) is an integer, \(\lambda\) is the wavelength of the incident X-ray beam, \(d\) is the lattice spacing of the given crystal, and \(\theta\) is the incidence angle.

Figure 3.3 Bragg’s law can be derived from the geometrical relation between the interplanar spacing \(d\) and the diffraction angle \(\theta\).\(^{[211]}\)

In this doctoral work, all the XRD measurements were performed using a GBC MMA X-ray generator and diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 1.5406 \text{ Å}\)). The powdered sample is mixed with ethanol to form a slurry which is then pasted onto a disk holder with a flattened surface. After drying, the holder is placed on the axis of the diffractometer at an angle \(\theta\). Graphical processing and data manipulation were based on Visual XRD and Traces software. The working voltage and current were 40 kV and 25 mA, respectively.
3.3.2 Raman Spectroscopy

Raman spectroscopy is a powerful characterization method to investigate the structure of a material. It can provide the vibrational, rotational, and other low frequency modes of a structure. In Raman spectroscopy, laser light from a monochromatic light source is employed to irradiate the sample, leading to both elastic scattering (Rayleigh scattering) and inelastic scattering (Stokes and anti-Stokes Raman scattering). Energy shifts from the incident radiation occur in Stokes and anti-Stokes Raman scattering, which are called the Raman effects. These energy shifts reflect the frequency or wavelength of a specific chemical composition and structure. By comparing the obtained spectra, materials with specific molecular features can be identified. Raman spectroscopy therefore is employed as a complementary measurement technique to XRD. In this doctoral work, the Raman spectroscopy was performed using a JOBIN YVON HR 800 Horiba Raman spectrometer with the laser wavelength at 632.8 nm. A neutral density filter was applied to adjust the laser intensity in the measurement.

3.3.3 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a commonly used means of analysis of absorption spectroscopy. The absorption, emission, photoconductivity, or Raman scattering in the infrared spectrum of a material can be collected. In the testing process, IR radiation interacts with the material through which the infrared radiation is transmitted or absorbed. After that, the chemical bonds in the molecules of the sample material can be detected from the spectral pattern of molecular absorption and transmission. In this doctoral work, FTIR spectra were collected on a Shimadzu
IRPresting-21 model Fourier transform infrared spectrometer. For measurement, the sample materials were mixed with potassium bromide (KBr) powder, which acts as the background, and pressed in a die with a barrel.

### 3.3.4 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic method to analyse the surface chemistry of a material. It can provide information on the elemental composition, empirical formula, chemical state, and electronic state of the elements within a material. When a beam of X-rays is employed to interact with the sample material, the kinetic energy and number of electrons that escape from the top surface of the material (0-10 nm) are simultaneously monitored, from which the XPS spectra are obtained. Then, the valence states and the ratios of the valence states of elements could be determined, based on the characteristic binding energies associated with electrons in their orbitals. In this doctoral work, XPS analysis was conducted on a VG Scientific ESCALAB 2201XL system using Al Kα X-ray radiation and fixed analyzer transmission mode. A commercial XPS 2.3.15 software package was used to analyse the XPS data. All the spectra were calibrated by C 1s = 284.6 eV.

### 3.3.5 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a widely utilized weight analysis technique. It shows the weight changes with the increasing temperature, revealing information on the physical and chemical properties of materials. This analysis could show some of the
material characteristics reflected by the precise weight changes caused by
decomposition, oxidation, or loss of volatiles (such as moisture) with increasing
temperature. In this doctoral work, a SETARAM Thermogravimetric Analyzer was
employed. TGA was used to determine the polypyrrole and carbon contents in the
composite materials. The temperature was heated to 800 or 900°C with a heating rate of
10 °C min⁻¹ in air atmosphere.

3.3.6 Brunauer-Emmett-Teller (BET) Analysis

Brunauer-Emmett-Teller analysis is an effective technique for evaluating the specific
surface area and pore size distribution of a sample material. It is based on the theory of
physical adsorption of gas molecules on a solid surface, and the pore size distribution
curve of the sample material can be determined from the N₂ isotherms. In this doctoral
study, all the samples were degassed before analysis to remove trace H₂O from them, in
order to gain more accurate results. The BET measurements were conducted at 77 K on
a Quantachrome Autosorb-IQ MP instrument.

3.3.7 Scanning Electron Microscopy equipped with Energy Dispersive
Spectroscopy

The scanning electron microscope (SEM) is a type of microscope that scans the material
with a high-energy beam of electrons to produce an image. It is the most commonly
used technique to characterize the morphology of a material. During the observation
process, the electrons interact with atoms in the material. Various signals, e.g.
secondary electrons (SE), back-scattered electrons (BSE), characteristic X-rays,
specimen currents under illumination, and transmitted electrons are generated. The detector then collects these signals to provide information on the morphology, composition, and other properties of the sample surface. SEM can provide images with resolution up to 1 nm when the detectors for secondary electrons are installed in the SEM system.

Some other detectors with specific analytical abilities, e.g. energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), are usually included on SEM systems. EDS can identify the different elements, because each element features a characteristic atomic structure. The analytical capabilities of EDS depend on the interaction between some source of X-rays, X-ray excitation, and the material. In this doctoral work, a field-emission scanning electron microscope (FE-SEM, JEOL JSM-7500FA, 15 kV) was used to characterise the morphologies of materials. Before SEM observation, the powdered material was directly applied on carbon conductive tape, which was mounted on an aluminium holder.

3.3.8 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a microscopy technique with significantly higher resolution than SEM that is used to observe the morphology, lattice spacing, crystal orientation, and electronic structure of sample materials. Unlike SEM, the beam of electrons in TEM is transmitted through an ultra-thin specimen and interacts with the specimen. After the electron transmission and interaction with the specimen, the image is magnified and focused on the imaging device. Selected area electron diffraction (SAED) is a crystallographic experimental technique that is usually coupled with the
TEM equipment. It has the ability to identify crystal structures and examine crystal defects.

In this doctoral work, the TEM observations were carried out on a JEOL 2011 TEM (200 keV) and a JEOL ARM-200F TEM (200 keV). Before observation, the sample was ultrasonically dispersed in ethanol. A holey carbon support film on a copper grid was used to load the dispersion. The grid was then loaded onto a sample holder, which was attached to the specimen stage.

3.4 Electrode Preparation and Coin-Cell Assembly

3.4.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the most commonly used electrochemical techniques and is based on a linear potential waveform, that is, the potential is changed as a linear function of time. The rate of change of potential with time is referred to as the scan rate. Through probing the thermodynamics and kinetics of the electron transfer during the electrochemical reaction, it can detect the electrochemical activity, determine the redox potential, determine the stability of the resultant products, and investigate the reversibility of a redox reaction.

In this doctoral work, the CV measurements were conducted on Princeton 2273 and 636 instruments (Princeton Applied Research).

3.4.2 Linear Sweep Voltammetry
Linear sweep voltammetry (LSV) is the simplest technique that uses the linear potential waveform, which was mentioned in connection with CV (2.4.1). Unlike CV, which involves reversible potential scans, the potential range in LSV is scanned starting from the initial potential and ending at the final potential. In this doctoral work, the LSV method was employed to test the steady state polarization curves of the fabricated electrocatalysts towards determining ORR and OER activities in 0.1 M KOH electrolyte with a scan rate of 10 mV s$^{-1}$.

3.4.3 Galvanostatic Charge and Discharge Measurement

The capacity, rate performance, and cycling stability of the Li-O$_2$ batteries were studied by galvanostatic discharge/charge tests. The charge or discharge capacity is equivalent to the total electron charge ($Q$) in the discharge or charge process. It was calculated from the applied current ($I$) and the time ($t$) consumed to fully charge or discharge the battery ($Q = I \times t$). In this doctoral work, all the tests were carried out on battery testers (Land CT 2001) in oxygen atmosphere at room temperature.

3.4.4 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a common important method to investigate electrochemical processes. The charge transfer, ion diffusion, mass transport, and chemical reactions can be studied from it. In a typical EIS impedance spectrum, a high frequency semicircle and a low frequency linear tail are included. The former corresponds to the kinetic processes, while the latter relates to the diffusion of ions (Li$^+$, Na$^+$) into the electrode material). In this doctoral work, EIS data were
collected on a Princeton 2273 workstation (Princeton Applied Research). The frequency range was from 100.00 kHz to 0.01 Hz.

3.4.5 Rotating Disk Electrode Measurement

The rotating disk electrode (RDE) technique is used in electrochemical studies when investigating reaction mechanisms related to the redox chemistry, among other chemical phenomena. A three electrode system is used for this hydrodynamic voltammetry. The working electrode contains a conductive disk, generally made of a noble metal or glassy carbon (GC), embedded in an inert non-conductive polymer or resin and is prepared by mounting the samples onto the pre-polished GC electrode. The working electrode is attached to an electric motor that can precisely control the electrode's rotation rate. Once a rotation speed with certain angular velocity is applied on the working electrode, the electrolyte solution is dragged along by the rotating electrode and flows away from the centre of the electrode. The solution jumps upwards from the bulk, perpendicular to the electrode, and replaces the boundary layer. The overall result is laminar flow of the solution towards and across the rotating electrode. The flow rate of the solution can be adjusted by applying an angular velocity on the electrode and modelled mathematically. The steady-state current is determined by the solution flow, not the diffusion. The RDE technique can provide abundant information on the characteristics and mechanisms of the reactions, mainly including multi-electron transfer, the kinetics of slow electron transfer, and adsorption/desorption steps.

In this doctoral work, Princeton 2273 and 636 instruments (Princeton Applied Research) were used to collect the ORR and OER characteristics of the as-prepared
materials. All measurements were carried out on a standard three electrode system at room temperature. A KCl saturated Ag/AgCl electrode acts as the reference electrode and a platinum wire acts as counter electrode.

3.4.6 Electrode preparation and coin cell assembly technique

For the preparation of the cathode, different proportions of catalyst, conductive regent, and poly(1,1,2,2-tetrafluoroethylene) (PTFE) (60% dispersion) were mixed in an isopropanol solution to form a homogeneous slurry. The resultant slurry was then coated onto carbon paper and dried at 120 °C in a vacuum oven for 12 h. The typical loading of slurry on each electrode is 0.5–1 mg/cm².

The Li-O₂ batteries were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) with both O₂ and H₂O levels less than 1 ppm. CR2032 coin type cells with holes in the cathode parts were used. A glassy fiber separator (Whatman GF/D) was applied to separate the cathode from the Li foil as the counter electrode. 1 M Li trifluoromethanesulfonylate (LiCF₃SO₃) in tetraethylene glycol dimethyl ether (TEGDME) was utilized as the electrolyte. All the assembled coin cells were stored in an O₂-purged chamber which was connected to a LAND CT 2001A multi-channel battery tester for 2 h before each test. Standard components of a CR2032 coin-cell Li-O₂ battery are shown in Figure 3.4 in their stacking sequence.
Figure 3.4 Stacking components of a CR2032 coin cell\textsuperscript{[154]}. 
CHAPTER 4 SELF-ASSEMBLED 3D FOAM-LIKE NiCo$_2$O$_4$ AS Efficient Catalyst for Lithium Oxygen Batteries

4.1 Preface

Intensive research efforts worldwide are being devoted to the realization of a new generation of lithium oxygen batteries, as a result of their high theoretical specific energy, which is almost ten times that of Li-ion batteries$^{[212-214]}$. Such batteries are the technology of choice for the electrification of transport and are expected to find application in static electricity storage, especially in grid distribution networks$^{[148, 215]}$. Although the reaction mechanism of lithium oxygen batteries is simple and straightforward, the practical use of lithium oxygen batteries has been restricted by numerous scientific challenges, including high discharge-charge over-potential, low energy efficiency, poor rate capability, and especially short cycle life. Sluggish kinetics of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) are major factors contributing to the unsatisfying performances$^{[147]}$. It has been studied that the performance of Li-O$_2$ batteries largely depends on the cathode material$^{[216, 217]}$.

Various catalysts have been studied for Li-O$_2$ batteries to overcome these challenges$^{[4,6,9-29]}$. Among them, NiCo$_2$O$_4$, a typical ternary spinel nickel cobalt oxide with the advantages of low cost, natural abundance, higher electronic conductivity than those of Co$_3$O$_4$ and NiO, and especially good bi-functional catalytic activity towards the ORR and OER, has aroused much interest for use as an electrocatalyst for Li-O$_2$ batteries$^{[118,121-125]}$. A NiCo$_2$O$_4$ nanowire array grown on carbon cloth was reported as cathode for Li-O$_2$. 
batteries, but only a capacity of approximately 1000 mAh g\(^{-1}\) was delivered, which was because the active sites only exist on the tips of the NiCo\(_2\)O\(_4\) nanowires\(^{[218]}\). To achieve a higher capacity, Wang et al. synthesized mesoporous NiCo\(_2\)O\(_4\) nanosheets via a hydrothermal method, and higher reversible capacity was demonstrated, as well as good cycling stability\(^{[219]}\). Although enhanced electrocatalytical performances of NiCo\(_2\)O\(_4\) have been reported, they are far from satisfactory, either due to low capacity or to high discharge-charge overpotential\(^{[126]}\), which may be largely due to their unfavourable cathode structure.

Generally speaking, an ideal oxygen electrode requires a highly conductive and porous structure to facilitate both electron and oxygen transportation\(^{[81, 220]}\). Typically, in a lithium oxygen battery, the formation of Li\(_2\)O\(_2\) only occurs on the triple junctions where electrolyte, catalytic active sites, and oxygen coexist \([40]\). The three-dimensional (3D) skeleton structure has drawn much attention for the design of the oxygen electrode, according to previous reports, due to the following advantages\(^{[63, 221-223]}\): a) it can provide suitable tunnels to supply continuous pathways for oxygen and meanwhile provide sufficient space for Li\(_2\)O\(_2\) formation according to the triple-junction oxygen reduction process, b) it can increase the electrical conductivity of the electrode and facilitate the charge transfer and electrochemical kinetics, c) it can enlarge the contact area between the electrolyte and the electrode to deliver high capacity and rate capability. Inspired by the 3D architecture, nickel foam has been widely employed by researchers as a porous catalyst support for Li-O\(_2\) batteries\(^{[46, 47]}\). Porous carbon derived from a graphene oxide gel in nickel foam was directly used as an O\(_2\) cathode, which facilitated a continuous O\(_2\) flow\(^{[224]}\). Liu et al.\(^{[225]}\) reported Co\(_3\)O\(_4\) grown on nickel foam with a 3D network structure.
as a cathode material for Li-O$_2$ batteries, and a voltage gap of no more than 0.5 V was achieved, which can be ascribed to the Ni foam skeleton, which provided continuous pathways for O$_2$. Although deposition of catalyst on nickel foam can form an interconnected porous structure, contact resistance still exists between the catalyst and the nickel foam, which inevitably causes overpotential during charge and discharge processes$^{[223]}$. Moreover, the pores and tunnels of the commercial nickel foam are large (usually 200 µm in diameter), which correspondingly decreases the surface area of the catalyst loaded on it. Meanwhile, these too large pores are usually flooded by the electrolyte, forming two-phase instead of three-phase regions$^{[225, 226]}$. Therefore, the development of a well-designed 3D foam-like cathode architecture by integrating small porous channels in it will be a good choice for enhanced Li-O$_2$ batteries$^{[227, 228]}$.

In this work, we used environmentally friendly starch as a template, and a self-assembled 3D foam-like NiCo$_2$O$_4$ framework with mesopores inside was obtained. It is expected that during discharge, the large macro-tunnels can function as “highways” to supply oxygen to the interior parts of the cathode, while the mesopores on nanowalls are the “exits” to provide the triple junctions (solid-liquid-gas) required for the oxygen reduction reaction and act as centres for Li$_2$O$_2$ crystallization.$^{[30]}$ Rotating disk electrode (RDE) measurements both in aqueous and non-aqueous electrolytes were employed to explore the electrocatalytical properties of the as prepared 3D foam-like NiCo$_2$O$_4$. Remarkably, the as-prepared hierarchically self-assembled 3D-structured NiCo$_2$O$_4$ manifested improved catalytic performance, with a high round-trip efficiency of 70% and a stable lifespan of 80 cycles for lithium oxygen batteries.
4.2 Experimental

*Synthesis of 3D foam-like NiCo$_2$O$_4$:* One gram of soluble starch was dissolved in 10.0 mL distilled water with stirring. Then, it was mixed with a 10 mL aqueous solution of nickel acetate (0.1 M) and cobalt acetate (0.2 M) to form a uniform suspension. The mixture was then placed in an oil bath preheated to 90 °C and maintained for 20 min under vigorous stirring until a pink gel was obtained. The gelatinized paste was kept at 90 °C for an additional 10 min without stirring to age. After cooling to room temperature, it was then freeze-dried for 24 h to obtain the light pink nickel acetate/cobalt acetate/starch precursor. Then, the precursor was calcined at a temperature of 380 °C with a heating rate of 5 °C min$^{-1}$ to obtain the hierarchically 3D foam-like NiCo$_2$O$_4$.

![Figure 4.1 Schematic illustration of the preparation of the 3D foam-like NiCo$_2$O$_4$. a) Starch/ Co$^{2+}$/Ni$^{2+}$ aqueous suspension, b) starch/ Co$^{2+}$/Ni$^{2+}$ gel, c) starch/Co$^{2+}$/Ni$^{2+}$ dry gel, d) NiCo$_2$O$_4$ calcined at 380 °C in air and e) high resolution SEM (HRSEM) image of the obtained NiCo$_2$O$_4$.](image)

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Characterization: X-ray diffraction (XRD) (GBC MMA) patterns were collected over a 2θ range of 10° - 80° with a scan rate of 4° min⁻¹ and analysed with Traces™ software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. X-ray photoelectron spectroscopy (XPS) was conducted on a VG Scientific ESCALAB 2201XL instrument using Al Kα X-ray radiation and fixed analyser transmission mode. The XPS data were analysed using CasaXPS software, and all the results were calibrated by C 1s at 284.6 eV for graphite. The morphologies of the samples were examined by field emission scanning electron microscopy (FE-SEM, JEOL 7500) and transmission electron microscopy (TEM, JEOL ARM-200F). High-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) images and corresponding element mapping images were collected with the same TEM equipped with a Centurio SSD energy-dispersive X-ray spectroscopy (EDS) detector. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were determined on a Micromeritics ASAP 2010 adsorption analyser at 196 °C (77 K).

Electrochemical performance: The electrochemical performances of lithium oxygen batteries were investigated using 2032 coin-type cells with air holes on the cathode side. For the preparation of the 3D foam-like NiCo₂O₄ cathode electrode, 50 wt % catalyst, 40 wt % Super P, and 10 wt % poly(1,1,2,2-tetrafluoroethylene) (PTFE) were mixed in an isopropanol solution. The resulting homogeneous slurry was coated onto a gas diffusion layer (GDL). The same procedure was applied to prepare pure Super P electrodes, which consisted of 90 wt. % Super P and 10 wt % poly(1,1,2,2-tetrafluoroethylene) (PTFE). After that, the electrodes were dried at 120 °C in a vacuum oven for 12 h. All the Li-O₂ batteries were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) with
water and oxygen contents below 0.1 ppm. They consisted of lithium metal foil as the counter electrode, a glass fiber separator (Whatman GF/D), non-carbonate electrolyte containing 1 M LiCF$_3$SO$_3$ in tetraethylene glycol dimethyl ether (TEGDME), and the air cathode electrode. All the assembled coin cells were stored in an O$_2$-purged chamber which was connected to a LAND CT 2001 A multi-channel battery tester for 2 h before each test. The galvanostatic discharge-charge tests were then conducted on the battery testing system with the voltage between 2.35-4.35 V (vs. Li$^+$/Li), and the capacity was calculated based on the mass of the carbon in the cathode. Cyclic voltammetry (CV) was conducted in O$_2$ saturated 1 M lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) in tetraethylene glycol dimethyl ether (TEGDME). The current densities and specific capacities were calculated based on the amount of carbon in the cathodes.

*Rotating disk electrode tests:* RDE tests were performed using a computer-controlled potentiostat (Princeton 2273 and 616, Princeton Applied Research) in a conventional three-electrode cell at room temperature. The glassy carbon (GC) working electrode (5 mm in diameter) was first polished with 1.0 and 0.05 μm alumina powder, rinsed with deionized water, and sonicated first in ethanol and then in double-distilled water. A platinum wire and Ag/AgCl (saturated KCl filled) were used as the counter and reference electrodes, respectively. Typically, the NiCo$_2$O$_4$ was redispersed in deionized water + isopropanol + 5% Nafion® (v/v/v = 4/1/0.05) to form a homogeneous catalyst ink with a concentration of 2 mg mL$^{-1}$. Then, 30 μL of this dispersion was pipetted onto the surface of the GC working electrode and dried under ambient conditions. For comparison, the control samples were Super P and commercial Pt/C (10 wt.% Pt on Vulcan XC-72), and were also obtained by the same method described above. Cyclic voltammograms (CVs)
were collected in O$_2$ saturated 0.1 M KOH solution from -0.9 V – 0.1 V at a scan rate of 10 mV s$^{-1}$. Linear sweep voltammograms (LSVs) to measure the ORR performance were collected in O$_2$ saturated 0.1 M KOH solution with different rotation speeds from 100 to 2500 rpm from -0.9 -0.1 V with a scan rate of 10 mV s$^{-1}$, while OER plots were obtained in Ar atmosphere from 0.1 -0.9 V with a scan rate of 10 mV s$^{-1}$ and a rotation speed of 1600 rpm. Koutecky-Levich (K-L) plots show the inverse current density ($j^{-1}$) as a function of the inverse of the square root of the rotation speed ($\omega^{-1/2}$) at different potential values. The number of electrons involved per O$_2$ in the ORR was determined by the Koutecky-Levich equation$^{[229]}$:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k}$$  \hspace{1cm} (4.1)

Where $j$, $j_k$, $j_d$ are the measured, the kinetically controlled and the diffusion controlled current densities, respectively, and $\omega$ is the electrode rotation rate. $B$ is determined from the slope of the K-L plot based on the Levich equation:

$$B = 0.2nF(D_{O2})^{2/3}v^{-1/6}C_{O2}$$  \hspace{1cm} (4.2)

Where $n$ represents the number of electrons gained per O$_2$, $F$ is the Faraday constant ($F = 96485$ C mol$^{-1}$), $D_{O2}$ is the diffusion coefficient of O$_2$ in 0.1 M KOH ($1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$), $v$ is the kinetic viscosity (0.01 cm$^2$ s$^{-1}$), and $C_{O2}$ is the bulk concentration of O$_2$ ($1.2 \times 10^{-6}$ mol cm$^{-3}$).

### 4.3 Results and Discussion

#### 4.3.1 Structure and morphology

Soluble starch was used as the template for the fabrication of 3D foam-like NiCo$_2$O$_4$, and the process is schematically shown in Figure 4.2. It was reported that starch is a natural polysaccharide polymer with abundant hydroxyl groups, which can facilitate
supramolecular associations by inter- and intramolecular hydrogen bonding\textsuperscript{33, 34}. Co\textsuperscript{2+} and Ni\textsuperscript{2+} cations, formed by the dissolution of nickel acetate and cobalt acetate in water, can thus favourably bind with the -OH containing groups on starch molecules when they are mixed together\textsuperscript{[230]}. Upon heating to 90 ºC, the aqueous dispersion of starch in a complex with Co\textsuperscript{2+} and Ni\textsuperscript{2+} became gel-like as a result of swelling and disruption of the starch granules. The resulting sponge-like pink gel consisted of a hydrated 3D porous network of predominantly amylose molecules. The as-prepared gel was directly dehydrated via a freeze-drying process to maintain the 3D architecture and then heated at 380 ºC for 5 h in air atmosphere. The final product from this process shows a black loose appearance with the same shape as the former gel. According to a previous report\textsuperscript{[231]}, the starch template can be completely removed at 380 ºC in air.

In the process, the starch template plays two main roles in the formation of the 3D foam-like porous structure: Firstly, it prevents small NiCo\textsubscript{2}O\textsubscript{4} units from growing into large particles before the decomposition of starch; secondly, the release of CO\textsubscript{2} produced by the decomposition of the starch results in a large number of mesopores in the NiCo\textsubscript{2}O\textsubscript{4} nanoparticles. Starch acts as not only as a template, but also as a passivated reagent. So, the resultant NiCo\textsubscript{2}O\textsubscript{4} possesses a 3D foam-like framework with continuous walls that consist of closely packed nanoparticles.

The structure of the as-prepared 3D foam-like NiCo\textsubscript{2}O\textsubscript{4} was confirmed by X-ray diffraction (XRD), as shown in Figure 4.2. Remarkably, the peaks (2θ values) at 31.1, 36.5, 44.6, 59.1, and 64.9 º correspond to the diffractions from the (220), (311), (400), (511), and (440) planes of spinel phase NiCo\textsubscript{2}O\textsubscript{4} (JCPDS card no.73-1702)\textsuperscript{[232]}. 

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Figure 4.2 XRD pattern of the as-prepared 3D foam-like NiCo$_2$O$_4$.

Figure 4.3 (a,b) HRSEM images, (c) TEM image, with the dashed lines indicating the nanowalls, and (d) HRTEM image of the as-prepared 3D foam-like NiCo$_2$O$_4$.

SEM images of the calcined NiCo$_2$O$_4$ reveal a 3D foam-like framework with continuous pores and walls that consist of closely packed nanoparticles (Figure 4.3 a and 3b). X-ray spectroscopy (EDS) pattern conducted from the 3D foam-like NiCo$_2$O$_4$ is shown in
Table 4.1 and Figure 4.4. Besides the Al and C peaks coming from the SEM holder and conductive adhesive tape, respectively, only the elements Ni, Co and O are detected in the EDS spectrum. The composition analysis reveals that the stoichiometry elemental ratio of Ni: Co: O in the sample is nearly 1: 2: 4, which proves that the whole 3D foam-like NiCo$_2$O$_4$ structure consists of NiCo$_2$O$_4$. The TEM image (Figure 3c) also proves that the sample has obvious nano-/mesoporous structure with interconnected nanoparticles. Nanowalls could also be observed in Figure 3c which are well consistent with the SEM images. It is noteworthy that besides the macro-sized foam-like structure, mesopores with a size of less than 8 nm can also be observed between the nanoparticles, and such mesopores have been reported to offer more diffusion pathways for oxygen and permit the electrolyte to easily penetrate, forming more of the triple-phase (solid-liquid-gas phases) regions required for efficient ORR and OER reactions$^{55,57}$. The high-resolution TEM (HRTEM) image (Figure 3d) indicates that the particles possess a typical crystalline texture, with space between lattice planes of 0.242 nm, which corresponds to the $d$ value of the (311) planes of spinel phase NiCo$_2$O$_4$.

Table 4.1 Elemental composition of the as-prepared 3D foam-like NiCo$_2$O$_4$.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>28.78314</td>
<td>56.04151</td>
</tr>
<tr>
<td>Cobalt</td>
<td>45.68487</td>
<td>26.35494</td>
</tr>
<tr>
<td>Nickel</td>
<td>23.73095</td>
<td>13.20083</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.6404</td>
<td>4.21581</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.16064</td>
<td>0.18691</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 4.4 SEM-EDS of the as-prepared 3D foam-like NiCo$_2$O$_4$. (inset is the corresponding SEM image)

Figure 4.5 (a) N$_2$ adsorption-desorption isotherms and (b) pore size distribution of the as-prepared 3D foam-like NiCo$_2$O$_4$.

The N$_2$ adsorption-desorption isotherms collected at 77 K and the pore-size distribution are shown in Figure 4.5 in the Supporting Information. The nitrogen sorption curves of the as-prepared NiCo$_2$O$_4$ exhibit the combined characteristics of type II/IV according to the IUPAC classification$^{[59, 116]}$, with a specific surface area of 46.4 m$^2$ g$^{-1}$ and a total
pore volume of 0.26 cm$^3$ g$^{-1}$. The H1 hysteresis loop in the P/P$_0$ range of 0.6-1.0 is indicative of mesoporosity$^{[116]}$. The pore-size distribution of the as-prepared NiCo$_2$O$_4$ calculated by the Barrett-Joyner-Halenda (BJH) method (Figure 4.5b) shows a large distribution of mesopores at sizes less than 10 nm and at 50 nm, respectively. These mesopores refer to the interspace voids between the aggregated nanoparticles, which can also be observed from the TEM results (Figure 4.3b and c). This unique porous structure combined with the 3D foam-like tunnels could be an ideal design for an O$_2$ electrode$^{[59]}$: during the discharge, the large tunnels can function as “highways” to supply oxygen to the interior parts of the cathode, while the mesopores on nanowalls are the “exits” that provide the triple junctions (solid-liquid-gas) required for the ORR reaction.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the as-prepared NiCo$_2$O$_4$, and the corresponding results are presented in Figure 4.6. The XPS spectra indicate the presence of Ni, Co, and O, as well as C from the graphite reference, and no other element peaks are detected (Figure 4.6a). By using a component fitting method, the Ni 2p emission spectrum (Figure 4.6b) is reasonably deconvoluted into four peaks, with two spin-orbit doublets characteristic of Ni$^{2+}$ and Ni$^{3+}$, and one shake-up satellite (indicated as “Sat.”). The binding energy peak at 855.6 eV and its satellite peak at 872.5 eV correspond to Ni$^{2+}$ while the binding energy peak at 861.4 eV and its satellite peak at 879.1 eV correspond to the Ni$^{3+}$. Similar to Ni 2p, the Co 2p (Figure 4.6c) was also fitted with two spin-orbit doublets and one shake-up satellite. Specifically, the fitting peaks at binding energies of 778.4 and 794.0 eV are attributed to Co$^{3+}$, whereas other fitting peaks sitting at 780.0 and 795.1 eV are ascribed to Co$^{2+}$.$^{[121,123]}$. The high resolution spectrum of the O 1s region (Figure 4.6d) shows three oxygen
contributions, which can be denoted as O1, O2, and O3, respectively. Usually, the O1 peak at 529.1 eV is typical of metal-oxygen bonds\textsuperscript{[121, 233]}, while the O2 peak located at 530.7 eV is assigned to the OH groups. The presence of this component in the O 1s spectrum indicates that the surface of the NiCo\textsubscript{2}O\textsubscript{4} is hydroxylated to some extent due to either surface oxyhydroxide or the substitution for oxygen atoms at the surface by hydroxyl groups\textsuperscript{[121, 234]}. The O3 contribution at 532.7 eV is usually associated with defects, contaminants, and a number of surface species, including chemisorbed oxygen, under-coordinated lattice oxygen, or species intrinsic to the surface of the spinel\textsuperscript{[30, 60, 61]}. These above data show that the surface of the as-prepared 3D foam-like NiCo\textsubscript{2}O\textsubscript{4} has a composition including Co\textsuperscript{2+}, Co\textsuperscript{3+}, Ni\textsuperscript{2+}, and Ni\textsuperscript{3+}, which may provide good electrocatalytic activity toward ORR/OER reactions.

![XPS spectra](image)

**Figure 4.6** (a) XPS survey spectrum of the as-prepared 3D foam-like NiCo\textsubscript{2}O\textsubscript{4}. High resolution XPS spectra of (b) Ni 2p, (c) Co 2p, and (d) O 1s.
4.3.2 Electrochemical characterizations

Figure 4.7 Linear sweep voltammetry (LSV) curves: (a) the as-prepared 3D foam-like NiCo$_2$O$_4$ in O$_2$-saturated 0.1 M KOH at a scan rate of 10 mV s$^{-1}$ in the potential range of -0.9-0.1 V (vs. AgCl/Ag), with the inset showing the corresponding Koutecky-Levich plots (J-1 vs. $\omega^{-0.5}$). (b) The as-prepared 3D foam-like NiCo$_2$O$_4$ and super P at a rotation speed of 1600 rpm. (c) Oxygen evolution curves for the 3D foam-like NiCo$_2$O$_4$ and Super P electrodes in the potential range of 0.2-0.9 V (vs. AgCl/Ag). (d) The as-prepared 3D foam-like NiCo$_2$O$_4$ and Super P at a rotation speed of 1600 rpm in O$_2$-saturated 0.5 M LiCF$_3$SO$_3$/TEGDME at a scan rate of 10 mV s$^{-1}$ in the potential range of 2.0-3.3 V (vs. Li$^+$/Li).
Figure 4.8 Linear sweep voltammetry (LSV) curves at various rotation speeds in \( \text{O}_2 \)-saturated 0.1 M KOH at a scan rate of 10 mV s\(^{-1}\) in the potential range of -0.9-0.1 V (vs. AgCl/Ag) for (a) 10% Pt/C and (c) Super P; K-L plots of (b) 10% Pt/C and (d) Super P.

The new 3D foam-like NiCo\(_2\)O\(_4\) was subjected to linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) in \( \text{O}_2 \)-saturated 0.1 M KOH at a scan rate of 10 mV s\(^{-1}\) in the potential range of -0.9-0.1 V (vs. AgCl/Ag). Super P and standard commercial Pt/C (10 wt% Pt on Vulcan XC-72 carbon) were tested as control samples. Compared with standard commercial Pt/C (Figure 4.8a) and Super P (Figure 4.8c), our as-prepared 3D foam-like NiCo\(_2\)O\(_4\) gives more defined diffusion-controlled LSV waves (Figure 4.7a). With increasing rotation speed, the limiting current density
also increases. Furthermore, the limiting current density of the ORR on the 3D foam-like NiCo$_2$O$_4$
n
electrode is always higher than that of the Super P electrode and much more stable than that of standard commercial Pt/C at each rotation rate, suggesting better ORR activity on the 3D foam-like NiCo$_2$O$_4$ electrode$^{[235]}$. The linearity of the Koutecky-Levich plots and the near parallelism of the fitting lines for the 3D foam-like NiCo$_2$O$_4$ electrode (inset of Figure 4.7a) suggest first order reaction kinetics toward the concentration of dissolved oxygen and similar electron transfer numbers for the ORR at different potentials$^{[62,63]}$. The electron transfer number ($n$) was calculated to be 4.0 at 0.45-0.75 V from the slopes of the Koutecky-Levich plots$^{[236]}$, suggesting that the 3D foam-like NiCo$_2$O$_4$ favours a 4e⁻ oxygen reduction reaction, as in the ORR catalysed by commercial Pt/C catalyst measured in the same 0.1 M KOH electrolyte ($n = 4$ for Pt/C, Figure 4.8a and b), while Super P could only catalyse a 2e⁻ oxygen reduction reaction (Figure 4.8c and d). Figure 4.7 b indicates that the catalytic activity of the as-prepared 3D foam-like NiCo$_2$O$_4$ significantly outperforms that of Super P at a rotation speed of 1600 rpm, as evidenced by the positive shifts of the onset potential and the half-wave potential ($E_{1/2}$) to -0.15 and -0.34 V (vs. AgCl/Ag), respectively. In contrast, the values for the Super P are -0.3 V and -0.43 V, respectively. Also, the diffusion current density of the 3D foam-like NiCo$_2$O$_4$ is notably stronger than that of Super P, suggesting synergistic effects on the ORR catalytic activity of 3D foam-like NiCo$_2$O$_4$.

We also extended the potential of the as-prepared 3D foam-like NiCo$_2$O$_4$ electrode and the control samples to 0.9 V (vs. AgCl/Ag) to the water oxidation regime and evaluated the electrocatalytic oxygen evolution reaction (OER) (Figure 4.7 c). In 0.1 M KOH, the
3D foam-like NiCo$_2$O$_4$ electrode offers a rather higher current density than Super P, with a value of 24 mA cm$^{-2}$ and an onset potential of 0.6 V. The above results show that the 3D foam-like NiCo$_2$O$_4$ is a powerful bi-functional catalyst for both oxygen reduction and oxygen evolution\textsuperscript{[237]}. Since the primary goal of this work is to develop an efficient ORR/OER catalyst for non-aqueous lithium oxygen batteries, the ORR activity of the 3D foam-like NiCo$_2$O$_4$ catalyst in O$_2$-saturated 1 M LiCF$_3$SO$_3$ in tetraethylene glycol dimethyl ether (TEGDME) was also studied using RDE with a rotation speed of 1600 rpm (Figure 4.7 d). With a similar trend to the ORR activity measured in aqueous electrolyte, a significant improvement in the ORR activity was observed on the 3D foam-like NiCo$_2$O$_4$ catalyst compared to the Super P catalyst in terms of more positive onset and half-wave potential. These direct ORR and OER assessments indicate that the as-prepared 3D foam-like NiCo$_2$O$_4$ is a promising catalyst for Li-O$_2$ batteries.

![Graphs showing cyclic voltammograms and charge-discharge curves](image)

Figure 4.9 (a) Cyclic voltammograms acquired at a scan rate of 0.2 mV s$^{-1}$ in 1 M LiCF$_3$SO$_3$ in TEGDME of the as-prepared 3D foam-like NiCo$_2$O$_4$ and Super P. (b)
Initial discharge-charge plots of the as-prepared 3D foam-like NiCo₂O₄ and Super P at a current density of 200 mA g⁻¹. (c) Rate performances of the as-prepared 3D foam-like NiCo₂O₄ and Super P at current densities of 200, 500, and 1000 mA g⁻¹. (d) Initial discharge-charge plots of the 3D foam-like NiCo₂O₄ and Super P with a capacity limitation of 1000 mAh g⁻¹ at a current density of 200 mA g⁻¹. (e) Discharge-charge curves for selected cycles of the 3D foam-like NiCo₂O₄ with a capacity limitation of 1000 mAh g⁻¹. (f) Cycling performances of the 3D foam-like NiCo₂O₄ and Super P with the capacity limitation of 1000 mAh g⁻¹ at a current density of 200 mA g⁻¹. Voltage window: 2.35-4.35 V (vs. Li⁺/Li).

The cathode performance using an electrolyte containing O₂-saturated 1.0 M LiCF₃SO₃ in TEGDME for the Li-O₂ battery is shown in Figure 4.9. All the capacities reported in this work are normalized by the mass of carbon used in the cathodes. Cyclic voltammetry (CV) curves of the as-prepared 3D foam-like NiCo₂O₄ and Super P control sample (Figure 4.9a) show that no redox phenomenon can be observed for the 3D foam-like NiCo₂O₄-based electrode in argon-saturated electrolyte, demonstrating the lack of any electrochemical reaction in such an atmosphere. Besides the more positive ORR peak potential, however, the as-prepared 3D foam-like NiCo₂O₄ exhibits an oxidation (OER) peak at 3.7 V (vs. Li⁺/Li), corresponding to the decomposition of discharge products, while there is no oxidation peak for Super P electrode below 4 V (vs. Li⁺/Li) in O₂-saturated electrolyte. The first discharge and charge curves of a lithium oxygen battery with the 3D foam-like NiCo₂O₄-based electrode are compared with those of the pure Super P electrode at the same current density (200 mA g⁻¹) in Figure 4.9b to enable an understanding of the excellence of the 3D foam-like NiCo₂O₄ in terms of its ORR and OER kinetics. The lithium oxygen battery with the pure Super
P sample exhibits a discharge and charge overpotential of 0.31 and 1.18 V, respectively, with a low round-trip efficiency of 64%. In contrast, the battery with the as-prepared 3D foam-like NiCo$_2$O$_4$ presents discharge-charge overpotentials of 0.2 and 0.97 V, respectively, which results in a higher round-trip efficiency of 70%. Additionally, the initial discharge capacity of the 3D foam-like NiCo$_2$O$_4$ electrode is 101376 mAh g$^{-1}$, which is significantly higher than that of the Super P electrode (5928 mAh g$^{-1}$). To the best of our knowledge, this is the first report that a lithium oxygen battery with NiCo$_2$O$_4$-based catalyst shows such low discharge-charge overpotential with such a high specific capacity based on the mass of carbon. Also, in order to make sure that all the capacity has resulted from the oxygen reduction reaction instead of from lithium insertion into the NiCo$_2$O$_4$ electrode, discharge curves in traditional R2032 cells without O$_2$ atmosphere were collected (Figure 4.10). A negligible capacity of 2 mAh g$^{-1}$ could be delivered when the discharge potential was cut to 2.35 V, suggesting that NiCo$_2$O$_4$ only functions as an oxygen reduction reaction catalyst.

Figure 4.10 Discharge curve of the as-prepared 3D foam-like NiCo$_2$O$_4$ in traditional R2032 cells without O$_2$ atmosphere at a current density of 200 mA g$^{-1}$. 

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Figure 4.11 (a) Initial discharge curves at various current densities, and (b) cycling performance with a capacity limitation of 1000 mAh g$^{-1}$ of the as-prepared 3D foam-like NiCo$_2$O$_4$.

Additionally, the rate performance of the 3D foam-like NiCo$_2$O$_4$ in comparison with Super P was further investigated at higher discharge current densities of 500 and 1000 mA g$^{-1}$, respectively, when the discharge potential was cut to 2.35 V (Figure 4.9c and Figure 4.11a). A specific capacity of 8202 mAh g$^{-1}$ was found for the 3D foam-like NiCo$_2$O$_4$-based electrode, while 4070 mAh g$^{-1}$ can be delivered by the Super P electrode at a current density of 500 mA g$^{-1}$. Even when the current density was increased to 1000 mA g$^{-1}$, the capacity of the 3D foam-like NiCo$_2$O$_4$ still remained as high as 5598 mAh g$^{-1}$, while the discharge plateau remained above 2.5 V. The good rate capability is likely to have benefited from its unique structure: during the discharge, large amounts of oxygen can be supplied by the “highways” of the macro-tunnels and stored in the interior parts of the cathode, facilitating the rapid oxygen reduction reaction at high current densities$^{[59, 228, 238]}$. 

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Figure 4.9d shows the typical initial discharge and charge profiles of the 3D foam-like NiCo$_2$O$_4$-based electrode and the Super P electrode with a fixed capacity of 1000 mAh g$^{-1}$ and a current density of 200 mA g$^{-1}$, from which a much lower discharge and charge overpotential can be observed for the 3D foam-like NiCo$_2$O$_4$-based electrode. Remarkably, the discharge-charge curves from the 5$^{th}$ to the 30$^{th}$ cycles even overlap (Figure 4.9e), and the specific capacity suffers no loss up to 80 cycles (Figure 4.11b) for the 3D foam-like NiCo$_2$O$_4$-based electrode, suggesting its good stability and reversibility. The stable cycling performance of the as-prepared 3D foam-like NiCo$_2$O$_4$-based electrode in comparison with the Super P electrode is also manifested by the terminal discharge-charge potential with a fixed capacity of 1000 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$. As shown in Figure 4.9f, after 80 cycles, the terminal discharge and charge potentials of the NiCo$_2$O$_4$-based electrode are 2.47 V and 4.35 V (vs. Li$^+/Li$), respectively, whereas, Super P electrode could only maintain such performance for less than 15 cycles. The better cycling stability of the 3D foam-like NiCo$_2$O$_4$-based electrode than that of the Super P electrode demonstrates its promising application as an effective ORR and OER catalyst for lithium oxygen batteries.
Figure 4.12 (a) XRD patterns of the 3D foam-like NiCo$_2$O$_4$ cathode before discharge, after discharge, and after recharge. SEM images of (b) fresh, (c) discharged, and (d) recharged 3D foam-like NiCo$_2$O$_4$ cathode.

Figure 4.13 Raman spectrum of the discharged 3D foam-like NiCo$_2$O$_4$ cathode.

To further understand the reaction mechanism of the 3D foam-like NiCo$_2$O$_4$, XRD measurements on the electrode at different discharge-charge stages of lithium oxygen
batteries and examination of the morphologies of the electrode at corresponding stages were also conducted. XRD patterns of the NiCo$_2$O$_4$ electrodes at different stages for the first cycle at a current density of 100 mA g$^{-1}$ are shown in Figure 4.12a. Compared with the XRD pattern of the fresh electrode, new diffraction peaks could be observed for the discharged electrode. They can be assigned to the (100), (101), and (110) peaks of Li$_2$O$_2$ (as highlighted in Figure 4.12a). These peaks indicate that Li$_2$O$_2$ is a major crystalline discharge product$^{[32, 239, 240]}$. The three diffraction peaks disappeared when the battery was recharged, however, which suggests that the discharge product Li$_2$O$_2$ is decomposed during the charging process. Meanwhile, before the discharge, the fresh NiCo$_2$O$_4$-based electrode shows a rather loose morphology with macro-tunnels (Figure 4.12b) that can permit oxygen flow and Li$_2$O$_2$ deposition. During the 1$^{st}$ discharge, the insoluble species precipitate on the surface of the cathode, and a less porous morphology was obtained compared to the pristine porous electrode before the discharge (Figure 4.12c). Moreover, the band at approximately 800 cm$^{-1}$ in the Raman spectrum of the electrode after discharge (Figure 4.13) is ascribed to O–O stretching vibrations of lithium peroxide, further confirming the presence of lithium peroxide$^{[241, 242]}$. After the 1$^{st}$ charge, the porous structure is essentially regained for the NiCo$_2$O$_4$-based electrode, indicating a reversible reaction (Figure 4.12d). Since the fundamental features of the ORR and OER processes in aqueous and non-aqueous electrolytes share similarities$^{[243]}$, catalysts that can favour a 4e$^-$ electron reaction in aqueous media have been reported to easily facilitate a 2e$^-$ reaction in non-aqueous electrolyte$^{[70]}$. Thus, it is not surprising that we acquired satisfactory electrocatalytical results for our as-prepared 3D foam-like NiCo$_2$O$_4$ in terms of reversible Li$_2$O$_2$ formation and decomposition, as well as reduced discharge-charge overpotential, based on the former RDE results involving a 4e$^-$ ORR reaction and excellent OER
performance. Moreover, the 3D foam-like structure not only provides more contact sites and larger space for Li$_2$O$_2$ deposition, it also simultaneously improves the transport of oxygen and electrolyte, which underpin enhanced discharge-charge capacity, as well as stable cycling capability.

4.4 Summary

In summary, self-assembled 3D foam-like NiCo$_2$O$_4$ was fabricated by an environmentally friendly starch template method and demonstrated superior bi-functional electrocatalytic activity towards both the ORR and the OER when employed as the catalyst for non-aqueous lithium oxygen batteries, as compared to traditional Super P catalyst. The assembled battery shows a relatively high round-trip efficiency of 70%, as well as a high discharge capacity of 10137 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$ and excellent electrochemical performance in such aspects as high rate capability and stable cycling behaviour. The specific discharge capacity at a current density of 1000 mA g$^{-1}$ reaches 5598 mAh g$^{-1}$, which is about 55% of that at the current density of 200 mA g$^{-1}$. When discharge-charge capacities are limited to 1000 mAh g$^{-1}$, the as-prepared 3D foam-like NiCo$_2$O$_4$ shows rather stable and reversible discharge-charge potentials and exhibits no capacity loss up to 80 cycles at a current density of 200 mA g$^{-1}$. These encouraging results are due to the unique, hierarchically self-assembled 3D foam-like structure, which facilitates continuous oxygen flow through the large tunnels to the interior parts of the electrode and provides enough triple junctions (solid-liquid-gas) for Li$_2$O$_2$ deposition and decomposition. This study highlights the importance of a novel electrode design and opens up a promising strategy to develop highly efficient oxygen electrodes for lithium oxygen batteries.
CHAPTER 5 NANOFIBROUS CO$_3$O$_4$/PPY HYBRID WITH SYNERGISTIC EFFECT AS BIFUNCTIONAL CATALYST FOR LITHIUM OXYGEN BATTERIES

5.1 Preface

The rechargeable lithium-oxygen battery currently enjoys great scientific interest because theoretically, it can store significantly more energy, which exceeds that possible with lithium ion batteries [5, 48, 244, 245]. Developing a stable porous cathode with high conductivity that is simultaneously capable of efficient ORR and OER reactions is at the heart of key technologies for Li-O$_2$ batteries [48, 247-249]. Nanostructured carbon has been extensively studied and found to offer sufficient ORR catalytic activity because of its high conductivity and large specific surface area, but the OER process kinetics of carbon is much slower than for the counterpart ORR process [216]. Recent investigations show that carbon support is unstable in Li-O$_2$ batteries [86, 97, 250], since it suffers from significant decomposition above 3.5 V during the charging process, while lithium carbonate arising from reactions involving the electrolyte and electrode will result in electrode passivation and capacity fading between 2-4 V [86].

To avoid corrosion of the carbon support, Wen and his co-workers [250] were the first to report a tubular structured conducting polymer, tubular polypyrrole (TPPy), as an alternate support material for the air electrode of Li-O$_2$ batteries, which demonstrated the effectiveness of the conductive polymer and indicated a new direction for support material design for the Li-O$_2$ battery cathode. Their electrodes with TPPy-supported
electrolytic manganese dioxide (EMD) catalyst showed improved reversible capacity of nearly 2000 mAh g\(^{-1}\), higher round-trip efficiency, and especially superior rate capability compared with conventional carbon supported cathodes. Composites of PPy grown uniformly on reduced graphene oxide (RGO) were also studied by Munichandraiah et al. as catalysts for Li-O\(_2\) batteries, and a discharge capacity of 3353 mAh g\(^{-1}\) was delivered\(^{[251]}\). Although the reversible formation and decomposition of Li\(_2\)O\(_2\) product was detected during the discharge/recharge process in the work of Wen’s group, no systematic investigation of the intrinsic discharge/recharge products or the stability during cycling of pristine polypyrrole (PPy) has been reported. Moreover, compared with one-dimensional (1D) or two-dimensional (2D) structures, the three-dimensional (3D) nanoweb structured support studied in this work could provide an ideal backbone for catalytically active sites in a Li-O\(_2\) battery cathode, since the 3D framework could not only offer continuous pathways for electron transport to increase the electrical conductivity of the cathode, but also ensures that the support and the second phase catalyst are in comprehensive contact to facilitate rapid charge transfer and improve the electrochemical kinetics in Li-O\(_2\) batteries\(^{[252, 253]}\). In this respect, the 3D PPy nanoweb as support is expected to deliver optimized oxygen/electrolyte diffusion and electron transport for cathode design in Li-O\(_2\) batteries.

Apart from the cathode support, it is highly challenging but desirable to develop an efficient bi-functional catalyst for both the ORR and the OER\(^{[30, 114, 254]}\). Co\(_3\)O\(_4\), a material possessing little ORR activity by itself, could offer high ORR and OER activities when attached on a highly conductive support due to the synergistic coupling effect\(^{[16; 19; 20]}\). Dai et al. found that physical mixtures of Co\(_3\)O\(_4\) with reduced mildly oxidized graphene oxide (rmGO) or N-doped rmGO (N-rmGO) afforded much lower
ORR activities than Co$_3$O$_4$ nanocrystals coupled on graphene$^{[254]}$, and Manthiram et al reported that Co$_3$O$_4$ grown on O-and N-doped carbon nanoweb could significantly enhance ORR and OER activities$^{[69]}$. Yuasa et al$^{[255]}$, Bashyam and Zelenay$^{[256]}$, and Chen et al$^{[257]}$ have all successfully synthesized cobalt-polypyrrole complex and used them as electrocatalyst for fuel cells or active material for Li-ion batteries due to the strong coordination between cobalt and N atom on polypyrrole matrix$^{[258]}$. So a synergetic hybrid catalyst for Li-O$_2$ battery can be expected by combination between PPy as high conductive support with Co$_3$O$_4$ nanocrystals as non-precious bifunctional catalyst.

Based on the inspiration of TPPy as support for the Li-O$_2$ battery, as reported by Wen’s group, and the concept of synergetic chemistry, we present strongly coupled Co$_3$O$_4$ nanocrystals with 3D structured PPy nanoweb as a bifunctional synergetic catalyst for Li-O$_2$ batteries, together with a thorough study of the electrocatalytic features of pristine PPy and the Co$_3$O$_4$/PPy hybrid as cathode for Li-O$_2$ batteries during discharge/recharge processes. Rotating disk electrode (RDE) measurements in both aqueous and nonaqueous electrolyte, and electrocatalytic testing were performed to identify their electrocatalytic activities. Characterizations involving X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Fourier transformation infrared (FTIR) spectroscopy were employed to analyse the reaction products at different stages of discharge and recharge.
5.2 Experimental

*Preparation of PPy nanofibers:* PPy nanofibres were synthesized via an oxidative template assembly route. Pyrrole (Py) was distilled before use. In a typical process, 0.72 g cetrimonium bromide (CTAB) was dissolved in 200 mL 1 M HCl solution by constant stirring in an ice bath (0-5 °C). Subsequently, 0.33 g distilled Py monomer was added into the above solution, and another 0.5 h stirring was carried out. Meanwhile, 1.13 g ammonium persulfate (APS) was dissolved in 20 mL distilled water, which was then dropped into the Py monomer-containing solution and allowed to react for 24 h in an ice bath (0-5 °C). After that, the black product was suction filtered and washed several times with 1 M HCl solution and distilled water, followed by drying in a vacuum oven at 80 °C overnight. Finally, a black powder was obtained and denoted as PPy nanofibers.

*Preparation of Co$_3$O$_4$/PPy:* In a typical synthesis, 0.4125 g cobalt (II) acetate was dissolved in 15 mL distilled water and 26 mL ethanol mixed solvent. Then, PPy nanofibers (50 mg) were added into the mixed solution and ultrasonically treated for 1 h. Secondly, 1.5 ml 25% ammonium persulfate was added under vigorous stirring. The mixture was stirred in air for about 10 min to form a homogeneous brownish-grey slurry. Then, the suspension was transferred into a 120 mL autoclave, sealed, and maintained at 150 °C for 3 h. After this, the autoclave was cooled to room temperature naturally. The resulting black solid products were washed with water via centrifugation and re-dispersion, dried in a vacuum oven at 80 °C overnight, and collected for characterization. Meanwhile, pristine Co$_3$O$_4$ was also prepared under the same hydrothermal conditions as a control.
Characterizations: X-ray diffraction (XRD) (GBC MMA) patterns were collected over a 2θ range of 15 º- 75 º with a scan rate of 4 ° min⁻¹ and analysed with Traces™ software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. The morphologies of the samples were examined by field emission scanning electron microscopy (FE-SEM, JEOL 7500) and transmission electron microscopy (TEM, JEOL ARM-200F). Scanning transmission electron microscope (STEM) images and corresponding element mapping images were collected with the same TEM equipped with a Centurio SSD energy-dispersive X-ray spectroscopy (EDS) detector. The XPS data were analysed using CasaXPS software, and all the results were calibrated by C 1s at 284.6 eV for graphite. Thermogravimetric analysis (TGA) was carried out using a SETARAM Thermogravimetric Analyzer (France). Fourier transform infrared (FTIR) spectra were collected using a FTIR Prestige-21 (Shimadzu). Raman spectroscopy was conducted on a JOBIN YVON HR800 Confocal system with 632.8 nm diode laser excitation using a 300 lines mm⁻¹ grating. Brunauer-Emmett-Teller (BET) surface area and pore size distribution (PSD) measurements were conducted by N₂ adsorption/desorption at 77 K on a Quantachrome Autosorb-IQ MP instrument.

Catalyst and electrochemical performance: The electrochemical performances of lithium oxygen batteries were investigated using 2032 coin-type cells with air holes on the cathode side. For the preparation of the porous cathode, 90 wt.% catalyst and 10 wt.% poly(1,1,2,2-tetrafluoroethylene) (PTFE) (60% dispersion) were mixed in an isopropanol solution. The resulting homogeneous slurry was coated onto nickel mesh. The same procedure was applied to prepare pristine PPy electrodes. After that, the electrodes were dried at 120 °C in a vacuum oven for 12 h. All the lithium oxygen
batteries were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) with both water and oxygen contents below 0.1 ppm. They consisted of lithium metal foil as the counter electrode, a glass fiber separator (Whatman GF/D), non-carbonate electrolyte containing 1 M LiCF$_3$SO$_3$ dissolved in tetraethylene glycol dimethyl ether (TEGDME), and the air cathode electrode. All the assembled coin cells were stored in an O$_2$-purged chamber which was connected to a LAND CT 2001 A multi-channel battery tester for 2 h before each test. The galvanostatic discharge-charge tests were then conducted on the battery testing system within a voltage window of 2.0-4.4 V (vs. Li$^+/\text{Li}$), and the capacity and current densities were calculated based on the active material on the cathode. The loading amount in each cathode was approximately 1 mg cm$^{-2}$. Cyclic voltammetry (CV) was conducted in an O$_2$ saturated solution of 1 M lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) in TEGDME.

Examination of the discharged and recharged electrodes involved disassembling the cell in the glove box, rinsing the cathode with tetraethylene glycol dimethyl ether, and removing the solvent under vacuum. For XRD, SEM, XPS, and FTIR tests, the electrodes were covered with a layer of Kapton film before moving from the glove box to the outside instruments.

*Rotating Disk Electrode Tests:* RDE tests were performed using a computer-controlled potentiostat (Princeton 2273 and 616, Princeton Applied Research) in a conventional three-electrode cell at room temperature. The glassy carbon (GC) working electrode (0.196 cm$^2$) was first polished with alumina powder, rinsed with deionized water, and sonicated first in ethanol and then in double-distilled water. A platinum wire and Ag/AgCl (filled with saturated KCl aqueous solution) were used as the counter and
reference electrodes, respectively. Typically, the catalyst was redispersed in deionized water + isopropanol + 5% Nafion® (v/v/v = 4/1/0.05) to form a homogeneous catalyst ink with a concentration of 2 mg mL$^{-1}$. Then, 30 μL of this dispersion was pipetted onto the surface of the GC working electrode and dried under ambient conditions. For comparison, commercial Pt/C (20 wt. % Pt on Vulcan XC-72) catalyst ink was also obtained by the same method described above. Linear sweep voltammograms (LSVs) to measure the ORR performance were collected in O$_2$ saturated 0.1 M KOH solution with different rotation speeds from 400 to 1600 rpm from -0.9 – 0.1 V with a scan rate of 10 mV s$^{-1}$, while OER plots were obtained in Ar atmosphere from 0.1 – -0.9 V with a scan rate of 10 mV s$^{-1}$ and a rotation speed of 1600 rpm.

Koutecky-Levich (K-L) plots show the inverse current density ($j^{-1}$) as a function of the inverse of the square root of the rotation speed ($\omega^{-1/2}$) at different potential values. The number of electrons involved per O$_2$ in the ORR was determined by the Koutecky-Levich equation$^{[259, 260]}$:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k}
\]  
(5.1)

where $j$, $j_k$, and $j_d$ are the measured, the kinetically controlled, and the diffusion controlled current densities, respectively, and $\omega$ is the electrode rotation rate. $B$ is determined from the slope of the K-L plot based on the Levich equation:

\[
B = 0.2nF(Do_2)^{2/3}v^{-1/6}C_{O_2}
\]  
(5.2)

where $n$ represents the number of electrons gained per O$_2$, $F$ is the Faraday constant ($F = 96485$ C mol$^{-1}$), $D_{O_2}$ is the diffusion coefficient of O$_2$ in 0.1 M KOH ($1.9 \times 10^{-5}$ cm$^2$ s$^{-1}$), $v$ is the kinetic viscosity (0.01 cm$^2$ s$^{-1}$), and $C_{O_2}$ is the bulk concentration of O$_2$ ($1.2 \times 10^{-6}$ mol cm$^{-3}$).
The non-aqueous electrochemical oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) tests were carried out using computer-controlled potentiostats (Princeton 2273) in a three-electrode system using Pt foil as the counter electrode, AgCl/Ag as the reference electrode, and a working electrode consisting of sample-coated glassy carbon (GC) (0 V vs. Li+/Li = −3.3 V vs. AgCl/Ag). A solution of 0.5 M LiCF₃SO₃/TEGDME was used as electrolyte. In detail, argon was introduced into the electrolyte for 30 min to ensure that the background data was measured in an inert atmosphere. Then, pure oxygen was purged into the electrolyte for 30 min to study the ORR.

5.3 Results and Discussion

The XRD pattern of the pristine Co₃O₄, pristine PPy and Co₃O₄/PPy hybrid in Figure 5.1a shows reflections due to face-centered cubic spinel Co₃O₄ (JCPDS 43-1003) with typical diffraction peaks of (111), (220), (311), (400), (511) and (440) [261, 262]. Figure 5.1b compares the Raman spectra of the as-prepared Co₃O₄/PPy composite and pristine Co₃O₄ as well as pristine PPy. The Raman shift of Co₃O₄ in both the pristine and hybrid match well at around 191 cm⁻¹ and 480 cm⁻¹ except that the shift at 680 cm⁻¹ for pristine Co₃O₄ increased to 687 cm⁻¹ for the hybrid, implying the decreased mode strength of Co-O due to the formation of Co-N coordination between Co₃O₄ and PPy [255, 257], which provides another evidence for the uniform dispersion of Co₃O₄ on the surface of PPy. Notably, the Raman shift of PPy in the composite maintains well with the pristine PPy which is in good agreement with the typical Raman modes of PPy [263], confirming that hydrothermal process has no negative effect on the PPy structure.
Figure 5.1 Some physical properties of the nanofibrous Co$_3$O$_4$/PPy hybrid: (a) X-ray diffraction patterns and (b) Raman spectra of the nanofibrous Co$_3$O$_4$/PPy hybrid, Co$_3$O$_4$, and PPy; (c) XPS survey spectra of PPy and the nanofibrous Co$_3$O$_4$/PPy hybrid; and high-resolution (d) C 1s, (e) N 1s, and (f) Co 2p XPS spectra of the nanofibrous Co$_3$O$_4$/PPy hybrid.
XPS spectra for C 1s, O 1s, N 1s, and Co 2p are shown in Figure 5.1c. Figure 5.1d-1f presents high-resolution XPS spectra of C 1s, N 1s, and Co 2p in the nanofibrous Co\textsubscript{3}O\textsubscript{4}/PPy hybrid. As shown in Figure 5.1d, the C1s spectra can be deconvoluted into five lines labelled C\textsubscript{beta}, C\textsubscript{alpha}, C-N, C-O/C-N, N-C=O/O-C=O and C=O/C=N bonds, respectively\textsuperscript{264,265}. In Figure 5.1e, the deconvolution of N 1s is depicted. The signal at approximately 399.0 eV is assigned to the NH group of the pyrrole unit. The C=N defects of PPy are at 397.4 eV, while the polaron (C-N+) and bipolaron (C=N+) structures are at 400.1 eV and 400.6 eV, respectively\textsuperscript{245}. The Co 2p spectrum in Figure 5.1f exhibits two peaks at 795.5 and 780.2 eV, which are indexed to the Co 2p\textsubscript{1/2} and Co 2p\textsubscript{3/2} binding energies, respectively\textsuperscript{16b}. The binding energies of Co 2p\textsubscript{1/2} and Co 2p\textsubscript{3/2}, and their difference value (about 15.3 eV, spin-orbit splitting) are identical to spinel Co\textsubscript{3}O\textsubscript{4} phase according to previous reports\textsuperscript{246,247}. The weight percentage of the Co\textsubscript{3}O\textsubscript{4} in the Co\textsubscript{3}O\textsubscript{4}/PPy hybrid is 78%, based on thermogravimetric analysis (TGA) from 25 to 800 °C with a heating rate of 10 °C min\textsuperscript{-1} in air, as shown in Figure 5.2.
Figure 5.3 (a) FESEM image of the pristine PPy nanofibers; (b)-(c) TEM images, and (d) high resolution TEM image of the nanofibrous Co$_3$O$_4$/PPy hybrid.

The growth of Co$_3$O$_4$ nanocrystals on the PPy nanofibers was confirmed by scanning electron microscope (SEM) and transmission electron microscope (TEM) images. It can be observed in Figure 5.3a that PPy features a homogeneous cross-linked nanofiber structure, with the diameters of the nanofibers in the range of 60-80 nm. Similarly, the Co$_3$O$_4$/PPy hybrid in Figure 5.3b maintains a nanofibrous-like web structure similar to that of PPy, except that the surface of the fibres has become rough and is decorated with a uniform layer of nanoparticles, which are verified to be Co$_3$O$_4$ by XRD in Figure 1a. TEM images of the Co$_3$O$_4$/PPy in Figure 5.3c confirm that small Co$_3$O$_4$ nanoparticles with a size distribution of 5-6 nm are tightly and homogeneously anchored on the surfaces of the PPy nanofibers. Such small Co$_3$O$_4$ particles are attributed to NH$_3$ coordination with cobalt cations in reducing particle size$^{234}$. From the high-resolution
TEM image in Figure 5.3d, it can be observed that several Co$_3$O$_4$ nanoparticles are grown on the PPy matrix with the typical interplanar distances of 0.47 and 0.24 nm, consistent with the $d$-spacing of the (111) and (311) crystal planes of or spinel phase Co$_3$O$_4$\textsuperscript{91,234}.

Figure 5.4 (a) Scanning transmission electron microscope (STEM) image, and (b)-(e) corresponding element mapping images of the nanofibrous Co$_3$O$_4$/PPy hybrid; (f) the corresponding SAED pattern.

A scanning TEM (STEM) image (Figure 5.4a) coupled with corresponding energy dispersive X-ray spectroscopy (EDS) mapping images (Figure 5.4b-e), and the corresponding selected area electron diffraction (SAED) pattern (Figure 5.4f) were employed to verify the uniform attachment of Co$_3$O$_4$ nanoparticles to the surfaces of PPy nanofibers. The indexed diffraction rings in the SAED pattern are assigned to the Co$_3$O$_4$, and they indicate that the growth directions of the Co$_3$O$_4$ are perpendicular to
the (111), (200), (311), (400), (511), and (440) planes, which is in line with the XRD observations. The EDS mapping images indicate the presence of the elements C, N, Co, and O with even distribution throughout the whole hybrid, which is further evidence that the Co$_3$O$_4$ nanoparticles are well-attached to the surfaces of the PPy nanofibers. Brunauer-Emmett-Teller (BET) measurement showed that the Co$_3$O$_4$/PPy hybrid possesses a specific surface area of 896 m$^2$ g$^{-1}$.

Figure 5.5 Linear sweep voltammetry (LSV) curves at various rotation speeds in O$_2$-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s$^{-1}$ in the potential range of -0.9-0.1 V (vs. AgCl/Ag) for (a) commercial 20 wt.% Pt/C, (b) the nanofibrous Co$_3$O$_4$/PPy hybrid, and (c) the pristine PPy.

The pristine PPy nanofibers and nanofibrous Co$_3$O$_4$/PPy hybrid were subjected to linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) in
O₂-saturated 0.1 M KOH solution at a scan rate of 10 mV s⁻¹ in the potential range of -0.9 - 0.1 V (vs. AgCl/Ag). Standard commercial Pt/C (20 wt% Pt on Vulcan XC-72 carbon) was tested as a control. RDE curves at various rotation speeds were collected to determine the samples’ ORR kinetic performances, as shown in Figure 5.5. As shown in the RDE curves in Figure 5.6a, compared with the pristine PPy nanofibers, the nanofibrous Co₃O₄/PPy shows more positive reduction peak potential, lower onset overpotential, and higher reduction current density, indicating a superior ORR activity. The Tafel plots of the measured potential vs. specific activity (Figure 5.6b) clearly show that the ORR kinetics of the nanofibrous Co₃O₄/PPy hybrid is definitely superior in terms of a smaller Tafel slope (~ 68 mV per decade) than that measured from the pristine PPy (~ 122 mV per decade). The electrocatalytic OER (Figure 5.6c) in 0.1 M KOH solution demonstrates that the nanofibrous Co₃O₄/PPy hybrid offers a rather higher current density than the pristine PPy nanofibers, with a value of more than 4 mA cm⁻² and an onset potential of 0.7 V vs. AgCl/Ag, suggesting a stronger OER activity in aqueous system. The above results show that with the utilization of Co₃O₄ nanocrystals, both oxygen evolution activities can be improved a lot. Since the fundamental features of the ORR and OER processes in aqueous and nonaqueous electrolytes share similarities, the similarities in both systems will provide some guidance for the development of new electrocatalysts when shifting Li-O₂ batteries from aqueous to nonaqueous systems. To confirm this concept, the ORR and OER catalytic capabilities of both the pristine PPy nanofibers and the nanofibrous Co₃O₄/PPy hybrid, which are shown in Figure 5.6d, were measured in O₂-saturated 0.5 M LiCF₃SO₃/tetraethylene glycol dimethyl ether (TEGDME) electrolyte. Obviously, the nanofibrous Co₃O₄/PPy hybrid exhibits a more positive ORR (2.7 V vs. Li⁺/Li) and much higher OER current density than the pristine PPy. The
consistency in both aqueous and non-aqueous electrolytes suggests that the pristine PPy may only act as an ORR catalyst with weak OER activity, while the nanofibrous Co$_3$O$_4$/PPy hybrid could reduce the ORR and OER overpotential and offer higher discharge and charge specific capacity when employed as cathode in lithium oxygen batteries.

Figure 5.6 (a) Linear sweep voltammetry (LSV) curves of commercial 20 wt.% Pt/C, nanofibrous Co$_3$O$_4$/PPy hybrid, and pristine PPy in O$_2$-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s$^{-1}$ in the potential range of -0.9-0.1 V (vs. AgCl/Ag); (b) Tafel plots showing the potential for commercial 20 wt.% Pt/C, nanofibrous Co$_3$O$_4$/PPy hybrid, and PPy as a function of the log of the kinetic current density, based on data from (a); (c) oxygen evolution curves for the commercial 20 wt.% Pt/C, nanofibrous Co$_3$O$_4$/PPy hybrid, and PPy in the potential range of 0.2-0.9 V (vs. AgCl/Ag), and (d) ORR and OER polarization curves of nanofibrous Co$_3$O$_4$/PPy hybrid
and PPy on a rotating disk electrode (RDE) at a rotation speed of 1600 rpm in O₂-saturated 0.5 M LiCF₃SO₃/TEGDME at a scan rate of 10 mV s⁻¹.

The electrochemical properties of the pristine PPy nanofiber and the nanofibrous Co₃O₄/PPy hybrid electrodes in an electrolyte containing O₂-saturated 1.0 M LiCF₃SO₃ electrolyte in TEGDME for the Li-O₂ battery are shown in Figure 5.7. All the capacities reported in this work are normalized by the mass of active material used in the cathodes. The initial galvanostatic discharge/charge curves at a current density of 100 mA g⁻¹ from 2.0 to 4.4 V (vs. Li⁺/Li) are presented in Figure 5.7a. It is observed that the lithium oxygen battery with the pristine PPy cathode exhibits discharge/charge capacities of 2529.6/1106.6 mAh g⁻¹, respectively, suggesting that PPy could act not only as a highly conductive support but also as an efficient ORR catalyst. It is not a desirable OER catalyst, however, with the recharge curve soaring to 4.4 V, which is consistent with the RDE results (Figure 5.6d). In contrast, the battery with the nanofibrous Co₃O₄/PPy hybrid electrode presents significantly enhanced ORR and OER activities, with a larger discharge capacity of 3585 mAh g⁻¹ and, in particular, a much higher charge capacity of 2784 mAh g⁻¹ with a much reduced discharge/charge gap of 1.24 V from 1.53 V for the pristine PPy nanofiber cathode, indicating that the nanofibrous Co₃O₄/PPy hybrid cathode has highly reversible charging and discharging characteristics.
Figure 5.7 (a) Initial discharge/charge plots of the nanofibrous Co$_3$O$_4$/PPy hybrid and the pristine PPy cathodes in lithium-oxygen batteries at a current density of 100 mA g$^{-1}$ in 1 M LiCF$_3$SO$_2$/TEGDME (2-4.4 V vs. Li$^+/Li$), (b) EIS plots of the nanofibrous Co$_3$O$_4$/PPy hybrid cathode and the pristine PPy cathode before and after the 1$^{\text{st}}$ recharge (RC). Representative discharge/charge curves for selected cycles (c), and the corresponding cycling performance (d) of nanofibrous Co$_3$O$_4$/PPy hybrid under a capacity limit of 500 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$. Representative discharge/charge curves for
selected cycles (e), and the corresponding cycling performance (f) of the pristine PPy cathode under a capacity limit of 500 mA h g\(^{-1}\) at a current density of 100 mA g\(^{-1}\).

We also conducted electrochemical impedance spectroscopy (EIS) of lithium oxygen batteries with the nanofibrous Co\(_3\)O\(_4\)/PPy hybrid and the PPy cathodes at different states in Figure 5.7b. The impedance shows that both interfacial resistance and charge-transfer resistance increase significantly in the recharged state for the PPy cathode, while both resistances almost recover to their initial state after recharging for the Co\(_3\)O\(_4\)/PPy hybrid. Thus, it is supposed that PPy has insufficient ability to decompose the discharge products, such as insulating Li\(_2\)O or Li\(_2\)CO\(_3\), which, in turn, explains its rather low recharge capacity compared with the nanofibrous Co\(_3\)O\(_4\)/PPy hybrid cathode.

Typical selected discharge/charge profiles of the nanofibrous Co\(_3\)O\(_4\)/PPy hybrid and the pristine PPy electrode with a fixed capacity of 500 mAh g\(^{-1}\) at a current density of 100 mA g\(^{-1}\) are presented in Figure 5.7c and Figure 5.7e, respectively, from which a lower discharge/charge overpotential at each cycle and rather stable discharge/charge profiles can be observed for the hybrid-based electrode. Figure 5.7d and Figure 5.7f exhibits the terminal discharge/charge voltages for each cycle of the nanofibrous Co\(_3\)O\(_4\)/PPy hybrid and the pristine PPy electrode, respectively. The discharge/charge profiles from the 10\(^{th}\) cycle to the 30\(^{th}\) cycle for the Co\(_3\)O\(_4\)/PPy hybrid cathode show almost no distinct polarization, with the end voltages of 2.58 V and 4.23 V after discharge and charge for 30 cycles, respectively. On the other hand, the terminal discharge voltage for the pristine PPy cathode becomes lower than 2 V after 15 cycles, with a capacity limit of 500 mAh g\(^{-1}\). From comparison of the above results for the Co\(_3\)O\(_4\)/PPy hybrid and the pristine PPy cathodes, it is believed that the uniform distribution of Co\(_3\)O\(_4\) nanocrystals
on the surface of the highly conductive support material can create substantial reaction sites for the $\text{O}_2/\text{Li}_2\text{O}_2$ conversion, and $\text{Co}_3\text{O}_4$ can take full advantage of its intrinsic catalytic activity, leading to an improved OER performance.$^{[9b]}$ Rate capabilities from 100 to 500 mA g$^{-1}$ for the $\text{Co}_3\text{O}_4$/PPy hybrid and the pristine PPy electrodes with a fixed capacity of 500 mAh g$^{-1}$ are presented in Figure 5.8a and Figure 5.8b, respectively. Although the pristine PPy can maintain a terminal voltage of 2.36 V at the current density of 200 mA g$^{-1}$, it suffers a sharp potential drop when the current density is increased to 500 mA g$^{-1}$ (Figure 5.8b). The nanofibrous $\text{Co}_3\text{O}_4$/PPy hybrid catalyst, however, shows improved bifunctional catalytic activity at high rates, which is confirmed by the terminal voltage of 2.51 V when the current density is increased to 500 mA g$^{-1}$, similar to the value at 200 mA g$^{-1}$ (2.52 V). The obtained improved electrocatalytic properties of the cathode with the nanofibrous $\text{Co}_3\text{O}_4$/PPy hybrid could be ascribed to the synergistic effects between the PPy nanofibers and the $\text{Co}_3\text{O}_4$ nanoparticles. On the one hand, $\text{Co}_3\text{O}_4$ has long been reported to be efficient OER catalyst for Li-O$_2$ batteries,$^{63, 91, 234, 252}$; On the other hand, PPy with a fibrous morphology that features a large specific surface area and a highly conductive web could offer advantages such as fast electron paths and facile O$_2$ diffusion throughout the whole cathode.$^{[9b, 22]}$ In particular, numerous reaction sites will be created when ultrafine $\text{Co}_3\text{O}_4$ nanoparticles are grown on PPy nanofibers. In this regards, $\text{Co}_3\text{O}_4$ can make full use of its ORR and OER catalytic activity.$^{63, 234}$
Figure 5.8 Discharge/charge curves of the lithium oxygen batteries at different current densities under a capacity limit of 500 mAh g\(^{-1}\) for a) the nanofibrous Co\(_3\)O\(_4\)/PPy hybrid cathode and b) the pristine PPy cathode.

Figure 5.9 Product detection. (a) FTIR spectra of nanofibrous Co\(_3\)O\(_4\)/PPy hybrid and pristine PPy cathodes after the 1\(^{st}\) discharge (1\(^{st}\) DC) and 1\(^{st}\) recharge (1\(^{st}\) RC) over wavenumber ranges of 2000-600 cm\(^{-1}\) (left panel) and 650-500 cm\(^{-1}\) (right panel), and (b) Li 1s XPS spectra of air electrode after the 1\(^{st}\) discharge (1\(^{st}\) DC, top) and 1\(^{st}\) recharge (1\(^{st}\) RC, bottom).
The initial discharged and recharged products of the Li-O₂ battery with the nanofibrous Co₃O₄/PPy hybrid and the pristine PPy nanofiber cathodes at a current density of 100 mA g⁻¹ were investigated by using ex-situ FTIR, XPS, and FESEM measurements. The IR transmission peaks at around 600 cm⁻¹ are derived from the characteristic peak of Li₂O₂ 32,253 in both the discharged nanofibrous Co₃O₄/PPy hybrid and the pristine PPy nanofiber cathodes, as displayed in Figure 5.9a. The Li₂O₂ peak of the nanofibrous Co₃O₄/PPy hybrid almost disappears in the charged state, indicating the decomposition of Li₂O₂. A weak Li₂O₂ signal can still be observed, however, after the recharge of the pristine PPy nanofiber cathode due to the limited capability for OER of PPy, which can explain the lower charge capacity of the pristine PPy compared with the nanofibrous Co₃O₄/PPy hybrid in Figure 5.7a. In addition to the peaks arising from Li₂O₂, the transmission peaks at around 1460 cm⁻¹ and 860 cm⁻¹ are the signature of the Li₂CO₃ signal 32. In both the discharged nanofibrous Co₃O₄/PPy hybrid and the pristine PPy cathodes, small transmission peaks ascribed to Li₂CO₃ are detected and may be attributed to the partial decomposition of the ether-based electrolyte. Although TEGDME is reported to be more stable compared with other organic solvents, ether-based electrolyte decomposition still occurs. 11c According to published reports, ether-based electrolyte is prone to auto-oxidation under oxygenated radicals, and decomposition occurs at voltages higher than 4 V, leading to the formation of non-reversible reaction products 5,189. These peaks are significantly weaker than those of the discharged pristine PPy electrode, however, probably due to the prevention of the side reactions between PPy, which may suffer oxidation of the carbon to CO₂ due to the high content of carbon atoms, and the discharge product Li₂O₂ to form Li₂CO₃ by the uniform dispersion of Co₃O₄ nanoparticles with higher OER capability on the surface of PPy nanofiber 32, 63, 91, 230, 254. The Li 1s spectra of the discharged and charged PPy
nanofiber cathode presented in Figure 5.9b is very consistent with the FTIR result, where the peaks at 54.3 eV and 55.4 eV can be assigned to the Li–O bond of Li$_2$O$_2$ and Li$_2$CO$_3$ respectively,$^{31,255-257}$ further indicating that Li$_2$O$_2$ and Li$_2$CO$_3$ are the main discharge products for the pristine PPy cathode. The presence of more Li$_2$CO$_3$ and less Li$_2$O$_2$ after recharge also confirms the incomplete decomposition of Li$_2$O$_2$ and explains its insufficient OER catalytic activity.

Figure 5.10 Product detection. SEM images of air electrodes at different stages: a)-c) pristine PPy electrode in (a) the fresh state, (b) after the 1$^{st}$ discharge (DC), and (c) after the 1$^{st}$ recharge (RC); (d)-(f) nanofibrous Co$_3$O$_4$/PPy hybrid electrode in (d) the fresh state, (e) after the 1$^{st}$ DC, and f) after the 1$^{st}$ RC.

The presence and disappearance of the products can be visibly confirmed from the FESEM observations of both the nanofibrous Co$_3$O$_4$/PPy hybrid and the pristine PPy nanofiber cathodes after the 1$^{st}$ discharge and recharge. As shown in Figure 5.10a-c, most of the PPy nanofibers in the pristine electrode are fully buried under the reaction
products after the 1st discharge (Figure 5.10b), even when in a charged state Figure 5.10c), which indicates that their access to the electrolyte would be seriously impeded. In sharp contrast, the nanofibrous Co₃O₄/PPy hybrid cathode after the 1st full discharge still clearly exhibits fiber-like morphology (Figure 5.10e), with vacant space and numerous holes allowing easy access of the electrolyte and oxygen, which is favourable for the oxygen release and for providing effective tri-phase (solid-liquid-gas) regions for the formation and the decomposition of Li₂O₂ in the subsequent processes. Note that after the 1st discharge, the diameter of the Co₃O₄/PPy nanofibers obviously becomes larger, and diamond-like crystal products with a size of 10 nm have grown on the surfaces of the Co₃O₄/PPy nanofibers. In this stage, even though Li₂O₂ product is formed on the surface of the Co₃O₄/PPy, the electrode still maintains its nanofibrous structure. After the 1st charging (Figure 5.10f), however, the diamond-like solid precipitate disappears, and nanofiber morphology similar to that of the fresh electrode is regained, indicating the complete decomposition of the recently-formed Li₂O₂ product.

Because Li-O₂ batteries are still relatively new, additional research efforts, including in-situ transmission electron microscope (TEM) observations, should be devoted to clarifying the effects of the crystallinity of Li₂O₂ on the charging process for Li-O₂ batteries.

We further conducted ex-situ XRD and high resolution SEM (HRSEM) measurements to identify the discharge products of Li-O₂ batteries with the nanofibrous Co₃O₄/PPy cathode. XRD patterns of the Co₃O₄/PPy cathode at different states for the first cycle and in the recharged state after 30 cycles at a fixed capacity of 500 mAh g⁻¹ and a current density of 100 mA g⁻¹ are shown in Figure 5.11a. As compared with the XRD pattern of the fresh electrode, new diffraction peaks are observed for the discharged
cathode. Although the peaks are weak, they could be reasonably assigned as the (100) and (101) peaks of crystalline Li$_2$O$_2$ (as highlighted in Figure 5.11a). These two peaks disappear when the battery is recharged to 4.4 V, suggesting high reversibility of the Li$_2$O$_2$ during the charging process. Only peaks attributed to Co$_3$O$_4$ can be found in the XRD pattern of the nanofibrous Co$_3$O$_4$/PPy cathode after the 30$^{th}$ cycle fixed-capacity charging process. Moreover, as shown in Figure 5.11b, the 3D framework with apparent nanoweb morphology in the Co$_3$O$_4$/PPy cathode is also well maintained after the 30$^{th}$ fixed-capacity cycle, further evidencing the fact that the nanofibrous Co$_3$O$_4$/PPy hybrid catalyst with high catalytic activity and 3D structure could promote efficient O$_2$/Li$_2$O$_2$ conversion for Li-O$_2$ batteries. The diagram in Figure 5.11c schematically illustrates the discharge and charge processes. The PPy nanofiber channels, which form a continuous
conductive network, could facilitate rapid O₂ and electrolyte diffusion throughout the whole ORR and OER process. The nanofibers also could provide a high density of reactive sites on the outside with their coating of ultrafine Co₃O₄ nanoparticles, in which Li₂O₂ can be deposited to achieve high energy density.

5.4 Conclusions

In summary, a novel nanofibrous Co₃O₄/PPy hybrid has been fabricated via a rapid hydrothermal method, and ultrafine Co₃O₄ nanocrystals have been grown in situ on the surface of the PPy nanoweb to form a 3D porous framework. By combining X-ray diffraction with FTIR and XPS spectroscopy, the discharge and recharge products of the pristine PPy and the nanofibrous Co₃O₄/PPy hybrid cathodes could be studied. It was discovered that PPy can act as a good support and ORR catalyst, but with poor OER capability, for Li₂O₂ batteries. With the uniform growth of Co₃O₄ nanoparticles on the PPy nanofibers, improved OER performance is achieved, involving lower charge overpotential and larger charge capacity, as well as better rate capability. Such a hybrid could deliver discharge/charge capacities of 3585/2784 mAh g⁻¹ at a current density of 100 mA g⁻¹, based on the reversible formation/decomposition of Li₂O₂. The as-acquired favourable electrocatalytic results probably benefit from the perfect synergistic effect between the PPy nanofiber support and the well-defined Co₃O₄ nanoparticles, in which the former not only acts as a highly electrically conductive web to facilitate efficient electron transfer, but also provides large surface area to load nanocrystalline Co₃O₄ ad nanocreates more tri-phase reaction sites throughout the whole cathode, while the latter offer highly catalytic sites, and more importantly, makes it possible for their ORR and
OER catalytic activity to be fully utilised when they are decorated onto the PPy nanoweb matrix.
CHAPTER 6 3D HIERARCHICAL POROUS CO$_3$O$_4$ NANOTUBE NETWORK AS EFFICIENT CATHODE FOR RECHARGEABLE LITHIUM-OXYGEN BATTERIES

5.5 Preface

Nanotechnology has definitely promoted the progress of material science and inspired the global chemists to think and act via a nano-perspective$^{258, 259}$. Increasingly significant achievements have been obtained in the research field of energy storage systems, electrocatalysis and fuel cells based on the concept of nanostructured materials$^{135, 260-266}$. Three dimensional (3D) hierarchical porous nanotube (HPNT) materials have shown further superiorities compared with the currently developed nanotechnology. Firstly, the continuous 3D conductive network can greatly improve the charge transport (in the electrolyte and the active materials) and charge transfer (in the two-phase interface), facilitating the electrode reaction kinetics and reaction rate$^{259, 267-270}$. Secondly, the nanoporous tubular structure with enlarged surface area can facilitate rapid ion and electron transport, improve adsorption of and immersion in electrolyte on the surfaces of electroactive materials, and enhance the capacity and energy density$^{263, 271-273}$. More importantly, the HPNT structured materials will be beneficial to the development of promising lithium oxygen battery which require optimal cathode structure to afford repaid oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics$^{4, 42, 86, 162, 274}$. The macroscale spaces in the 3D network skeleton can function as “highways” to continuously supply oxygen to the interior parts of the electrode$^{40, 275}$. 3D nanoporous tubes are instinctively connected to a whole network, which greatly reduce the interface
contact impedance compared to the reported 1D nanoporous tubes\textsuperscript{276}. Moreover, the larger porosity on the nanotube can create more abundant tri-phase (catalyst-electrolyte-oxygen) regions required by ORR and OER\textsuperscript{40}, because O\textsubscript{2} and electrolyte can enter into the hollow cavities of porous nanotubes via not only the two narrow ends but also holes in the tube walls. In addition, the macropores and nanopores provide sufficient space for the deposition of the discharge product (Li\textsubscript{2}O\textsubscript{2}), which enlarges the discharge capacity\textsuperscript{263, 277}. To the best of our knowledge, however, there has not been reported yet on the synthesis of the 3D HPNT network structure for Li-O\textsubscript{2} battery application.

In the previous reports, fabrication of 1D porous nanotubes has been evidenced a critical challenge, since it involves either a multistep synthetic route\textsuperscript{40, 278, 127} or precious metal as a template\textsuperscript{279, 280}. We present here a facile and scalable fabrication scheme for a 3D hierarchical porous Co\textsubscript{3}O\textsubscript{4} nanotube (Co\textsubscript{3}O\textsubscript{4} HPNT) network by employing polypyrrole nanofiber (PPyNF) as a sacrificial template. The PPy nanofiber template with its unique 3D nanoweb morphology is cheaper, easier to be synthesized by a facile chemical polymerization method in a large scale compared with other templates e.g. Al\textsubscript{2}O\textsubscript{3} array that needs complicated electrochemical deposition\textsuperscript{281, 282}. Its easy and thorough removal by a direct heat treatment in air atmosphere makes it undoubtedly a much superior approach to the fabrication of tubular structures compared with other inorganic templates to produce porosity\textsuperscript{283, 284}. Take SiO\textsubscript{2} template as an example, its removal not only needs etching with a special solution of hydrogen fluoride (HF) and multiple repurifying, but also may introduce ionic impurities if they are not rinsed incompletely. Therefore, it is expected that the present technique will open up a promising strategy to
develop 3D structured nanotubular metal oxides, as well as perovskite oxides, with different sizes, based on adjusting the size of the PPy template.

When employed as cathode in the Li-O₂ battery, the as-prepared Co₃O₄ HPNT exhibited relatively low charge overpotential of 99 mV and high discharge/charge capacity of 4164/4299 mAh g⁻¹. This superior performance is ascribed to the 3D web-like nanoporous tubular structure. It provides rapid oxygen flow, increases the catalytic utilization of Co₃O₄, and offers sufficient volume for insoluble Li₂O₂ deposition. In addition, the hierarchical porous structure, including meso/nanopores on the walls of the nanotubes, facilitates O₂ diffusion, wetting by the electrolyte, and mass transport of all the reactants.

5.6 Experimental

*Synthesis of PPy nanofibers:* PPy nanofibers were synthesized via an oxidative template assembly route. Pyrrole (Py) was distilled before use. In a typical process, 0.72 g cetrimonium bromide (CTAB) was dissolved in 200 mL of 1 M HCl solution by constant stirring in an ice bath (0-5 ºC). Subsequently, 0.33 g distilled Py monomer was added into the above solution, and another 0.5 h stirring was carried out. Meanwhile, 1.13 g ammonium persulfate (APS) was dissolved in 20 mL distilled water which was then dropped into the Py monomer-containing solution and allowed to react for 24 h in an ice bath (0-5 ºC). After that, the black product was suction filtered and washed several times with 1 M HCl solution and distilled water, followed by drying in a vacuum oven at 80 ºC overnight. Finally, a black powder was yielded and denoted as PPy nanofiber.
Synthesis of 3D hierarchical porous Co₃O₄ nanotube (HPNT) network: In a typical synthesis, 0.4125 g cobalt (II) acetate was dissolved in 15 mL distilled water and 26 mL ethanol mixed solvent. Then, 50 mg of PPy nanofibers was added into the mixed solution, which was ultrasonically treated for 1 h. Secondly, 1.5 ml 25% ammonium was added under vigorous stirring. The mixture was stirred in air for about 10 min to form a homogeneous dark slurry. Then, the suspension was transferred into a 120 mL autoclave, sealed, and maintained at 150 ºC for 3 h. Afterwards, the autoclave was cooled to room temperature naturally. The resulting black solid products were washed with water via centrifugation and re-dispersion and dried in a vacuum oven at 80 ºC overnight, which was followed by a heat-treatment at 450 ºC for 6 h in air atmosphere. Meanwhile, pristine Co₃O₄ under the same hydrothermal conditions without PPy nanofiber as template was also prepared as a control sample, with the sample denoted as Co₃O₄ NP.

Characterizations: X-ray diffraction (XRD) (GBC MMA) patterns were collected over a 2θ range of 20°-70° with a scan rate of 4° min⁻¹ and analysed with Traces™ software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. The morphologies of the samples were examined by field emission scanning electron microscopy (FE-SEM, JEOL 7500) and transmission electron microscopy (TEM, JEOL ARM-200F). The XPS data were analysed using CasaXPS software, and all the results were calibrated by C 1s at 284.6 eV for graphite. Thermogravimetric analysis (TGA) was carried out using a SETARAM Thermogravimetric Analyzer (France). Brunauer-Emmett-Teller (BET) surface area and pore size distribution (PSD) measurements were conducted by N₂ adsorption/desorption at 77 K on a Quantachrome Autosorb-IQ MP instrument.
Electrochemical performance: The electrochemical performance of lithium-oxygen batteries containing the samples as active materials was investigated using 2032 coin-type cells with air holes on the cathode side. For the preparation of the porous cathode electrode, 60 wt.% catalyst, 30 wt.% Ketjen Black (KB), and 10 wt.% poly(1,1,2,2-tetrafluoroethylene) (PTFE) (60% dispersion) were mixed in an isopropanol solution. The resulting homogeneous slurry was coated on carbon paper. The same procedure was applied to prepare pristine KB electrodes. After that, the electrodes were dried at 120 ºC in a vacuum oven for 12 h. All the lithium-oxygen batteries were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) with both water and oxygen contents below 0.1 ppm. They consisted of lithium metal foil as the counter electrode, a glass fiber separator (Whatman GF/D), non-carbonate electrolyte containing 1 M LiCF$_3$SO$_3$ dissolved in tetraethylene glycol dimethyl ether (TEGDME), and the air cathode electrode. All the assembled coin cells were stored in an O$_2$-purged chamber which was connected to a LAND CT 2001 instrument, a multi-channel battery tester, for 2 h before each test. The galvanostatic discharge-charge tests were then conducted on the battery testing system with the voltage between 2.35-4.35 V (vs. Li$^+$/Li), and the capacities reported in this work were normalized by the mass of active material and carbon used in the cathodes. The loading amount in each cathode was approximately 1 mg cm$^{-2}$. Cyclic voltammetry (CV) was conducted in O$_2$-saturated 0.2 M lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) in tetraethylene glycol dimethyl ether (TEGDME) with a scan rate of 10 mV s$^{-1}$.

Examination of the discharged and recharged electrodes involved disassembling the cell in the glove box, rinsing the cathode with tetraethylene glycol dimethyl ether, and removing the solvent under vacuum. For ex-situ XRD, SEM, and XPS tests, the
electrodes were covered by a layer of Kapton film before moving them from the glove box to the outside instruments.

*Rotating disk electrode tests:* Rotating disk electrode (RDE) tests were performed using a computer-controlled potentiostat (Princeton 2273 and 616, Princeton Applied Research) in a conventional three-electrode cell at room temperature. The glassy carbon (GC) working electrode (0.196 cm\(^{-1}\)) was first polished with alumina powder, rinsed with deionized water, and sonicated, first in ethanol and then in double-distilled water. A platinum wire and Ag/AgCl (filled with saturated KCl aqueous solution) were used as the counter and reference electrodes, respectively. Typically, the catalyst was redispersed in deionized water + isopropanol + 5% Nafion\(^\circledast\) (v/v/v = 4/1/0.05) to form a homogeneous catalyst ink with a concentration of 2 mg mL\(^{-1}\). Then, 30 μL of this dispersion was pipetted onto the surface of the GC working electrode and dried under ambient conditions. For comparison, commercial Pt/C (20 wt. % Pt on Vulcan XC-72) catalyst ink was also obtained by the same method described above. Linear sweep voltammograms (LSVs) to measure the ORR performance were collected in O\(_2\) saturated 0.1 M KOH solution with different rotation speeds from 400 to 1600 rpm from -0.9 − 0.1 V with a scan rate of 10 mV s\(^{-1}\), while OER plots were obtained in Ar atmosphere from 0.1 − 0.9 V with a scan rate of 10 mV s\(^{-1}\) and a rotation speed of 1600 rpm.

Koutecky-Levich (K-L) plots show the inverse current density (j\(^{-1}\)) as a function of the inverse of the square root of the rotation speed (ω\(^{-1/2}\)) at different potentials. The number of electrons involved per O\(_2\) in the ORR was determined by the Koutecky-Levich equation:\(^{[8a, 28]}\)

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \tag{6.1}
\]
where \( j, j_k \), and \( j_d \) are the measured, the kinetically controlled, and the diffusion controlled current densities, respectively, and \( \omega \) is the electrode rotation rate. \( B \) is determined from the slope of the K-L plot based on the Levich equation:

\[
B = 0.2nF(Do_2)^{2/3}v^{-1/6}Co_2
\]

where \( n \) represents the number of electrons gained per O\(_2\), \( F \) is the Faraday constant \((F = 96485 \text{ C mol}^{-1})\), \( Do_2 \) is the diffusion coefficient of O\(_2\) in 0.1 M KOH \((1.9 \times 10^{-5} \text{ cm}^2 \text{s}^{-1})\), \( v \) is the kinetic viscosity \((0.01 \text{ cm}^2 \text{s}^{-1})\), and \( Co_2 \) is the bulk concentration of O\(_2\) \((1.2 \times 10^{-6} \text{ mol cm}^{-3})\).

## 5.7 Results and Discussion

### 5.7.1 Structure and morphology

The preparation process for the 3D Co\(_3\)O\(_4\) HPNT was illustrated (Figure 6.1). Firstly, PPy nanofibers were prepared via a polymerization method. Next, Co\(_3\)O\(_4\)/PPy precursor was achieved by a hydrothermal reaction at 150 °C for 3 h\(^{241, 285}\), in which PPy nanofibers were uniformly dispersed in a mixed solvent of distilled water and ethanol with cobalt (II) acetate dissolved. Finally, the Co\(_3\)O\(_4\)/PPy precursor was heated at 450 °C for 6 h in air atmosphere to obtain the 3D hierarchical porous Co\(_3\)O\(_4\) nanotube (Co\(_3\)O\(_4\) HPNT) network.
Figure 0.1 Schematic illustration of the fabrication of Co₃O₄ HPNT network.

A scanning electron microscope (SEM) image of PPy shows that PPy features a homogeneous cross-linked nanofibrous web structure, with the diameters of the nanofibers in the range of 80-90 nm (Figure 6.2a). After the hydrothermal reaction, the Co₃O₄ coating on the PPy nanofibers keeps the nanofibrous web structure (Figure 6.2b), except that the surfaces of the fibers become rough and are decorated with a uniform layer of Co₃O₄ nanoparticles. Such small Co₃O₄ particles are attributed to NH₃ coordination with cobalt cations, which tends to reduce particle size ⁴⁰, ²³⁴. The low magnification SEM image of the as-prepared Co₃O₄ HPNT shows a 3D cross-linked net structure consisting of homogeneous nanotubes approximately 100 nm in diameter (Figure 6.2c). The tubular structure is definitely attributed to the complete burning of PPy fiber. Numerous pores between the small Co₃O₄ nanocrystals on the walls of the tubes can be observed from the high magnification SEM image (Figure 6.2d).
transmission electron microscope (TEM) image shows the apparent tubular structure of the as-prepared Co₃O₄, in which the wall thickness of the tube is about 10 nm (Figure 6.2e). Furthermore, obvious mesopores about 4 nm in size on the nanowalls can be clearly observed (Figure 6.2f). Note that the particle size (~10 nm) of the Co₃O₄ HPNT is slightly larger than that in the Co₃O₄/PPy composite, which may be due to the crystal growth during the heat treatment. Co₃O₄ nanoparticles (Co₃O₄ NP) prepared without the PPy nanofiber template was used as a control, from which serious agglomeration of nanoparticles can be clearly observed (Figure 6.3). The nanotube consists of several Co₃O₄ nanoparticles connected tightly to each other with the typical interplanar spacings of 0.28, 0.24, and 0.2 nm, consistent with the d-spacing of the (220), (311), and (400) crystal planes of spinel phase Co₃O₄, respectively (Figure 6.2g). The indexed diffraction rings in the selected area electron diffraction (SAED) pattern also confirmed the spinel phase of Co₃O₄ (Figure 6.2h). Several typical diffraction peaks of the (220), (311), (400), (511), and (440) planes, assigned to spinel Co₃O₄ (JCPDS 43-1003), can be observed both from the X-ray diffraction (XRD) patterns of the Co₃O₄ HPNT and the Co₃O₄/PPy precursor (Figure 6.2i).
Figure 0.2 Physical characterization. (a) SEM image of the PPy nanofibers; (b) SEM image of the nanofibrous Co$_3$O$_4$/PPy with inset TEM image, inset bar: 100 nm; (c-d) SEM and (e-f) TEM images of Co$_3$O$_4$ HPNT network; (g) High magnification TEM image of Co$_3$O$_4$ HPNT network, (h) SAED pattern of Co$_3$O$_4$ HPNT network, and (i) XRD patterns of nanofibrous Co$_3$O$_4$/PPy and Co$_3$O$_4$ HPNT network.
Figure 0.3 SEM image of Co$_3$O$_4$ nanoparticles (Co$_3$O$_4$ NP).

Figure 0.4 (a) N$_2$ adsorption-desorption isotherms and (b) pore size distribution of the as-prepared Co$_3$O$_4$ HPNT network, with the inset showing an enlargement of the indicated range.
Figure 0.5 TGA plots of the Co$_3$O$_4$/PPy precursor and the as-prepared Co$_3$O$_4$ HPNT network.

The N$_2$ adsorption-desorption isotherms and the pore-size distribution of the as-prepared Co$_3$O$_4$ HPNT are characterized (Figure 6.4). The nitrogen sorption curves exhibit the combined characteristics of type II/IV, according to the International Union of Pure and Applied Chemistry (IUPAC) classification$^{29}$, with a specific surface area of 38.1 m$^2$ g$^{-1}$ and a total pore volume of 0.43 cm$^3$ g$^{-1}$. The H1 hysteresis loop in the relative pressure ($P/P^0$) range of 0.6-1.0 is indicative of mesoporosity$^{287}$. The pores in size of 3.8 nm are attributed to the interspace voids between the Co$_3$O$_4$ nanoparticles on the tube, which is well consistent with the TEM (Figure 6.2f). The pores of 96 nm in size correspond to the internal diameter of the Co$_3$O$_4$ nanotubes due to the pyrolysis of the PPy nanofibers. The specific surface area of the Co$_3$O$_4$ NPs was measured to be 29.8 m$^2$ g$^{-1}$, much lower than that of the Co$_3$O$_4$ HPNT network. Thermogravimetric (TGA) measurements of the Co$_3$O$_4$/PPy precursor in air atmosphere (Figure 6.5) show that all the mass loss from PPy took place below 450 °C, 450 °C was then chosen for heating.
the Co$_3$O$_4$/PPy precursor. The as-obtained Co$_3$O$_4$ HPNT shows no mass loss in the TGA plot, indicating that no PPy is remained in the target Co$_3$O$_4$ HPNT network product.

### 5.7.2 Electrochemical characterization

![Electrochemical characterization](image)

Figure 0.6 Linear sweep voltammetry (LSV) curves at various rotation speeds in O$_2$-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s$^{-1}$ in the potential range of -0.9-0.1 V (vs. AgCl/Ag) for (a) commercial 20 wt.% Pt/C, (b) the Co$_3$O$_4$ HPNT network, and (c) Co$_3$O$_4$ NP. (d) Calculated electron transfer numbers of the Co$_3$O$_4$ HPNT, Co$_3$O$_4$ NP and 20% Pt/C from the LSV curves.
Figure 0.7 (a) Linear sweep voltammetry (LSV) curves of commercial 20 wt.% Pt/C, the \( \text{Co}_3\text{O}_4 \) HPNT network, and \( \text{Co}_3\text{O}_4 \) NP in \( \text{O}_2 \)-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s\(^{-1}\) in the potential range of -0.9-0.1 V (vs. AgCl/Ag). (b) Tafel plots showing the potential for commercial 20 wt.% Pt/C, the \( \text{Co}_3\text{O}_4 \) HPNT network, and \( \text{Co}_3\text{O}_4 \) NP as a function of the log of the kinetic current density, based on the data from (a). (c) Oxygen evolution curves for the commercial 20 wt.% Pt/C, \( \text{Co}_3\text{O}_4 \) HPNT network, and \( \text{Co}_3\text{O}_4 \) NP in the potential range of 0.1-0.9 V (vs. AgCl/Ag). (d) Cyclic voltammograms of the as-prepared \( \text{Co}_3\text{O}_4 \) HPNT network, \( \text{Co}_3\text{O}_4 \) NP, and KB acquired at a scan rate of 10 mV s\(^{-1}\) in 0.2 M LiCF\(_3\)SO\(_3\)/TEGDME electrolyte.

Electrochemical measurements of the as-prepared \( \text{Co}_3\text{O}_4 \) HPNT and \( \text{Co}_3\text{O}_4 \) NP were carried out on a rotating disk electrode (RDE) in 0.1 M KOH solution at a scan rate of 10 mV s\(^{-1}\). Standard commercial Pt/C (20 wt% Pt on Vulcan XC-72 carbon) was also tested for comparison. Linear sweep voltammetry (LSV) curves at various rotation
speeds in the potential range of -0.9 - 0.1 V (vs. AgCl/Ag) in O₂-saturated atmosphere were collected to determine the ORR kinetic performance of the samples (Figure 6.6). As shown in the LSV curves (Figure 6.7a), compared with the Co₃O₄ NP, the Co₃O₄ HPNT network shows a slightly more positive onset potential and a higher reduction current density, indicating its higher ORR activity. Electron transfer number of the Co₃O₄ HPNT reached 3.5, it is much higher than that of the Co₃O₄ NP with 2.6 (Figure 6.6d), but a bit lower than commercial 20% Pt/C, which offers a 4e⁻ oxygen reduction reaction, suggesting that the Co₃O₄ HPNT delivers a more efficient electron transfer process. The Tafel plots of the measured potential vs. specific ORR activity (Figure 6.7b), indicate that the ORR activity of the Co₃O₄ HPNT network is definitely better in terms of a smaller Tafel slope (~ 175 mV per decade) than that of the Co₃O₄ NP (~ 230 mV per decade). We also extended the potential to 0.9 V (vs. AgCl/Ag) to the water oxidation regime and evaluated the electrocatalytic OER activities of the above samples. The electrocatalytic OER plots (Figure 6.7c) demonstrates that the Co₃O₄ HPNT network offers a higher current density than commercial Pt/C, with a value of more than 12 mA cm⁻² and an onset potential of 0.7 V vs. AgCl/Ag, suggesting strong OER activity of the Co₃O₄ HPNT network in the aqueous system. The above electrochemical evaluations prove that the Co₃O₄ HPNT network possesses powerful bifunctional electrocatalytic activities towards both the ORR and the OER. This is because the fundamental features of the ORR and OER processes in aqueous and non-aqueous electrolytes share similarities, which will provide some enlightenment for developing efficient catalysts when shifting Li-O₂ batteries from aqueous to non-aqueous systems. To certify this, the as-prepared Co₃O₄ HPNT network, Co₃O₄ NP, and Ketjen Black (KB) catalyst were then subjected to steady-state cyclic voltammetry (CV) within a potential window of 2.35 - 4.35 V (vs. Li⁺/Li) in
O₂-saturated 0.2 M LiCF₃SO₃ in tetrathylene glycol dimethyl ether (TEGDME) at a scan rate of 10 mV s⁻¹ (Figure 6.7d). Compared with the Co₃O₄ NP and KB, the as-prepared Co₃O₄ HPNT network exhibits obviously more apparent ORR and OER peaks in the O₂-saturated non-aqueous electrolyte, which indicates that the Co₃O₄ HPNT network features bifunctional catalyst performance during the anodic and cathodic scan processes.

Figure 0.8 (a) Initial discharge-charge plots of the as-prepared Co₃O₄ HPNT network, Co₃O₄ NP, and KB cathodes in lithium-oxygen batteries at a current density of 25 μA cm⁻² in 1 M LiCF₃SO₃/TEGDME, with a voltage window of 2.35-4.35 V (vs. Li⁺/Li). (b) Initial discharge/charge plots of the Co₃O₄ HPNT network, Co₃O₄ NP, and KB cathodes in lithium-oxygen batteries at a current density of 25 μA cm⁻² in 1 M LiCF₃SO₃/TEGDME with discharge/charge capacities fixed at 1000 mAh g⁻¹. Representative discharge/charge curves of (c) as-prepared Co₃O₄ HPNT network, (d) Co₃O₄ NP, and (e) KB under a capacity limit of 1000 mA h g⁻¹ at a current density of 25
μA cm\(^{-2}\) in 1 M LiCF\(_3\)SO\(_3\)/TEGDME. (f) The corresponding terminal discharge voltage of the Co\(_3\)O\(_4\) HPNT network, Co\(_3\)O\(_4\) NP, and KB under a capacity limit of 1000 mA h g\(^{-1}\) at a current density of 25 μA cm\(^{-2}\) in 1 M LiCF\(_3\)SO\(_3\)/TEGDME.

The electrochemical properties of the as prepared Co\(_3\)O\(_4\) HPNT network were studied in a coin-type lithium-oxygen cell using O\(_2\)-saturated 1.0 M LiCF\(_3\)SO\(_3\) in TEGDME. Co\(_3\)O\(_4\) NP and Ketjen Black (KB) were also investigated as controls. All the capacities reported in this work are normalized by the mass of active material and the carbon used in the cathodes. The initial galvanostatic discharge/charge curves of a lithium oxygen battery with a Co\(_3\)O\(_4\) HPNT network cathode and those of Co\(_3\)O\(_4\) NP and KB cathodes at a current density of 25 μA cm\(^{-2}\) from 2.35 to 4.35 V (vs. Li\(^+\)/Li) were measured (Figure 6.8a). Clearly, the lithium oxygen battery with the as-prepared Co\(_3\)O\(_4\) HPNT network cathode yields the largest discharge/charge capacity of 4299/4164 mAh g\(^{-1}\) compared with the other two cathodes, and in particular, the charge overpotential is much reduced to 99 mV from 125 mV for the Co\(_3\)O\(_4\) NP and 111 mV for the KB cathode, showing that the as-prepared Co\(_3\)O\(_4\) HPNT network cathode has the highest reversible discharge/charge characteristics compared to the Co\(_3\)O\(_4\) NP and KB cathodes.

The initial discharge/charge curves of the Co\(_3\)O\(_4\) HPNT network, Co\(_3\)O\(_4\) NP, and KB cathodes with a fixed capacity of 1000 mAh g\(^{-1}\) at a current density of 25 μA cm\(^{-2}\) were tested (Figure 6.8b), from which the lowest discharge/charge overpotential can also be observed for the Co\(_3\)O\(_4\) HPNT network cathode. The typical selected discharge/charge profiles with a fixed capacity of 1000 mAh g\(^{-1}\) at a current density of 25 μA cm\(^{-2}\) of the as-prepared Co\(_3\)O\(_4\) HPNT (Figure 4c), Co\(_3\)O\(_4\) NP (Figure 6.8d), and KB (Figure 6.8e) cathodes demonstrate a lower discharge/charge overpotential at each cycle and rather stable discharge/charge profiles for the Co\(_3\)O\(_4\) HPNT network cathode. The terminal
discharge voltages for each cycle of the above three cathodes at a fixed discharge/recharge capacity of 1000 mAh g⁻¹ is shown (Figure 6.8f). The discharge/charge profiles from the 1ˢᵗ to the 20ʰ cycle for the Co₃O₄ HPNT network cathode almost overlap (Figure 6.8c), and the specific capacity suffers no loss, with terminal discharge/charge voltages of 2.71/4.11 V after 20 cycles and 2.22/4.56 V after 40 cycles, respectively. The terminal discharge voltage becomes lower than 2 V after 28 cycles, however, for the Co₃O₄ NP cathode and 15 cycles for the KB cathode with such a capacity limitation. From the comparison of the above results for the as-prepared Co₃O₄ HPNT network, Co₃O₄ NP, and KB cathodes, it is believed that the as-prepared 3D hierarchical porous nanotube network with Co₃O₄ nanocrystals connected to each other on the tube surface can create a substantial amount of tri-phase and reaction sites for the Li₂O₂ formation and meanwhile provide sufficient deposition space for Li₂O₂. In addition, Co₃O₄ can take full advantage of its intrinsic catalytic activity, leading to improved ORR and OER performance.

5.7.4 Analysis of the discharge/charge product

The XRD patterns of the as prepared Co₃O₄ HPNT network cathode in different states for the first cycle between 2.35-4.35 V (vs. Li⁺/Li) and the recharge state after 40 cycles at a fixed capacity of 1000 mAh g⁻¹ with a current density of 25 μA cm⁻² are shown (Figure 6.9a). As compared with the XRD pattern of the fresh electrode, two new diffraction peaks appear in the discharged cathode, which could be reasonably assigned to the (100) and (101) peaks of crystalline Li₂O₂ (as highlighted in Figure 6.9a)²⁷⁷. These two peaks disappear when the battery is recharged to 4.35 V, suggesting almost complete decomposition of the Li₂O₂ during the recharge process. Only peaks
attributable to Co$_3$O$_4$ can be found in the XRD pattern of the as-prepared Co$_3$O$_4$ HPNT network cathode after 40 fixed capacity cycles, further evidencing the highly stable catalytic activity of the as-prepared Co$_3$O$_4$ HPNT network as the catalyst.

Figure 0.9 (a) XRD patterns of the Co$_3$O$_4$ HPNT network cathode at different discharge/charge stages, (b) Li 1s XPS spectra of the Co$_3$O$_4$ HPNT network cathode at different discharge/charge stages.

The Li 1s spectra of the 1$^{st}$ cycle discharged, 1$^{st}$ cycle recharged, and 40$^{th}$ cycle recharged states with a fixed capacity of 1000 mAh g$^{-1}$ for the as-prepared Co$_3$O$_4$ HPNT network cathode (Figure 6.9b) are well consistent with the XRD results discussed above, where the peak at 54.6 eV can be assigned to the Li–O bond of Li$_2$O$_2$ after the 1$^{st}$ discharge $^{31, 255-257}$. Upon charging, the Li 1s peak at 54.6 eV corresponding to Li$_2$O$_2$ disappears, and no other peaks are left, showing almost complete decomposition of Li$_2$O$_2$. After the 40$^{th}$ cycle recharge, an obvious Li–O bond of the Li$_2$CO$_3$ signal appears in the X-ray photoelectron spectroscopy (XPS) spectrum $^{31}$. Although TEGDME is reported to be more stable compared with other organic solvents, ether-based electrolyte decomposition still occurs $^5$. According to published reports, ether-based electrolyte is
prone to auto-oxidation under oxygenated radicals, and decomposition occurs at voltages higher than 4 V, leading to the formation and accumulation of non-reversible reaction products\textsuperscript{5,189}.

Figure 0.10 (a) Typical initial discharge/recharge curves of Co\textsubscript{3}O\textsubscript{4} HPNT network cathode at a current density of 25 $\mu$A cm\textsuperscript{-2} in the voltage range of 2.35-4.35 V (vs. Li$^+$/Li) with (b), (c), (d), (e), and (f) stages. (b-f) SEM images of Co\textsubscript{3}O\textsubscript{4} HPNT network cathode corresponding to (b), (c), (d), (e), and (f) stages in (a), respectively. (g) Schematic illustration of the Co\textsubscript{3}O\textsubscript{4} HPNT cathode in the Li-O\textsubscript{2} battery system.

The Co\textsubscript{3}O\textsubscript{4} HPNT network cathode was monitored during the discharging and charging processes at a current density of 25 $\mu$A cm\textsuperscript{-2}, using ex-situ scanning electron microscopy.
(SEM) (Figure 6.10b-f), corresponding to the states (b-f) in Figure 6.10a. The fresh Co$_3$O$_4$ HPNT network cathode (Figure 6b) reveals a porous morphology because of the web-like Co$_3$O$_4$ nanotubes with KB particles aggregated on the surfaces of the nanotubes. When the Co$_3$O$_4$ HPNT network cathode is discharged to 1500 mAh g$^{-1}$, a small amount of film consisting of the discharge product Li$_2$O$_2$ grown on the cathode surface can be observed (Figure 6c). When the discharge voltage goes down to 2.35 V, there is a large amount of porous Li$_2$O$_2$ discharge product, consisting of many nanofilms that completely cover the cathode (Figure 6d). It is noteworthy that the Li$_2$O$_2$ discharge product formed on the catalytic Co$_3$O$_4$ HPNT network cathode is in sharp contrast to the conventional toroidal 97, 256, 290-292 or plate 293 morphology of the Li$_2$O$_2$ discharge product. Nazar et al. 292 found that large toroidal-shaped crystalline Li$_2$O$_2$ tends to form at low current densities, while higher current densities favor film formation of Li$_2$O$_2$. Zhang et al. 255, however, reported that the film-like Li$_2$O$_2$ with low crystallinity may contain many defects (for example, lithium vacancies) that facilitate electron transportation and especially ion conduction, thus reducing the charge overpotential 294, 295, which further explains the much reduced charge overpotential of the as-prepared Co$_3$O$_4$ HPNT network cathode. When the Li-O$_2$ battery with the Co$_3$O$_4$ HPNT network cathode was recharged to the capacity of 3000 mAh g$^{-1}$, only a little film-like Li$_2$O$_2$ was left, as shown in Figure 6e. All the discharge products disappear when the Li-O$_2$ battery is fully charged to 4.35 V. Also, the porous and 3D web-like nature of the Co$_3$O$_4$ HPNT network cathode is regained (Figure 6.10f), similar to the fresh one in Figure 6.10b, indicating the reversible reaction of Li$_2$O$_2$. Schematic illustration of the Co$_3$O$_4$ electrode (Figure 6.10g), in which carbon particles (Ketjen Black) dispersed in Co$_3$O$_4$ nanoweb ensuring rapid charge transfer. Macropores between Co$_3$O$_4$ nanotubes facilitate high O$_2$ transportation whereas nano- and
meso-pores in the Co$_3$O$_4$ HPNT provide quantities of active catalytic sites and benefit electrolyte wetting. Combined with sufficient triple-phase sites, porous Li$_2$O$_2$ consisting of nano films grows uniformly on the surface of the cathode after the discharging process and disappears after the charging process. Since Li-O$_2$ batteries are still in their infancy stage, further research efforts, including in-situ TEM observations, should be devoted to clarifying the effects of the morphology of Li$_2$O$_2$ on the discharging/charging process of Li-O$_2$ batteries.

Figure 0.11 Electrochemical impedance spectroscopy (EIS) plots of the as-prepared Co$_3$O$_4$ HPNT network in fresh, 1$^{st}$ cycle discharged, 1$^{st}$ cycle recharged, and 40$^{th}$ cycle recharged states.

Electrochemical impedance spectroscopy (EIS) tests of the as-prepared Co$_3$O$_4$ HPNT network cathode at different discharge/recharge stages (Figure 6.11) were performed to further identify the discharge and recharge characteristics. A larger charge-transfer resistance is observed after the first discharge compared with the fresh electrode due to
the formation of Li$_2$O$_2$, which has high electrical resistivity and is hypothesized to prevent the transfer of electrons$^{296}$. After the battery was recharged, however, the charge-transfer resistance of the Co$_3$O$_4$ HPNT network electrode was little changed compared with the fresh state, suggesting reversible reaction product formation and decomposition. The charge-transfer resistance increases again after the 40$^{th}$ recharge due to the formation and accumulation of non-reversible reaction products$^{5,189}$, which is well consistent with the results of XRD and the field emission SEM image in Figure 5 and Figure 6, respectively. This provides electrochemical evidence that the as-prepared Co$_3$O$_4$ HPNT network can effectively catalyze both the ORR and OER reactions in rechargeable lithium-oxygen batteries.

5.8 Conclusions

In summary, this work describes a facile and large-scale approach to the fabrication of a 3D hierarchical porous Co$_3$O$_4$ nanotube (HPNT) network by using polypyrrole nanofiber as the sacrificial template. The as-prepared 3D Co$_3$O$_4$ HPNT network demonstrated superior bifunctional electrocatalytic activity towards both the ORR and the OER when employed as the catalyst in non-aqueous lithium oxygen batteries, as compared to Co$_3$O$_4$ nanoparticles (Co$_3$O$_4$ NP) and Ketjen Black (KB) catalysts. The Li-O$_2$ battery based on Co$_3$O$_4$ HPNT network cathode shows a relative low charge overpotential of 99 mV and high discharge/charge capacity of 4164/4299 mAh g$^{-1}$, as well as a long lifespan of 40 cycles at a fixed capacity of 1000 mA g$^{-1}$. These encouraging results may provide insights into the use of polymer nanofiber as new template to develop 3D porous tubular structured catalyst for Li-O$_2$ batteries on a large scale and in a rapid way.
CHAPTER 7 FACILE FABRICATION OF SILVER
NANOCRYSTALS ENCAPSULATED IN NITROGEN-DOPED
CARBON FIBERS AS EFFICIENT CATALYST FOR LITHIUM
OXYGEN BATTERIES

6.1 Preface

Nonaqueous rechargeable Li-O₂ batteries have emerged as a major candidate for future alternative energy storage since they were first introduced ¹², ¹⁸⁶, ²⁹⁷. They have aroused worldwide scientific attention because of their ultrahigh energy density, which is almost ten times that of traditional Li-ion batteries and their relatively simple configuration ³², ³⁶. Typically, three essential components are included in nonaqueous Li-O₂ battery: (1) a metallic lithium anode, (2) a porous cathode (usually carbon-based materials with or without catalysts), and (3) a nonaqueous electrolyte (Li⁺-containing solution) in between. So far, exploration of the Li-O₂ battery is still in its infancy, because several critical challenges have hindered its market application ²⁰, ³⁹, ¹⁴⁶. Among them, the huge polarization during charging, with a typical 1-2 V voltage gap between the charge and discharge, is the most urgent one to be addressed. The large polarization, arising from the sluggish kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reduction (OER), will also induce irreversibility and cause poor cycling stability in the Li-O₂ battery. The electrolyte is another key problem causing performance decay due to its instability against oxygen radicals ⁵, ¹⁷, ²¹, ¹⁶³. Fortunately at present, certain electrolytes, e.g. tetraethylene glycol dimethyl ether (TEGDME) and dimethyl sulfoxide (DMSO), appear to be relatively stable and can support the reversible formation and decomposition of Li₂O₂ against oxygen radicals ²³, ³³, ²⁷⁷, ²⁹⁸.
In addition to a stable electrolyte, the optimized cathode architecture and the chosen efficient catalyst are crucial for determining the kinetics of the ORR and OER. In general, a highly conductive cathode structure with large surface area is most desirable to facilitate rapid electron and mass transportation. Many experimental and computational studies have demonstrated exciting performances of nitrogen-doped carbon (N-C) materials as cathode materials for Li-O_2 batteries. Nitrogen doping is well known to induce beneficial changes in both the electronic and the structural properties of carbon materials. When N atoms are doped into carbon lattices, the electronic and geometric structures of the carbon are significantly modified. The incorporation of electron-accepting nitrogen atoms in the conjugated nanotube carbon planes will impart a relatively high positive charge density on adjacent carbon atoms in nitrogen-doped carbon nanotubes, leading to high electrocatalytic activity for the ORR. Very recently, it was reported that pyridinic N in nitrogen-doped carbon materials have the ability to create ORR active sites and exhibit high electrocatalytic activity toward the ORR for fuel cell applications, because the doping process leads to non-uniform distributions of the spin and atomic charge densities, which is very important for oxygen adsorption and activity enhancement. Since the ORR in aqueous and nonaqueous electrolytes shares some similarities in the process for adsorbing O_2, many researchers have discovered that pyridinic N in carbon is also beneficial for the ORR in the nonaqueous Li-O_2 battery system from both experimental observations and computational investigation. In addition, fibrous carbon materials are more favourable for efficient electron and oxygen transportation. The coexistence of active N sites on the carbon skeleton favours Li⁺ diffusion and electrolyte immersion.
Apart from the N-Carbon matrix, great efforts have been made in searching for an efficient catalyst to further mitigate the discharge/charge polarization in Li-O\textsubscript{2} batteries. Silver crystal, as a less precious catalyst compared with Pt, Pd, or Ru-based catalysts, is one promising alternative\textsuperscript{138-140}. It has been proposed that the optimal metal-oxygen interaction strength is a critical criterion for evaluating a Li-ORR electrocatalyst. The interaction of Ag and O atoms is a bit lower than for Pt or Pd metal with O, although Ag outperforms Au and Ru metal\textsuperscript{306}. Taking the trade-off between cost and performance into account, Ag decoration on an N-C matrix should be a smart choice as a promising catalyst for the Li-O\textsubscript{2} battery.

In this work, we propose a rather facile approach to the synthesis of Ag nanocrystals encapsulated in N-doped carbon fibers (Ag/NCFs). A cable consisting of Ag encapsulated in polypyrrole (PPy) was fabricated as precursor. It has been reported that Ag\textsuperscript{+} has the ability to polymerize pyrrole monomer, and meanwhile, Ag\textsuperscript{+} would be reduced to Ag\textsuperscript{0}\textsuperscript{307,308}. This is based on the following principles: FeCl\textsubscript{3} is usually used as the oxidizing agent for PPy synthesis. The standard reduction potential of Fe\textsuperscript{3+} to Fe\textsuperscript{2+} is 0.771 V. The standard reduction potential of Ag\textsuperscript{+} to Ag is 0.800 V. Inspired by the above concept, we designed a one-pot synthesis for Ag/PPy cable with methyl orange (MO) as additive to stabilize the cable structure. In previous reports, fabrication of metal/N-C composite usually involved initial preparation of the NC matrix, followed by either a complicated heat-reflux operation or thermal reduction under a protective atmosphere to obtain elemental metal\textsuperscript{309,310}. In this work, the Ag crystal is synchronously introduced in the process of PPy fabrication. Meanwhile, the introduction of Ag crystals into the NCF facilitates the kinetics of the ORR and OER. A much reduced discharge/charge gap of 0.89 V was achieved for Ag/NCF compared with
1.38 V for NCF cathode. The as-acquired favorable electrocatalytic results probably benefit from the perfect synergistic effects between the NCF matrix and the encapsulated Ag nanocrystals, in which the former acts as a highly electrically conductive web to facilitate efficient electron transfer, while the latter offer highly catalytic sites.

6.2 Experimental

6.2.1 Preparation of Ag/NCF Composites

N-C fiber (NCF): 16.3 mg methyl orange (MO) was dispersed in 25 mL deionized water, followed by the addition of 3.61 mmol FeCl₃. Then, 83.3 μL pyrrole (Py) monomer was added into the above dispersion, and the mixture was stirred at room temperature for 36 h. The thus-formed precipitate was washed with deionized water/ethanol several times until the filtrate was colourless and neutral, and it was then dried under vacuum at 60 °C for 12 h. Finally, the dried precipitate was heated to 600 °C and kept for 2 h to obtain the nitrogen doped carbon fiber, which was denoted as NCF.

Ag/N-C fiber (Ag/NCF): 16.3 mg methyl orange (MO) was dispersed in 25 mL deionized water, followed by the addition of 1.2 mmol AgNO₃. Then, 83.3 μL pyrrole (Py) monomer was added into the above dispersion and the mixture was stirred at room temperature for 36 h. The thus-formed precipitate was washed with deionized water/ethanol several times until the filtrate was colourless and neutral, and it was finally dried under vacuum at 60 °C for 12 h to obtain the Ag/PPy precursor. The
precursor was heated to 600 °C and kept for 2 h to promote encapsulation of the Ag crystals in the nitrogen-doped carbon cables, with the product denoted as Ag/NCF.

*Ag/N-C particles:* The same procedure as for the preparation of Ag/N-C, except for the absence of methyl orange.

### 6.2.2 Physical Characterization

X-ray diffraction (XRD) (GBC MMA) patterns were collected over a 2θ range of 20°-70 ° with a scan rate of 4° min⁻¹ and analyzed with Traces™ software in combination with the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction files. The morphologies of the samples were examined by field emission scanning electron microscopy (FE-SEM, JEOL 7500) and transmission electron microscopy (TEM, JEOL ARM-200F). The XPS data were analyzed using CasaXPS software, and all the results were calibrated by C 1s at 284.6 eV for graphite. Thermogravimetric analysis (TGA) was carried out using a SETARAM Thermogravimetric Analyzer (France). Raman spectroscopy was conducted on a JOBIN YVON HR800 Confocal system with 632.8 nm diode laser excitation using a 300 lines mm⁻¹ grating.

### 6.2.3 Electrochemical Measurements

The electrochemical performances of lithium oxygen batteries were investigated using 2032 coin-type cells with air holes on the cathode side. For the preparation of the porous cathode electrode, 80 wt % NCF or Ag/NCF, 10 wt % Ketjen Black (KB), and 10 wt % poly(1,1,2,2-tetrafluoroethylene) (PTFE) (60% dispersion) were mixed in an isopropanol solution. The resulting homogeneous slurry was coated onto carbon paper. After that, the electrodes were dried at 120 °C in a vacuum oven for 12 h. All the
lithium oxygen batteries were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) with both water and oxygen contents below 0.1 ppm. The batteries contained lithium metal foil as the counter electrode, a glass fiber separator (Whatman GF/D), 1 M LiCF$_3$SO$_3$ dissolved in tetraethylene glycol dimethyl ether (TEGDME) as the electrolyte, and the air cathode.

electrode. All the assembled coin cells were stored in an O$_2$-purged chamber, which was connected to a LAND CT 2001 A multi-channel battery tester 2 h before each test. The galvanostatic discharge-charge tests were then conducted on the battery testing system with the voltage between 2.35-4.25 V (vs. Li$^+$/Li). All the capacities reported in this work are normalized by the mass of active material in the cathodes. The loading amount in each cathode is approximately 0.6 mg cm$^{-2}$.

The non-aqueous electrochemical oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) tests were carried out using computer-controlled potentiostats (Princeton 2273) in a three-electrode system using Pt foil as the counter electrode, AgCl/Ag as the reference electrode, and a working electrode consisting of sample-coated glassy carbon (GC). A solution of 0.5 M LiCF$_3$SO$_3$/TEGDME was used as the electrolyte. In detail, argon was introduced into the electrolyte for 30 min to ensure that the background data was measured in an inert atmosphere. Then, pure oxygen was bubbled into the electrolyte for 30 min to study the ORR.

Examination of the discharged and recharged electrodes involved disassembling the cell in the glove box, rinsing the cathode with tetraethylene glycol dimethyl ether, and removing the solvent under vacuum. For ex-situ XRD, SEM, FTIR, and XPS
observations, the electrodes were covered by a layer of Kapton film before moving from the glove box to the outside instruments.

6.3 Results and Discussion

6.3.1 Formation mechanism of Ag/NCF

Figure 6.1 Schematic representation of the synthesis process for the Ag/NCF and Ag/NC bulk.

As illustrated (Figure 7.1), typical amounts of methyl orange (MO) and FeCl₃ were dissolved in aqueous solution. Afterwards, a fixed amount of pyrrole monomer was added, and the fibrous structured precursor PPy was formed with the fibre diameters approximately 250 nm, which is shown in Figure 7.2a. When AgNO₃ is substituted for FeCl₃, a fibrous precursor Ag/PPy was also achieved (Figure 7.2b) with more or less the same size as the precursor without Ag⁺. As described in the introduction, Ag⁺ has the ability to polymerize pyrrole monomer, while itself being reduced to Ag. It has been reported that methyl orange (MO) and FeCl₃ can form a fibrillary complex as a reactive seed template during polypyrrole polymerization ⁴ⁱ. Here FeCl₃ is replaced by AgNO₃. We speculate therefore that the formation of fibrous structured Ag/PPy resulted from
the adoption of methyl orange (MO). The contrast is that bulk Ag/PPy was precipitated without the presence of MO (Figure 7.2c). To confirm the formation of Ag and PPy, XRD and Raman measurements were conducted on the fibrous precursor PPy, fibrous precursor Ag/PPy, and bulk precursor Ag/PPy. The Raman spectra show characteristic Raman modes of PPy (Figure 7.3a), confirming the formation of PPy in the three precursors. Several strong typical diffraction peaks for the (111), (200), (220), and (311) reflections due to the face-centred cubic structure of Ag (JCPDS file 04-0783) occur in the XRD patterns (Figure 7.3b) of fibrous precursor Ag/PPy and bulk precursor Ag/PPy, indicating the formation of Ag in these precursors. Nitrogen-doped carbon fibers (NCF) and Ag encapsulated in nitrogen-doped carbon (Ag/NCF) are obtained by heating the fibrous precursors of PPy and Ag/PPy (Figure 7.1).

Figure 6.2 FESEM images of a) polypyrrole fiber, b) Ag/polypyrrole fiber, and c) Ag/polypyrrole particles.
6.3.2 Structure and morphology characterization

The field emission SEM (FE-SEM) images demonstrate that both NC and Ag/NCF feature the fibrous morphology (Figure 7.4a-b). It can be observed from the insets in the above two images that the diameters of the fibers are more or less 250 nm. The transmission electron microscope (TEM) image of the Ag/NCF shows that Ag nanocrystals are well-embedded in the NCF, with the particle size varying from 40 nm to approximately 200 nm (Figure 7.4c). Characteristic peaks of the elements N, C, and Ag appear in the energy dispersive X-ray spectroscopy (EDS) spectrum (Figure 7.4d). To access the distribution of Ag crystals in the NCF, EDS mapping images were also captured (Figure 7.4e). The red spots in the EDS mapping image correspond to the presence of the element N, and the green spots correspond to the element C. The blue spots associated with the element Ag are distributed throughout the whole area of the composite, providing further evidence that the Ag nanoparticles are well-dispersed in the NCF. As a control, characteristic peaks of the elements N, C, and Ag are shown in the EDS spectrum of an Ag/polypyrrole particle in Figure 7.5a. In addition, EDS
mapping images (Figure 7.5b-e) were also captured, from which Ag nanoparticles were observed to be well-dispersed in the bulky nitrogen-doped carbon matrix.

Figure 6.4 FESEM image of the NCF (a) and the Ag/NCF (b), Scale bars for insets in (a) and (b) showing higher magnification: 200 nm. TEM image of the Ag/NCF (c), with the inset showing higher magnification. EDS spectrum of the Ag/NCF(d), SEM image of the selected area for SEM element mapping (e), and corresponding element mapping images of the Ag/NCF(f)-(h).
Figure 6.5 (a) EDX spectrum, (b) scanning transmission electron microscope (STEM) image, and (b)-(e) corresponding element mapping images of the Ag/NC particles.

XRD patterns of NCF and Ag/NCF consists of a broad peak near 23 °C, which is assigned to the (002) planes of carbon in NCF (Figure 7.6a)\(^{315}\). The low intensity peak indicates that the as-obtained NCF possesses low degree of graphitization, as is expected with PPy as the carbon source\(^ {316}\). Several strong typical diffraction peaks for the (111), (200), (220), and (311) reflections due to the face-centred cubic structure of Ag (JCPDS file 04-0783) in the XRD pattern of Ag/NCF\(^ {140, 314}\) indicates that the heating process had no negative effect on the Ag particles in the composite. Raman measurements were conducted to further characterize the components of the NCF and Ag/NCF, and two typical graphitic peaks in Raman spectrum (Figure 7.6b) are clearly
observed from the pure NCF and the Ag/NCF. The G-band peak at 1590 cm\(^{-1}\) is associated with E\(_{2g}\).

![Graph](image-url)

**Figure 6.6** (a) X-ray diffraction patterns for NCF and Ag/NCF, (b) Raman spectra of NCF and Ag/NCF, (c) XPS survey spectrum of the Ag/NCF, and high-resolution (d) C 1s, (e) N 1s, and (f) Ag 3d spectra.

The D-band at around 1335 cm\(^{-1}\) corresponds to the defect-induced mode\(^{317}\). The intensities of the D band are evidently stronger than those of the G band, which suggest that large amounts of defects were formed in the carbon matrix because of the incorporation of nitrogen atoms into the carbon atomic layers\(^{305}\).

X-ray photoelectron spectroscopy (XPS) spectra for C 1s, O 1s, N 1s, and Ag 3d are shown in Figure 7.6c. Figure 7.6d-f presents high-resolution XPS spectra of C 1s, N 1s, and Ag 3d in the Ag/NCF. The high-resolution XPS spectrum of C 1s (Figure 7.6d) could be deconvoluted into four individual component peaks, labelled as C-C (284.6
eV), C-N (285.3 eV), C-O (286.1 eV), and C=O (287.8 eV), respectively. Two peaks at 400.8 eV and 398.6 eV in the high-resolution XPS spectrum of N 1s (Figure 7.6e) can be assigned to pyrrolic-N and hexagonal pyridinic-N, respectively, suggesting the transformation of part of the pyrrolic-N within the five-membered rings of PPy into pyridinic-N in the NCF in the carbonization process. The XPS spectrum of Ag consists of a doublet at 369.0 eV and 375.0 eV (Figure 7.6f). The separation of 3d_{5/2} and 3d_{3/2} by 6.0 eV is in good agreement with a previous report, indicating the metallic nature of Ag in NCF.

6.3.3 Electrochemical performances on RDE

The pristine NCF and the Ag/NCF were subjected to linear sweep voltammetry (LSV) measurements on a rotating disk electrode (RDE) at a rotation speed of 1600 rpm in O_2-saturated 0.1 M KOH solution at a scan rate of 10 mV s^{-1} in the potential range of -0.9 – 0.1 V (vs. AgCl/Ag). Standard commercial Pt/C (20 wt% Pt on Vulcan XC-72 carbon) was tested as a control. The RDE curves of the Ag/NCF show a more positive onset potential and higher reduction current density, suggesting better ORR activity compared with the NCF (Figure 7.7a). The electrocatalytic OER in 0.1 M KOH solution (Figure 7.7b) demonstrates that the Ag/NCF offers a rather higher current density than the NCF and the standard commercial 20% Pt/C in the range of testing, with a value of approximately 4 mA cm^{-2} and an onset potential of 0.6 V vs. AgCl/Ag, suggesting stronger OER activity in the aqueous system. Since the fundamental features of the ORR and OER processes share similarities in aqueous and nonaqueous electrolytes, this will provide some guidance for the development of new electrocatalysts when shifting Li-O_2 batteries from aqueous to nonaqueous systems. To confirm this concept, the ORR
and OER catalytic capabilities of both the NCF and the Ag/NCF were measured in O₂-saturated 0.5 M LiCF₃SO₃/tetraethylene glycol dimethyl ether (TEGDME) electrolyte with a rotation speed of 1600 rpm (Figure 7.7c-d). It can be observed that NCF and Ag/NCF present more or less the same features during ORR process, although Ag/NCF exhibits a much higher current density than the NCF (Figure 7.7c). Enhanced OER performance for Ag/NCF in terms of a reduced overpotential and enlarged current density can also be found in Figure 7.7d. The consistency in both aqueous and non-aqueous electrolytes suggests that the Ag/NCF may play a positive role in reducing the overpotential, especially for the OER when employed as cathode in lithium oxygen batteries.

Figure 6.7 (a) Linear sweep voltammetry (LSV) curves of commercial 20 wt.% Pt/C, Ag/NCF, and NCF in O₂-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s⁻¹ in the potential range of -0.9-0.1 V (vs. AgCl/Ag) at a rotation speed of 1600 rpm;
(b) oxygen evolution curves for the commercial 20 wt.% Pt/C, Ag/NCF, and NCF in the potential range of 0.2-0.7 V (vs. AgCl/Ag); and (c) ORR and (d) OER polarization curves of Ag/NCF, and NCF on a rotating disk electrode (RDE) at a rotation speed of 1600 rpm in O₂-saturated 0.5 M LiCF₃SO₃/TEGDME at a scan rate of 10 mV s⁻¹.

6.3.4 Electrochemical performances in Li-O₂ batteries

Coin cells containing a Li foil anode and the as-prepared NCF and Ag/NCF cathodes were tested under an O₂ atmosphere. 1.0 M LiCF₃SO₃ in TEGDME was selected as the electrolyte because it was recently demonstrated to be relatively stable toward the discharge product, Li₂O₂. All the capacities reported in this work are normalized by the mass of active material used in the cathodes. The initial galvanostatic discharge-charge measurements were conducted at a current density of 100 mA g⁻¹ from 2.35 to 4.25 V (vs. Li⁺/Li) (Figure 7.8a). The first discharge plateaus for both Ag/NCF and NCF based batteries are almost identical (around 2.75 V), indicating that Ag crystal plays almost no obvious role in enhancing the ORR capability based on the NCF. It has been suggested that the ORR performance during discharge may be governed by the oxygen diffusion in the cathodes. This phenomenon agrees well with the RDE results (Figure 7.7c). During the reverse process, one charge plateau at about 4.1 V is observed for the NCF cathode, which is comparable to the performance of other reported N-doped carbon materials. Ag/NCF cathode presents two charge plateaus, however, one at a low potential of 3.5 V with the other at a higher potential of 4.1 V. It was reported that the charge overpotential is sensitive to the size of Ag particles. Aggregation of Li₂O₂ particles into rod shapes easily occurs around Ag particles with size of several hundred nm. Li₂O₂ with rod and even agglomerated shapes will cause dramatic charge
polarization, with increased overpotential of the second plateau\textsuperscript{140}. The typical initial discharge and charge profiles of the Ag/NCF and NCF electrodes with a fixed capacity of 500 mAh g\textsuperscript{-1} and a current density of 200 mA g\textsuperscript{-1} are shown in Figure 7.8b. There is a much reduced discharge/charge gap of 0.89 V, up from 1.38 V for the NCF cathode, indicating that the introduction of Ag crystals into NCF facilitates the reversible charging and discharging characteristics of the battery. The capacity-limited method has been widely used to evaluate the cycling performance of Li-O\textsubscript{2} batteries\textsuperscript{86,277}. Typical selected discharge/charge profiles of the Ag/NCF and NCF electrodes with a fixed capacity of 500 mAh g\textsuperscript{-1} at a current density of 100 mA g\textsuperscript{-1} are presented in Figure 7.8c and Figure 7.9, respectively, from which a lower charge overpotential at each cycle and rather stable discharge/charge profiles can be observed for the Ag/NCF cathode. The cycling performances of the Ag/NCF and NCF cathodes were tested under a capacity limit of 500 mA h g\textsuperscript{-1} at a current density of 100 mA g\textsuperscript{-1} with a voltage limitation of 2.5 V (Figure 7.8d). The Ag/NCF cathode features a much more stable cyclability of 32 cycles, while the NCF electrode only sustained 21 cycles with a voltage limitation of 2.5 V. The obtained improved properties of the cathode, especially the OER performance of the Ag/NCF, could be ascribed to the high electrocatalytic performance of Ag nanocrystals embedded in the NCF matrix.
Figure 6.8 (a) Initial discharge/charge plots of the Ag/NCF and NCF cathodes in lithium-oxygen batteries at a current density of 100 mA g$^{-1}$ in 1 M LiCF$_3$SO$_3$/TEGDME (2.35 - 4.25 V vs. Li$^+/Li$); (b) Initial discharge-charge plots of the Ag/NCF and NCF cathodes with a capacity limitation of 500 mAh g$^{-1}$ at a current density of 100 mA g$^{-1}$; (c) Representative discharge/charge curves for selected cycles of Ag/NCF cathode under a capacity limit of 500 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$; (d) cycling performance of the Ag/NCF and NCF cathodes under a capacity limit of 500 mA h g$^{-1}$ at a current density of 100 mA g$^{-1}$ with a voltage limitation of 2.5 V.
6.3.5 Analysis of the Discharge/Recharge Products

The initial discharged and recharged products of the Li-O₂ battery with the Ag/NCF cathode at a current density of 100 mA g⁻¹ were investigated by using *ex-situ* XRD, Raman, and FESEM measurements, in order to further understand the reaction mechanism over the whole process. As compared with the XRD pattern of the fresh electrode (Figure 7.10a), new diffraction peaks are observed from the discharged cathode. Although the peaks are weak, they could be reasonably assigned as the (100) and (101) peaks of crystalline Li₂O₂ (as highlighted in the inset)³³,³²⁰. Besides the two Li₂O₂ diffraction peaks, one weak peak assigned to LiOH was also detected, which may be ascribed to the reaction of Li₂O₂ with trace H₂O during the ex-situ tests¹⁴⁹,³²¹. The three diffraction peaks disappeared when the battery was recharged, however, which suggests that the discharge product Li₂O₂ is decomposed during the charging process. During the 1st discharge, the slight peak at approximately 800 cm⁻¹ in the Raman spectrum (Figure 7.10b) of the electrode after discharge (inset) is ascribed to O–O
stretching vibrations of lithium peroxide, further confirming the presence of lithium peroxide. The peak disappeared after the 1st recharge, the same as in the fresh state, providing evidence that Li₂O₂ was completely decomposed during the recharge process.

The Ag/NCF cathode before discharge clearly shows its fibrous structure (Figure 7.10c). Dense solids with irregular protrusions were precipitated on the surface of the fibers after the battery was fully discharged in the 1st cycle to 2.35 V (Figure 7.10d). After full charging however, this solid product disappears, and the fibrous structure of the cathode was regained after the cell was fully charged in the 1st cycle to 4.25 V (Figure 7.10e), indicating the complete decomposition of the recently-formed Li₂O₂ product. The fibrous structure of the Ag/NCF cathode is also maintained after the 30th fixed-capacity cycle (Figure 7.10f). Some sediment accumulated on some fibers can be observed, however, which may be Li₂CO₃ formed via the reaction between carbon matrix and Li₂O₂ during the cycling process. The schematic illustration shows the discharge and charge processes (Figure 7.10g). The one-dimensional (1D) NC fiber channels, which form a conductive network, could facilitate rapid O₂ and electrolyte diffusion throughout the whole ORR and OER process. The dispersion of Ag nanocrystals in the NCF could provide efficient electrocatalytic active sites toward Li₂O₂ formation and decomposition to achieve high round-trip efficiency and stable cyclability.
Figure 6.10 Product detection. (a) XRD patterns at different discharge/charge stages of Ag/NCF cathode, with the inset showing higher resolution of the indicated region; (b) Raman spectra at different discharge/charge stages of Ag/NCF cathode, with the inset showing a lower range of wavenumbers; SEM images of Ag/NCF cathode at different stages: (c) the fresh state, (d) after the 1\textsuperscript{st} discharge, (e) after the 1\textsuperscript{st} recharge, (f) after the 20\textsuperscript{th} recharge, (g) schematic diagram of the formation and decomposition of Li$_2$O$_2$ on Ag/NCF cathode.

### 6.4 Conclusions

Ag nanocrystals encapsulated in nitrogen-doped carbon fibers were prepared by the simultaneous reaction of pyrrole and Ag$^+$ ions in an aqueous medium followed by a heat treatment. The as-prepared Ag/NCF demonstrated favourable electrocatalytic ability
especially towards the OER in lithium oxygen batteries. A much reduced discharge/charge gap of 0.89 V was achieved from Ag/NCF compared with 1.38 V from NCF cathode, indicating that the introduction of Ag crystals into NCF facilitates the reversible charging and discharging characteristics of the battery. X-ray diffraction analysis coupled with Raman spectroscopy confirmed the reversible formation and decomposition of $\text{Li}_2\text{O}_2$ on the Ag/NCF cathode. The as-acquired favourable electrocatalytic results probably benefit from the perfect synergistic effects between the NCF matrix and the encapsulated Ag nanocrystals, in which the former acts as a highly electrically conductive web to facilitate efficient electron transfer, while the latter offer highly catalytic sites.
CHAPTER 8 CONCLUSIONS AND OUTLOOK

7.1 General Conclusion

This doctoral work investigated four kinds of efficient electrocatalyst materials for the rechargeable Li-O₂ battery: three-dimensional (3D) foam-like NiCo₂O₄, nanofibrous Co₃O₄/PPy hybrid, 3D hierarchical porous Co₃O₄ nanotube (Co₃O₄ HPNT) network, and Ag/nitrogen-doped carbon fiber. The synthesis, physical features and electrochemical performances of these electrocatalysts were thoroughly characterized. The above obtained materials exhibited improved electrocatalytic performances, in terms of decreased discharge/charge overpotential, increased capacity, and prolonged cycle life. These improvements are credited to abundant catalytic active sites of the materials and to optimized structures with large surface area, which are helpful for promoting reversible Li₂O₂ formation and decomposition. A summary of the results are provided in the following sections.

A self-assembled three-dimensional (3D) foam-like NiCo₂O₄ catalyst has been synthesized via a simple and environmental friendly approach, wherein starch acts as the template to form the unique 3D architecture. Interestingly, when employed as cathode for lithium oxygen batteries, it demonstrated superior bi-functional electrocatalytic activities towards both the oxygen reduction reaction and the oxygen evolution reaction, with a relatively high round-trip efficiency of 70% and high discharge capacity of 10137 mAh g⁻¹ at a current density of 200 mA g⁻¹, which is much higher than those in previously reported results. Meanwhile, rotating disk electrode measurements in both aqueous and non-aqueous electrolyte were also employed to
confirm the electrocatalytic activity for the first time. This excellent performance is attributed to the synergistic benefits of the unique 3D foam-like structure and the intrinsically high catalytic activity of NiCo₂O₄.

Co₃O₄ nanocrystals strongly coupled with a three-dimensional (3D) structured polypyrrole (PPy) nanoweb via a rapid hydrothermal method are presented for the first time as a bifunctional synergetic catalyst for Li-O₂ batteries. The obtained Co₃O₄/PPy hybrid material showed improved oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) performances, specifically, a larger discharge/charge capacity of 3585/2784 mAh g⁻¹, respectively, at a current density of 100 mA g⁻¹ and lower recharge overpotential, as well as better rate capability compared to pristine PPy cathode. Rotating disk electrode measurements and electrocatalytic testing, as well as characterization after cycling showed that the pristine PPy could act as a good support and good ORR catalyst, but it was only a poor OER catalyst, with Li₂O₂ and Li₂CO₃ as its main discharge products, while the nanofibrous Co₃O₄/PPy hybrid could catalyze reversible Li₂O₂ formation and decomposition in Li-O₂ batteries. The improved performance is attributed to the synergistic effects from the PPy matrix with its highly conductive 3D nanoweb structure and the Co₃O₄ nanoparticles with intrinsically high catalytic activity.

Three-dimensional (3D) hierarchical porous Co₃O₄ nanotube (Co₃O₄ HPNT) networks were prepared by using polypyrrole nanofiber (PPyNF) as a sacrificial template. When employed as cathode for lithium oxygen batteries, the 3D Co₃O₄ HPNT network demonstrated superior bi-functional electrocatalytic activities towards both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), with a rather low
charge overpotential of 99 mV and high discharge/charge capacity of 4164/4299 mAh g$^{-1}$. High resolution scanning electron microscope, X-ray diffraction, and X-ray photoelectron spectroscopy measurements on the Co$_3$O$_4$ HPNT based cathode after discharge/recharge showed reversible formation and decomposition of Li$_2$O$_2$. This superior performance is ascribed to the 3D web-like porous tubular structure, which facilitates rapid oxygen flow, provides enough void volume for insoluble Li$_2$O$_2$ deposition, and increases the catalytic utilization of Co$_3$O$_4$. Meanwhile, the hierarchical porous structure with meso/nanopores on the walls of the Co$_3$O$_4$ nanotubes facilitates O$_2$ diffusion, electrolyte penetration, and mass transport of all the reactants.

A facile synthesis of Ag nanocrystals encapsulated in nitrogen-doped carbon fiber (NCF) has been achieved via the simultaneous reaction of pyrrole and Ag$^+$ ions in an aqueous medium followed by a heat treatment. The as-prepared Ag/NCF demonstrated a much reduced discharge/charge gap of 0.89 V compared with 1.38 V for the NCF cathode with a fixed capacity in lithium oxygen batteries, indicating that the introduction of Ag crystals into NCF facilitates the ORR/OER kinetics. X-ray diffraction analysis coupled with Raman spectroscopy confirmed the reversible formation and decomposition of Li$_2$O$_2$ on the Ag/NCF cathode. The as-acquired favourable electrocatalytic results probably benefit from the ideal synergistic effects between the NCF matrix and the encapsulated Ag nanocrystals, in which the former acts as a highly electrically conductive web to facilitate efficient electron transfer, while the latter offer highly catalytic sites.
7.2 Outlook

Although real advances in improving the electrocatalytic performance of nonaqueous Li-O₂ batteries have been made, challenges remain, which need to be addressed in order to realize practical commercial applications. Low round-trip efficiency, low capacity and practical energy density, poor cycleability, and low rate capability have hindered their further development. Seeking low-cost, low-mass, conductive, and highly stable porous gas diffusion cathodes to reduce the overpotential, especially during the charge process, is the primary task in the future to develop rechargeable non-aqueous Li-O₂ batteries. The research strategy to fabricate high performance cathodes presented in this thesis could be of considerable interest and is expected to bring some inspiration to other researchers.

3D porous NiCo₂O₄ was successfully synthesized by using starch as the template in Chapter 4, a method which offers a high possibility of fabricating other 3D porous structured metal oxides (di-metal oxides) e.g. MₓOₙ or MNₓOₙ (M, N: Mn, Co, Fe, Ru, etc.) by the same method. The newly designed 3D MₓOₙ or MNₓOₙ materials with high surface area are expected to show promising performances when used as electrode materials for Li-O₂, Li-ion, or even Na-ion batteries. The introduction of PPy nanofiber in Chapter 7 could also open up a promising strategy to develop 3D structured nanotubular metal oxides, as well as perovskite oxides, with different sizes.

In addition to these, some further research efforts could be conducted based on the thesis as follows:

The reaction conditions for preparation of nanofibrous PPy/Co₃O₄ hybrid material via hydrothermal method in Chapter 5 could be adjusted, including by changing the
amount, concentration, and pH of the precursor solution, the reaction temperature, and the duration time, to form nanoparticles with designed morphologies and structures, which can strongly regulate the electrochemical performance of the electrode material.

The morphology and properties of the discharge product Li$_2$O$_2$ play a critical role in the charge process, e.g. charge overpotential and reversibility. A deep investigation of Li$_2$O$_2$ formation and decomposition will be beneficial to understanding the catalytic process during discharge and charge processes in a Li-O$_2$ battery. In this thesis, however, all physical characterizations of the Li$_2$O$_2$ at different discharge/charge states were conducted via ex-situ methods, such as ex-situ HRSEM, XRD, Raman, XPS, etc. In-situ characterization methods, including in-situ SEM, TEM, Raman, XRD, and synchrotron techniques, therefore, are essential for investigating the intermediates, surface kinetics, chemical bonding, and the related structural and compositional variations in the discharge and charge processes. Moreover, the combination of computational and experimental investigations is also needed to systematically study the electrode materials and the processes between Li$^+$ and O$_2$ reactions.

With the above mentioned challenges and insufficiencies solved, a brighter future for the next generation of batteries is expected to come.
REFERENCES


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APPENDIX A: LIST OF PUBLICATIONS


Papers listed were all written during my PhD study.

The publications with an asterisk mark are exclusively related to this thesis.