

# **Literature Summary of Recent Research About Na-ion, Li-S, and Li-O<sub>2</sub> Batteries**

A Book Auto-generated By ChemDataWriter

January 30, 2023



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**Part I**

**Na-ion Batteries**



# Chapter 1

## Na-ion Cathode Materials

### Contents

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### 1.1 Introduction

It is expected that SIBs will become one of the alternatives to lithium-ion batteries. Iron-based materials have developed into the most suitable energy storage conversion systems on the grid scale. Many studies on iron-based cathode materials have been carried out and some progress has been made. The proposed strategies to address these challenges will analyse several technical challenges. [1]

A cost-effective, simple and efficient method for producing compliant coating layers on the primary particles of sodium layer oxide materials to improve battery performance. The cells with these coated cathode materials provide a significantly improved cycle life while maintaining a relatively high reversible capacity and performance. Structural stability and water resistance are improved, which can help to simplify the storage protocol of cathode powder before battery production. [2]

Plate-shaped micron coated copper-substituted  $\text{Na}_{0.67}\text{Cu}_x\text{Mn}_{1-x}\text{O}_2$  loads and is demonstrated to discharge within 5 minutes. The materials have excellent stability and maintain more than 70% of the original capacity after 500 cycles at  $1000 \text{ mA g}^{-1}$ . [3]

The low electrochemical kinetics of sodium-ion batteries is a major problem that restricts its large-scale application. This report will provide better instructions for pyrophosphate electrode materials used in advanced batteries. The remaining challenges and opportunities of these systems are also discussed and made available. [4]

SIBs are increasingly attracting attention as one of the most promising candidates for cost-effective, energy-rich rechargeable batteries. Due to their high theoretical capacity and energy density, they have a rich electrochemical interaction with  $\text{Na}^+$  ( $\text{V}^{2+}$  to  $\text{V}^{5+}$ ). A large number of vanadium (V)-based cathode materials, including vanadium oxides (e.g.  $\text{V}_2\text{O}_5$  and  $\text{VO}_2$ ) and F-containing V-based polyanions, have been researched. [5]

$\text{Na}_2\text{Fe}_{1.96}\text{V}_{0.96}(\text{PO}_4)_3$  (NFVP) is a new cathode material for Na-Ion batteries with excellent cycle life and high power density. At  $30^\circ \text{C}$ , which means fast charging/discharging, 74% of the theoretical capacity was provided. [6]

Sodium layer cathode materials are usually multicomponent transition metal oxides (TM). Each TM plays a unique role in the cathode chemistry, e.g. redox activity, structural stabilisation. In the construction of

the three-dimensional (3D) distribution of TM cations into individual cathode particles, a deep-dependent charging mechanism can be used. [7]

Stable cathode materials are highly desirable for sodium ion batteries and a challenge. Below the authors report on the production of a layer cathode material,  $\text{P2-Na}_{0.67}\text{Co}_{0.67}\text{Mn}_{0.5}\text{O}_2$ , with a hierarchical architecture, through a simple and simple sun-yellow route. The material provided a high discharge capacity of  $147 \text{ mA h g}^{-1}$  at  $0.1 \text{ }^\circ\text{C}$ . [8]

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) is one of the most promising cathode materials with a NASICON structure. It was produced on a graphene surface using a simple method that combines sun gel and solid body reaction. [9]

Organic compounds with multifunctional groups that can be used as electrode materials for SIBs due to their low weight, their multi-electron reactions, their redox stability and their structural diversity. The organic compound 4,8-dihydrobenzo [1,2-b: 4,5-b'] was produced with a simple solution method. BDT-G as a cathode material showed a significantly improved electrochemical performance. [10]

Hybrid layer cathode materials  $\text{Na}_x\text{Li}_{1.5-x}\text{Ni}_{0.167}\text{Mn}_{0.67}\text{O}_2$  offer a initially reversible capacity of  $222 \text{ mA h g}^{-1}$  at  $20 \text{ m}^{-1}$ . The materials consist of P2 structure,  $\alpha$ - $\text{NaFeO}_2$  structure and a small amount of  $\text{Li}_2\text{MnO}_3$ . [11]

The analysis using X-ray and electron bending shows that the new materials are initially mixtures of rhomboedric and monoclinic phases. They were examined as highly capacitive positive electrode materials for Na-ion batteries with a initially reversible capacity  $\geq 200 \text{ mA h g}^{-1}$ . [12]

Layer-structured  $\text{Na}_2\text{V}_6\text{O}_{16}$  nanobelts (NVON) are synthesized using a simple, effective, cost-effective, one-top and template-free method. The NVON is inspired by its structural advantages as a cathode material for Na-ion batteries. [13]

Ni-based cathode materials have received great attention as advanced electrode materials for sodium ion batteries, but suffer from rapid loss of capacity, which leads to poor cycle performance. In this study the authors formed an artificial CEI layer (ACEI) on  $\text{O}_3\text{-NaFe}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (NFNO) through a simple electrochemical discharge step. [14]

$\text{P2-Na}_{0.67}\text{Co}_{0.25}\text{Mn}_{0.75-x}\text{Nb}_x\text{O}_2$  cathode materials were obtained by a simple solid matter method.  $\text{Nb}_5+$  + -doped effects on the improvement of the structural and electrochemical properties of the  $\text{Na}_{0.67}$  source material for sodium ion batteries were investigated. [15]

Two types of  $\text{MnO}_2$  polymers have been synthesized using a hydrothermal method: their crystalline phases, morphologies and crystal structures have been characterised by X-ray, FESEM and TEM analysis. The electrochemical properties of  $\alpha$ - $\text{MnO}_2$  and  $\beta$ - $\text{MnO}_2$  nanorods as cathode materials in Na-Ion batteries have been investigated by electro-static charging/discharge. [16]

A chain of nickel hexacyanoferrate (NiHF) nanotube is cultivated coaxially on a CNT @ bipolar conductive polymer (BCP) on a simple electrochemical path. The preserved cathode has a surprisingly high specific capacity of  $194 \text{ mA h g}^{-1}$ , a good cycle performance and an excellent performance at first discharge. [17]

$\text{FeF}_2$ -reduced graphene oxide nano-bond is synthesized in-situ and added to an electrode with poly (acrylic acid) binder as a novel sodium ion cathode. Electrode has superior electrochemical performance: high capacity of  $175 \text{ mAh g}^{-1}$  at  $0.2 \text{ A g}^{-1}$ . [18]

Sodium ion batteries (SIBs) at room temperature are promising candidates for intelligent power grids and large-scale energy storage. Among the already reported cathode materials for SIBs, coated transition metal oxides and polyanion-like materials are considered the most attractive options. We hope that this review can provide some insights into the development of polyanionic materials. [19]

Sodium ion batteries are the main candidates in the race for large-scale electrochemical energy storage. The obvious cost advantage as well as attractive electrochemical properties, including excellent cycle stability and high performance potential, make them the main candidates for high-performance power applications on the grid scale. [20]

Cobalt substitution in  $\text{Na}_{0.67}\text{MnO}_2$  reduces the lattice parameters "a" and "c", leading to the contraction of the  $\text{MO}_6$  octahedron and to the increase of the "d" distance between the layers.  $\text{Co}^{3+} / \text{Co}^{4+}$  has high structural stability and superior capacity retention, while Mn-rich phases release higher capacities. [21]

$\text{Na}_x\text{FeFe}(\text{CN})_6$  (NFF) is considered to be potential cathode material for aqueous sodium ion batteries due to its low cost and high theoretical capacity. However, a low sodium content, a low Columbian efficiency (CE) and a rapid capacity reduction hinder their practical application. NFF, which was substituted with 23%  $\text{Ni}^{2+}$ , showed the best electrochemical behaviour. [22]

Various  $\text{Ti}^{4+}$  levels have been successfully allocated to the grids of  $\text{Cr}^{3+}$  in  $\text{NaCrO}_2$  due to the two-stage solid matter reaction. Analysis results of the crystal structure show that the intermediate plate spacing ( $\text{NaO}_2$ ) is increased with the  $\text{Ti}$ -dose content. This contributes to the expansion of the sodium ion channel and then facilitates the rapid (de) intercalation of sodium ions. [23]

Cathode materials are crucial for the energy density, power density and safety of sodium ion batteries.  $\text{Na}_x\text{Ni}_{1/3}$  co-structured materials with intergrowth  $\text{P}_2/\text{O}_3/\text{O}_1$  structure showed a better electrochemical performance and thermal stability than  $\text{Na}_x\text{Ni}_{1/2}/\text{Mn}_{1/2}$  with binary phase integration. Interaction microassemblies can serve as an indispensable bridge for future design and synthesis of high-performance battery materials. [24]

$\text{Li}_2\text{FeSiO}_4$  has been studied far as promising cathode material due to its theoretical capacity of  $330 \text{ mAh g}^{-1}$  over two electron reactions. However, its Na equivalent has not yet been reported, although it could significantly reduce potential product costs due to the abundance of sodium resources in nature. [25]

Carbon-coated  $\text{NaCrO}_2$  cathode material has an excellent capacity reserve with superior performance up to a rate of  $150 \text{ C}$  ( $99 \text{ mA h (g Oxid)}^{-1}$ ). This study has the potential to promote the development of sodium ion batteries for a large number of applications. [26]

Mn-based  $\text{P}_2$  material is considered one of the most promising cathode materials for sodium ion batteries. The maximum discharge capacity of the  $\text{Mo}$ -doped cathode is  $131.9 \text{ mAh g}^{-1}$  at a capacity retention rate of 91.51% after 100 cycles. [27]

Lithium-Ion Batteries (SIBs) have shown great interest as alternatives to grid and mobile energy storage applications in the modern world. In order to accelerate the practical application of SIB systems, the electrochemical performance of cathode materials should be further improved in order to meet the increasing global demand. Layer Metal Oxides (LTMOs) have a high specific capacity and high energy density due to their suitable voltage window. [28]

## 1.2 Literature Reviews

### 1.2.1 Advanced iron-based cathode materials for sodium-ion batteries

The annual consumption of fossil fuels accounts for more than 85%. Sodium Ion Batteries (SIBs) have attracted great attention worldwide due to their abundance of resources, their low price and their environmental friendliness. SIBs are battery systems that have been developed in the 1970s. They are expected to use and store wind, heat, solar and water power. Iron has many advantages in terms of natural wealth, refining production and price and would be the most logical choice for a redox centre of SIBs. Using the valenzredox reaction of iron, the potential of the iron-based cathode material can be up to 3.5 V, thus achieving a high energy density. In this review, the authors have mainly summarized core research on various iron-based positive electrode materials for SIBs and discussed the development of some sodium-free cathodes. Crystal structures, synthetic methods, characterisation, characterisation and electrochemical properties are also examined in this review. [1]

### 1.2.2 Surface transformation by a “cocktail” solvent enables stable cathode materials

The promise is based on its superior affordability compared to other energy storage systems, such as lithium-ion batteries. Cathode materials influence the performance characteristics of alkali-metal ion batteries, including power density, energy density, output voltage and cycle life. To achieve further progress, the authors need to overcome the cathode problems through the development of novel cathode chemistry and processes.

To improve battery power without significant cost losses, cheap elements from Cu, Fe and Mn were used to synthesize the air-stable  $O_3\text{-Na}_{0.9}[\text{Cu}_{0.22}\text{Fe}_{0.30}\text{Mn}_{0.48}]\text{O}_2$ . The cells containing this material provided excellent electrochemical performance. The degradation mechanisms for lithium layer oxides are well developed, including surface reconstruction, irreversible oxygen activity, electrolysis, metal dissolution in transition, formation of micro cracks and defects of the cationic antisite. Most of these failure mechanisms are associated with the degradation of the interface between cathode particles and electrolytic solution. A new method for extending battery cycle life by selective transformation of the surfaces of cathode materials into conformal coating layers. With such coating layers the authors detect a significantly improved electrochemical performance, including extended cycle life, excellent voltage stability, increased water resistance and structural stability. Our research highlights the importance of controlling cross-border chemistry in sodium ion batteries and provides a cost-effective and efficient "cocktail" method. [2]

### 1.2.3 High-power sodium-ion battery cathode

Lithium-ion batteries (LIBs) are often used to operate portable devices such as laptops, mobile phones and power tools. However, the limited lithium resources and the geographical location of these reserves have led to a high price for LIBs. Cheap alternatives such as sodium-ion batteries (SIBs) attracted great attention due to the high and even abundance of sodium around the world. Manganese-based cathodes ( $\text{P}_2\text{-Na}_x\text{Mn}_y\text{M}_z\text{O}_2$ ) have attracted a lot of attention because Manganese is inexpensive and earthy. These materials can offer an impressive initial capacity of up to  $210 \text{ mA h g}^{-1}$  at low current rate and a voltage plateau of about 2.0-2.2 V vs. Na / Na<sup>+</sup> due to the redox pair  $\text{Mn}^{3+} / \text{Mn}^{4+}$ .  $\text{P}_2\text{-Na-Mn-O}$ -cathodes with a high potential of about 3.6 V compared to Na/Na<sup>+</sup> are comparable to LIBs. With increasing Cu-content, the average potential increases while the entire discharge capacity decreases. Most importantly, the cycle stability of the materials is improved by Cu-substitution, even at high power rates. [3]

### 1.2.4 A review on pyrophosphate framework cathode materials for sodium-ion

Lithium-Ion Batteries (LIBs) have been used in various electronic products and energy storage systems since 1991. Due to their abundant resources and low costs, SIBs are considered one of the most promising energy storage technologies and their electrochemical properties are similar to those of LIBs. Three main assessment criteria, namely lifetime, energy density and discharge rate, must be taken seriously for SIBs. No material is perfect and each type of electrode material has its own advantages and disadvantages. Oxide, polyanionic compounds, organic substances and Prussian blue analogues can be divided into four main categories. Phosphates, pyrophosphates and sulphates are the three most important research systems. Phosphates have good thermal stability, long cycle stability and high performance as the most widely studied cathodes. Sulphates have a higher operating voltage derived from the stronger electronegativity of the sulphates, but unfortunately poor thermal stability and crystallinity will be responsible for their unpredictable prospects. [4]

### 1.2.5 Research progress on vanadium-based cathode materials for sodium ion batteries

Lithium-ion batteries (LIBs) have dominated the market of portable and intelligent electronic devices for almost three decades. However, due to resource scarcity, high costs and geographical distribution of Li in the earth crust, a candidate for LIBs is needed. Alternatively, sodium-ion batteries have regained attention mainly due to the abundance of Na (2.83 % by weight vs. 0.01 % by weight) and similar chemical properties of Na to Li (the alkali metal family) as well as the electrochemical mechanisms of SIBs. First research on room temperature SIBs dates back to the 1980s, not far beyond the original LIBs developed in the 1970s. This is mainly due to the lower energy density and safety problems caused by the use of Na. Significantly, the exploration and optimization of cathode materials with a suitable voltage window, high reversible capacity and stable structure are applied. Recently, intelligent design and nano-engineering of electrode materials for high-performance LIBs are applied. Vanadium-based cathode materials (V) have attracted more attention

due to their high operating voltages, theoretical capacities and energy densities. V (atomic number 23 in the periodic table) of the VB group has a valence electron layer of  $3d^34s^2$ . All five V atom valence electrons can be involved in the binding, resulting in a multivalent V from  $V^{2+}$  to  $V^{5+}$ . [5]

### 1.2.6 Alluaudite-based cathode material with high power and long cyclability

Na-Ion batteries (NIBs) have attracted considerable attention due to their low production costs due to the essentially unlimited Na-resources as one of the best alternatives to LIBs. However, several problems should be solved to achieve commercialisation of NIBs: the redox potential of  $Na^+ / Na$  is lower than that of  $Li^+ / Li$ , and water contamination is caused by the reaction between water and cathode materials with an average voltage of less than 2.7 V vs.  $Na^+$ . [6]

### 1.2.7 Empowering multicomponent cathode materials for sodium ion batteries by exploring

Lithium and sodium ion batteries are considered to be excellent batteries of choice for energy storage in the grid or for electric vehicles. The design of these batteries can follow the configuration of a two-stage rocking chair. Layer oxides are considered one of the most promising cathode materials for both battery families. Interaction reactions between a layer oxide cathode and electrolytic solution influence the electrochemical properties of the cathode. These reactions hinder efforts to increase the energy/performance density and cycle life of alkali metal ion batteries. In order to achieve further progress in sodium ion batteries, sodium layer cathode materials must be stabilized against undesirable interface reactions. The best battery performance was achieved for  $Na_{0.9}Cu_{0.2}Fe_{0.28}Mn_{0.52}O_2$  materials. The cells that contained this material provided practical discharge capacity of  $125 \text{ mA h g}^{-1}$  at  $C / 10$ . The authors expect the study to shed light on the way to developing composite heterogeneities for high-energy and long-lasting sodium ion batteries. [7]

### 1.2.8 A P2- $Na_{0.67}Co_{0.5}Mn_{0.5}O_2$ cathode

In view of the rapidly increasing demand for large energy stores in electric vehicles and intelligent power grids, rechargeable batteries are the best candidates among the various energy storage technologies. In recent decades, lithium-ion batteries have been widely used in portable electronic devices due to relatively mature technologies. However, lithium is not present on earth in excess, and rising costs have restricted its use. Layer oxides, polyanion compounds and other electrode materials have been fully investigated.  $Na_xMO_2$  can be further classified into many subtypes, namely P2, P3 and O3, due to the stoichiometric ratio of sodium and synthetic temperature of the compounds. P2 materials, which are considered promising candidates for SIBs, generally have excellent reversibility and high discharge capacity. Despite the advantageous crystal structure and correspondingly high capacity, however, the P2 phase has a poor cycle life and poor performance compared to the O3 phase. To meet the demand for practical applications, huge challenges remain to be met. P2-NCM55 showed excellent performance in terms of high capacity, long cyclic stability and excellent derivation performance. It offered a discharge capacity of  $88 \text{ mA h g}^{-1}$  at  $30^\circ\text{C}$  and the capacity retention was 47% over 2000 cycles. It paves the way for practical applications of SIBs. [8]

### 1.2.9 $Na_3V_2(PO_4)_3$ as a high rate cathode

Lithium-ion batteries are widely recognised for a high energy density and a long life span. It is questionable whether the cost of lithium for use in wider markets such as electric vehicles and energy stores would be sufficiently low. Most sodium-based electrode materials have low C values regardless of the crystal structures. Graphene, a 2D form of carbon allotrope, is the basic building block of all graphic materials. It was used to form composites or hybrids as a highly electronic conductive network in the area of rechargeable batteries. While many groups have previously demonstrated the effect of graphs in LIBs, sodium-based electrode materials

with graphs have rarely been reported. NASICON-structured materials have aroused widespread interest in high ionic conductivity, but it is difficult to use materials such as electrodes in rechargeable batteries, as the electronic conductivity is poor. Here, for the first time, a high-crystalline NVP / graphene composite was synthesized as cathode material for rechargeable sodium ion batteries. [9]

### 1.2.10 C<sub>10</sub>H<sub>4</sub>O<sub>2</sub>S<sub>2</sub>/graphene composite as a cathode material for sodium-ion batteries

Lithium-ion batteries rule the portable electronic market at present and would be the best choice for electric vehicles because of their high energy density, power density, and output voltage. Lithium resources are too geographically constrained and limited to be sufficient to satisfy the demands of widespread application in electric vehicles and smart grids. In contrast to LIBs, SIBs would be one of the most attractive alternative rechargeable systems. Organic compounds have been studied as electrode materials for sodium-ion batteries because of their processability, light weight, multi-electron reactions, redox stability, structural diversity, and availability from biomass and environmentally friendly materials. Graphene possesses a large specific surface area and excellent conductivity. The introduction of graphene into organic compounds would have the potential to improve the materials' electrochemical performance. BDT was composited with graphene as an electronic conductivity promoter by the dispersion-deposition process. It is found that BDT-G exhibits the high capacity of 217 mA h g<sup>-1</sup> for the first cycle (theoretical capacity: 243 mA . g<sup>-1</sup>) along with a long cycle life and excellent rate performance when graphene is added. [10]

### 1.2.11 Na<sub>x</sub>Li<sub>1.5-x</sub>Ni<sub>0.167</sub>Co<sub>0.167</sub>Mn<sub>0.67</sub>O<sub>2</sub>

Lithium-ion batteries have been intensively researched as energy sources in the last two decades and are used in portable electronics, electric vehicles and hybrid electric vehicles. Such materials should be environmentally friendly to combat global warming and combat global warming [1-3]. After the successful development of lithium ion batteries, a number of cathode materials were synthesized and examined on sodium ion-ion batteries, which were divided into prismatic P2 types and octahedral O3 types in early literature (Na<sub>x</sub>MO<sub>2</sub> (M = Mn, Ni, Co, Fe, Cr...)). The discharge capacities of these materials are always below 150 mA h g<sup>-1</sup> which is much lower than those of Li-ion batteries. LiMnO<sub>2</sub> [12,13], LiNi<sub>0.33</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>O<sub>2</sub> [14] and LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> (LiNi's (M = Ni, Co, Mn) are Li-rich materials (discharge capacity > 250 mA h g<sup>-1</sup>) This high capacity supplied by Li-rich cathode materials is mainly due to their specific composite structures and their high lithium content. The authors propose novel cathode materials with Li and Na as alkali ions. For the synthesis of a number of alkaline hybrid layer cathode materials, a co-fall was used in combination with a calcination method. The effects of the original sodium / lithium content on structure and electrochemical performance have been systematically investigated. The authors believe that the hybrid cathode with composite structures for the development of powerful cathode for sodium ion batteries is of high relevance. [11]

### 1.2.12 Na-ion battery cathode materials prepared by electrochemical ion exchange from

The importance of Na-Ion batteries is based on the high sodium content in the earth's crust, which ensures an unlimited supply that promises low costs. Sodium ion is 0.3 A<sup>2</sup> greater than lithium ion and approximately three times heavier (6,9 and 23 g mol<sup>-1</sup>) The specific gravimetric capacity is three times lower for the Na-Metal than for lithium. Li- and Mn-rich metal layer materials are structurally integrated two-component solid solutions that have a specific capacity > 250 mA h g<sup>-1</sup> in the potential range of 4.6-2.5 V (after activation) with a mean discharge voltage of approximately 3.7 V compared to Li. Recent reports on Na-Insertion cathode materials present compositions of Na<sub>2</sub>MnO<sub>3</sub>-NaMO<sub>2</sub>. The ion exchange process described in literature included three steps: First, lithium cells were produced and loaded to 4.6 V versus Li, leading to the de-insertion of lithium ions from electrodes and activation of the cathode material. Further contaminations and cycles were carried out with these cells. The aim of the present work was to prepare analogue cathode materials with a high na-insertion capacity. Two approaches were investigated: high na-insertion and low

na-insertion. The aim was to prepare the materials for the cathode material with a high na-insertion capacity. The materials were examined in two approaches: na-insertion capacity. Synthesis of Li- and Mn-rich cathode materials such as  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$  and  $\text{Li}_{1.13}\text{Mn}_{0.54}\text{Ni}_{0.2}\text{O}_2$ , followed by their use as precursors for Li-Na-Ion exchange. The synthesis of Na-Insertion cathode materials similar to the composition of methods such as self-combustion reactions proved to be extremely effective in the production of Li-Insertion cathode materials. The methods were developed to prepare Li-Insertion cathode for the use of the cathode material. In our synthesis by ion exchange, the initial Li- and Mn-rich cathodes were activated (dissolved) and cyclically in Na-cells containing sufficient amounts of free Na-ion. The electrochemical reactions in the cells were dominated by Na-ion reactions. The main source material  $\text{Li}_{1.13}\text{Mn}_{0.54}\text{Ni}_{0.2}\text{Co}_{0.13}\text{O}_2$  (Li-a) was converted directly into  $\text{Na}_1 + x\text{Li}_{0.05}\text{Mn}_{0.54}\text{Co}_{0.2}\text{O}_2 - z$  by an electrochemical ion exchange procedure. The secondary objective of this study was to reduce harmful reactions between cathode and electrolyte solutions by creating a protective layer that allows the diffusion / migration of sodium ions. These materials were coated with aluminium oxide by means of the atomic layer separation method (ALD) by applying the ion exchange method to coated precursor materials from Li- and Mn-rich cathodes. [12]

### 1.2.13 Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub> nanobelts as promising cathode and symmetric

Na-Ion batteries (NIBs) have recently aroused great interest in large-scale energy storage in renewable energy sources. The larger size of Na-Ion (-1.02 Å) makes it difficult to identify economic cathode materials. Some candidate materials face the problem of low capacity or even complete electrochemical inactivity in NIBs. In recent years, various materials have been examined to develop cost-effective and highly secure cathode materials for energy storage on the grid scale. Layer compounds such as  $\text{P}_2\text{-Na}_7 / 9\text{Cu}_2 / 9\text{Fe}_1 / 9\text{Mn}_2 / 3\text{O}_2$  [11],  $\text{NaMO}_2$  (M: Transition Metal) [12],  $\text{VOPO}_4$  [13] polyanionic compounds such as  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$  (NVPF) and  $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$  [15] are currently the most frequently studied.  $\text{Na}_2\text{V}_6\text{O}_{16}$  (NVO) nanobelts (NVON) are synthesized by a simple, cost-effective and one-stage, surfactant-free method. Inspired by this structural advantage, the NVON is tested as a NIB cathode between 1.2 and 4.5 V. They have significant electrochemical performance, including a high specific capacity of 194.6 mAh g<sup>-1</sup>. [13]

### 1.2.14 Effect of the interfacial protective layer on the NaFe<sub>0.5</sub>Ni<sub>0.5</sub>

Rechargeable sodium-ion batteries (NIBs) have attracted a lot of attention compared to lithium due to their frequency, low cost and easy accessibility. Common anode materials such as hard coal and snow are reported to have capacity of over 200 mAh g<sup>-1</sup> and have stable cycle performances.  $\text{Na}_x\text{MO}_2$  (M = Fe, Mn, Ni, Cr, Co.) has been extensively studied due to its high theoretical capacities and simple synthesis processes. However, its practical application still poses significant challenges such as low specific capacity, poor cycle performance and structural instability. Pre-disposed  $\text{NaFe}_{0.5}\text{Ni}_{0.5}\text{O}_2$  (PS-NFNO) has a high reversible capacity, superior performance and excellent cycling capability. It has a high capacity retention of 86% after 50 cycles, which is 23% higher than the unspoiled NFNO. [14]

### 1.2.15 Nb<sup>5+</sup>-doped P<sub>2</sub>-type Mn-based layered oxide cathode

Lithium-ion batteries (LIBs) play a dominant role in the global market for rechargeable batteries due to their excellent power density and superior energy efficiency. However, there are still restrictions on the large-scale use of LIBs, in particular their increasing costs due to the limited lithium resources and their unequal distribution in the earth. SIBs were considered a more practical alternative to LIBs. The layer oxides  $\text{Na}_x\text{MO}_2$  (M = transition metals) can be divided into P and O types, as Na<sup>+</sup> ions can be distributed in prismatic (P) or octahedral (O) places in the crystal grid.  $\text{P}_2\text{-Na}_{0.67}\text{Fe}_{0.5-x}\text{Mn}_{0.3-x}\text{Co}_{2x}\text{O}_2$  samples developed an exceptional cyclic stability compared to the unspoiled (P<sub>2</sub>) material. Co-doping contributed to the reduction of the Mn<sup>3+</sup> content and delivered Mn<sup>3.7+</sup>, which could effectively overcome the Jahn plate effects.  $\text{Nb}_2\text{O}_5$  was considered as promising transitional metal oxide for the Li<sup>+</sup> switch-on [32, 33], which contributed to a better high rate

[34] and safer energy storage for LIBs. Nb<sup>5+</sup>-doped P2-Na<sub>0.67</sub>Co<sub>0.25</sub>Mn<sub>0.75</sub>O<sub>2</sub> cathode material with layer architecture using solid body method. [15]

### 1.2.16 Hydrothermal synthesis of -MnO<sub>2</sub> and -Mn materials

The high cost of Li-Ion batteries and the limited Li-Reserves made their application difficult for large-scale energy storage devices such as renewables and intelligent power grids. The higher ionization potential and the larger ion diameter of Na restrict the structural variability and selection of Na-Introduction materials in crystalline materials. [16]

### 1.2.17 a string of nickel hexacyanoferrate nanocubes coaxial

The rechargeable sodium ion battery (SIB), which works at room temperature, is considered a promising alternative to the current Li-ion battery. Sodium ion (Na<sup>+</sup>) has a greater radius than Li<sup>+</sup>, so it is difficult to find a suitable cathode material with sufficient electrochemical capacity and reversibility for the Na<sup>+</sup> intercalation reaction. In this study the authors found an interesting structure in the production of a 3D hybrid cathode for SIBs in a simple electrochemical way. A chain of nickel hexacyanoferrate (NiHCF) nanocathodes was anchored coaxially to bipolar conductive polymer (BCP) coated CNTs. In the following context, this type of cathode is called CNTs @ NiHCF-BCP. Also the pathways for Na<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> diffusion and electron conduction are schematically depicted. [17]

### 1.2.18 FeF<sub>2</sub>-rGO hybrid cathode with poly (acrylic acid) binder

Lithium-ion batteries have been successfully used in portable electronic devices and electric vehicles, but their use in ESS is limited due to their high costs and limited natural lithium sources. Sodium-ion batteries (SIBs) are a promising alternative for ESS systems on the grid scale due to their low costs and abundant sodium resources. Due to its high potential, metal fluoride is considered a promising material for the SIBs cathode due to the strong ionic bond between metal and fluorine. However, the lack of sodium before discharge can be corrected by the use of metal Na as anode by the use of solid or polymer-like batteries. Disposal and aggregation of active materials as well as the collapse of the electrode structure during the cycle can lead to too low capacity and poor cyclical performance. To solve such problems, different strategies such as reducing particle size and hybridization with leading materials have been introduced. Fe-rGO composite material has a capacity of 120 mAh g<sup>-1</sup> with good cycle stability at a current density of 0.1 A g<sup>-1</sup>. Zhang et al. [19] describe amorphous FeF<sub>3</sub> / C-Nanoverbundung materials. FeF<sub>2</sub> can be considered an attractive candidate for high-performance cathode materials for SIBs. Poly (acrylic acid) (or PAA) is an aspirating binder with improved mechanical properties. PAA has been successfully used in alloy and conversion electrodes and has shown the ability to improve the cyclic and high performance of LIBs electrodes [24-26]. Despite its successful use in SIB's anode electrodes, the use of PAA in sodium ion battery cathodes has to be further investigated. FeF<sub>2</sub>-rGO (reduced graphene oxide) -PAA electrode is produced by in-situ rGO hybridization and binder optimization. It has a higher discharge capacity as well as improved speed and cycle stability. The mechanisms for electrochemical reaction and improved performance are determined by analysing changes in morphologies and phases before and after the cycle. [18]

### 1.2.19 Polyanion-type cathode materials for sodium-ion batteries

Lithium-Ion Batteries (LIBs) have developed into primary energy storage candidates since their first marketing by Sony in the 1990s. Sodium (Na) has similar physical and chemical properties to Li because they belong to the same main group in the periodic table. Na is the fifth most common element on the earth crust. SIBs have great potential for use in large ESS. The output voltage of a battery is based on the potential difference between anodes and cathodes. Hard carbon has been used successfully and its performance is already comparable to

that of graphite in LIBs. However, the development of cathodes is relatively slow. Therefore, the development of suitable cathode materials with high capacity and voltage is crucial for increasing the energy density of SIBs. Polyanion-like materials have a higher operational potential, stable scaffolding and superior safety. They are considered one of the most promising cathode materials in SIBs. Nevertheless, some bottlenecks hinder their practical application, such as limited capacity and low electrical conductivity. In this review the authors focus on the conception of materials, the characterisation of reaction mechanisms and strategies to improve electrochemical performance. the authors try to provide insights into the research and application of polyanion-like materials for SIBs. In addition, the challenges and bottlenecks are highlighted. [19]

### 1.2.20 Design of fast ion conducting cathode materials for grid-scale sodium-ion batteries

We need to explain why the authors want to use this tool to improve our chances of getting to the future. the authors are happy to explain the motivation behind the project. the authors hope to use the project as a tool to help others achieve the same success as the authors do. Large electrochemical energy storage systems with revolutionary energy density and efficiency are needed to control electricity networks based on intermittent renewable energy sources and to put urban mobility on a sustainable basis. The goals of large energy storage systems include mainly electrochemical energy storage. As the main motivation for the transition from Li- to Na-based cell chemistry, the low cost and soil availability of sodium is generally cited. Nevertheless, a large part of this new research into sodium-based batteries only imitates approaches that have proven successful in Li-Ion battery technology (LIB). External design restrictions for sodium-ion batteries. Sodium-ion batteries can be used to produce larger batteries that can be compressed into smaller packs. The materials are designed to meet the design requirements of sodium-ion batteries. They can also be used for other types of batteries that need to be converted into smaller batteries. The cost advantage of Na will only be able to be applied to commercially feasible NIBs on a large scale if the concept of earthiness is consistently applied to the entire system design. The design of NIB electrode materials should focus on the most common transition metals Fe, Ti and Mn. NIB materials need to focus on the specificities of Na compounds. According to the authors of the study, polyanionic oxides, oxyfluoride or oxynitride, which contain ample transition metals, are the most promising class of NIB electrode materials. We will analyse for a number of such polyanionic NIB cathode materials how suitable the respective structure type is for fast Na + mobility and thus for high-performance NIBs. It is shown that a stretched exponential functional description provides a rational quantitative measurement of performance. The slightly lower cell voltage of NIBs affects the energy density available, but tends to increase both cycle and durability. The larger size of Na + tends to cause volume changes in cyclic insertions. The rate capability of historical NIB cathode materials is often affected by the order of Na +, as the distance between the layers Na + -Na + becomes a decisive structural factor. The higher order number and the larger size of the Na + ions mean that Na + is more polarizable and less polarizing than Li +. Na + is less attached to vibrations in the motionless oxide substructure and therefore less harmonious than Li +. This mobility advantage should be directly reflected in possibilities for applications that require a high performance. The mobility of electrons in mixed conductive electrode materials is often higher and, if not, can be improved by conductive additives such as carbon coating. An exception are extremely nano-sized materials with low electronic conductivity, where cathodes have high performance when the unloaded structure acts as p-type and the loaded as n-type semiconductor. In this work the authors discuss the speed performance assuming that it is limited by ion mobility in cathode material. This will be the standard case for Na or Li-based batteries with metal anodes as well as for most practical Li and Na-ion batteries. The results will also remain applicable in cases where the speed limitation process concerns an anode of the insertion type. [20]

### 1.2.21 P2-Na<sub>0.67</sub>Mn<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> cathode

Sodium-based energy storage overcomes the problems associated with lithium's cost and scarce resources. Sodium storage is attractive for niche applications such as stationary power storage that require cost-effective, safe and durable solutions while providing flexibility in terms of energy density. Sodium introduction electrodes with capacities comparable to commercial Li-ion cathodes. 2D sodium laminate oxides of the generic formula Na<sub>x</sub>MO<sub>2</sub> are widely studied as cathode materials due to their structure and their high specific capacity. In the case of type P2 compounds, the single cell contains two MO<sub>2</sub> layers with an elongated MO<sub>6</sub> octahedron, while Na-Ions are present at the prismatic site. Na<sub>0.67</sub>MnO<sub>2</sub> of type P2 contains two MnO<sub>6</sub> octahedrons with Na<sup>+</sup> in a trigonal prismatic environment. In this compound, almost two thirds of the manganese are in the oxidation state + 3. The presence of Jahn plates Mn<sup>3+</sup> + high spin ions reduces the diffusion coefficient of sodium and destabilizes the structure. Cobalt substitution in P2-Na<sub>x</sub>MnO<sub>2</sub> is expected to improve electrode performance as it improves electrical conductivity and diffusion of Na-Ions. The diffusion coefficient D<sub>Na<sup>+</sup></sub>, calculated at different redox potentials, could provide insights into the mechanical understanding of the Na-Ion transport phenomenon and the charging storage properties. Cobalt-doped sodium manganese oxide layers, Na<sub>0.67</sub>Mn<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> (x = 0.25, 0.75) as cathode materials for Na-Ion batteries. By structural analysis, cyclic voltammetry and impedance spectroscopy, the authors understand the positive role of co-doping. [21]

### 1.2.22 High performance cathode for sodium ion batteries with nickel doping

Sodium has similar physical and chemical properties to lithium, so sodium has proven to be higher than the energy supply due to enormous sodium resources and cheaper material costs. The ion radius of Na<sup>+</sup> (1.02 Å) is greater than Li<sup>+</sup> (0.76 Å), which leads to slow and difficult Na<sup>+</sup> introduction/extraction into an electrode. Due to its simple synthesis, its open frame structure, its chemical stability, its adaptable redox potential and its excellent electrochemical activity, PBAs have been identified as suitable cathode in aqueous SIBs. PBAs have a metal organic open framework with a general composition of A<sub>x</sub>M [Fe (CN)<sub>6</sub>]<sub>y</sub> · nH<sub>2</sub>O. This structure contains large intrinsic channels and intermediate spaces that allow for rapid use/extraction of Na<sup>+</sup>. Na-iron hexacyanoferrate (Na<sub>x</sub>Fe [Fe (CN)<sub>6</sub>]<sub>6</sub>) has a high theoretical capacity (170 mAh g<sup>-1</sup>) and cost-effective Fe resources. Recent reports on Na-rich PBAs with low defects have demonstrated superior electrochemical performance in organic SIBs [27.43.44]. Due to grid gaps in the crystal structure, PBAs generally show poor cycle stability, low CE and high potential polarization [25.46]. Transport kinetics can be improved by changing the composition of PBAs by substitution of inactive/electroactive elements and by promoting their electrochemical performance. [22]

### 1.2.23 Ti-doped NaCrO<sub>2</sub> as cathode materials

Lithium-ion batteries have become an indispensable power source for energy storage and have penetrated all aspects of our lives. Sodium-ion batteries (SIBs) have similar functional mechanisms to LIBs. SIBs have increasingly attracted the attention of researchers, especially for cathode materials [4-6]. O<sub>3</sub>-NaCrO<sub>2</sub> material, which is characterised by low-cost synthesis, rich soil treasures and a relatively high voltage platform, is considered to be the most promising candidate for SIBs. Material always suffers from a rapidly dwindling capacity and disappointing performance caused by electrode-electrolyte side reactions and multiple phase transitions. In this work, a small amount of titanium (≤ 10%) was allocated to the crystal structure of NaCrO<sub>2</sub>. In a systematic study, the effects of Ti-doping on the structure, morphology and electrochemical properties of the materials were investigated. The results obtained are useful to promote the development of high-performance cathode materials for SIBs. [23]

### 1.2.24 Structure and structural effects of layered cathode materials

Recently, rechargeable sodium-ion batteries (SIBs) are attracting increasing interest as an attractive alternative to Li-ion batteries. However, as usual in any new chemistry, there are always setbacks in the development of high-performance electrode materials for SIBs. Layer metal oxides ( $\text{Na}_x\text{TMO}_2$ , TM = Fe, Co, Ni, Mn, Cr, V, Cu, etc.) have attracted particular attention due to their potentially high capacity. The relatively low standard electrochemical potential of electrode materials for sodium ion batteries requires that these are operated in a larger range of voltages in order to achieve energy density comparable to lithium ion batteries. Earlier research into sodium ion oxide has shown that the O3 cathode material has relatively good sodium/disposal reversibility below 4.0 V. However, once these materials are charged over this voltage, they significantly dissipate with large irreversible capacity losses due to either sodium-controlled structural irreversible changes or increasing catalytic decomposition of the Na-based electrolytes. On the other hand, layer-structured cathode materials are usually produced by a calcination process between transitional metal precursors (e.g.  $\text{Ni}_1 / 3\text{Co} / 3\text{Mn} / 3(\text{OH})_2$ ) and sodium salts. The calcination temperature, sintering time, temperature rise/cooling, calcination atmosphere etc. play a major role in the morphologies and phase structures of the resulting cathode material. The thermal stability of deep-charged cathodes at high temperature and/or in the presence of electrolytes is an important factor for the safety properties of cathode materials. In recent years, the thermal stability of disinfected cathodes such as O3  $\text{NaCrO}_2$  and  $\text{NaNi}_{0.6}\text{Co}_{0.05}\text{Mn}_{0.35}\text{O}_2$  has been reported. Interaction microstems could serve as an indispensable bridge for the design and synthesis of high-voltage SIB cathode materials with excellent cycle stability and thermal stability. A high initial reversible capacity of 142,8 mA h g<sup>-1</sup> was achieved with a high initial coulombic efficiency of 95%. [24]

### 1.2.25 Metastable $\text{Na}_2\text{FeSiO}_4$ as a cathode material

$\text{Li}_2\text{FeSiO}_4$  is known as various polymorphics that have similar electrochemical properties during the cycle [11.12] Nevertheless, its low electronic conductivity and its strong polarization need to be further improved during loading/discharge. For the first time in the production of sodium iron silicate, the solvothermal synthesis was used, and its feasibility as a cathode material for Na-Ion batteries has also been investigated.  $\text{Na}_2\text{MSiO}_4$  as a possible cathode candidate due to the abundance of sodium resources in nature. [25]

### 1.2.26 $\text{NaCrO}_2$ cathode for high-rate sodium-ion batteries

Lithium-ion batteries (LIB) have attracted a lot of attention as an alternative source of energy and electricity to fossil fuels. However, the percentage of lithium in the earth crust is only 0.006%. Lithium and lithium compounds could increase and lithium sources could be exhausted if the use of electric vehicles increases in the near future. Recently Komaba et al. investigated the layer-structured  $\text{NaCrO}_2$  layer of the O3 type into which Na-Ions could be inserted due to their greater distance between the plates compared to  $\text{LiCrO}_2$  / from the host structure. A theoretical capacity of about 250 mA h g<sup>-1</sup> has been reported, but the practical reversible capacity is about 110 mA.  $\text{NaCrO}_2$  cathodes with excellent capacity retention, impressive performance and feasibility in full cells that are suitable for advanced energy storage and conversion. Our work allows us to determine with a high degree of security that the carbon-coated  $\text{NaC}_2$  cathode is excellent for use in high-performance Na-ion batteries. [26]

### 1.2.27 $\text{Na}_{0.59}\text{Co}_{0.20}\text{Mn}_{0.77}\text{Mo}_{0.03}\text{O}_2$ cathode

Lithium-ion batteries are widely used as rechargeable batteries due to their high energy density, but the cost of lithium-ion batteries increases year after year due to the limitation of lithium resources. Therefore, it is necessary to explore a substitute for lithium-ion batteries [3-5]. Since sodium-resources are present in excess and the functional principle of sodium-ion equivalent to lithium-ion batteries is considered to be effective substitutes. The layer oxide- $\text{Na}_x\text{TMO}_2$  material is produced by stacking TMO6 plates. The structure of the

layer oxide material provides a stable and relaxed three-dimensional scaffolding. It also provides a sufficient electrode-electrolyte border area to allow the redox reaction of the active metal to run completely. The doped method was used to replace Mn in the layer oxide with other transitional metal elements to stabilize the structure of the material and improve electrochemical performance. Chu et al. [3] prepared a pseudo-ternary  $\text{Na}_2/3\text{Mn}_1/2\text{Fe}_1/4\text{O}_2$  material as a cathode of a sodium ion battery. Zang et al. [24] used Mo as a replacement for Mn in  $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$  material. The material was able to deliver a discharge capacity of up to 260.8 mAh g<sup>-1</sup> when operated at 1 °C in a voltage range of 2.0-4.8 V. Although it could provide a high discharge capacity, the capacity reduction at 1 °C and 10 °C is not very optimistic. Mo doping is an effective method to improve the electrochemical performance of manganese-based layer oxide cathode material for sodium ion batteries. Mo for a part of Mn does not change the structure of the P2-phase layer, but can obviously improve the cycle performance and the kinetic performance of the source material. [27]

### 1.2.28 Ni- and Mn-based layered transition metal oxides as cathode materials

In recent years, two main aspects have driven the development of rechargeable batteries: demand for the propulsion of mobile electronic devices such as electric vehicles and PCs. Clean and renewable energies such as wind, solar and tidal energy have been widely used to reduce the consumption of conventional fossil fuels. Therefore, large grid EES systems are urgently needed to store excess electrical energy from clean energy sources. The lithium-ion battery (LIB) has been a real success story since its first marketing in the early 1990s by Sony. Sodium-ion batteries (SIBs) are promising candidates for next generation power sources. SIBs could be more attractive for large-scale power storage than LIBs. Recent advances in SIBs are remarkable, as enormous efforts have been made in this area. However, relatively poor electrochemical performance limits their commercialization both in mobile and stationary energy storage. Among all cathode materials, layered metal oxides (LTMOs), polyanionic oxides and Prussian-blue analogues (PBAs) have been widely proven as promising candidate materials for SIBs. Recent progress on three types of LTMO cathode materials (including Ni-based, Mn-based and Ni/Mn-based LTMOs) for use in SIBs is summarised. [28]

## 1.3 Conclusions

Sodium-ion batteries have proven to be one of the crucial research priorities in the field of energy storage and conversion technologies. Suitable cathode materials are necessary components between the various components of SIBs. Iron-based materials have a massive influence due to their low cost, ideal voltage and environmental friendliness. The theoretical capacities of transition metal oxides are high, but there are problems related to their poor structural stability and difficult preparation methods. Carbon coatings or the design of porous nanostructures can effectively improve the electrochemical performance of the materials. Some polyanionic compounds have the advantages of high voltage and good structural stability. Despite progress in the development of iron-based electrodes for SIBs, some scientific and practical problems remain to be overcome in the direction of commercialisation. Several points should be highlighted as follows: Several points need to be highlighted in order to overcome the challenges of SIB electrodes. Although SIBs are similar to LIBs, it does not seem so easy to apply the iron-based cathode materials of the LIBs directly to SIB, as sodium ions have a larger ion radius. LIB cathode have a different structure than SIB. Further research of new materials with high energy and power density and long life of SIB cathode is necessary. At present, the synthesis methods of iron-based materials for SIB cathodes are not yet sufficient to achieve high performance for practical application. Traditional solid phase methods and gel-sol methods are the most important preparation techniques. The methods must be optimised to control morphologies and structures. Structures and electrochemical reaction mechanisms of iron-based cathode materials can be investigated and understood. It is expected that the development of in situ characterization technologies such as situ-electron microscopy and in situ-Raman spectroscopy will support the research of the material functional and reaction mechanisms. The identification and detailed characterisation of the Na<sup>+</sup> ion and electron transport within the materials

will benefit the rational design and optimized synthesis of the materials. The electrolyte is an important component that affects the safety performance of the entire battery. The properties of the electrolyte greatly limit the electrochemical performance of sodium ion batteries. Therefore, the compatibility between cathode material and electrolyte should be optimised in order to achieve high performance. Among all developed SIB cathode materials, both iron-based Prussian blue compounds, polyanion compounds and O<sub>3</sub>-like layer oxides have good commercial prospects for grid-scale applications due to their low cost and low electrochemical properties. However, there are still some problems that limit their commercialization progress. [1]

We developed a conceptually new method for producing compliant coating layers (also known as artificial CEIs) on NaNi<sub>1/3</sub>Fe<sub>1/3</sub>O<sub>2</sub> particles. This was a cost-effective and efficient method, whereby battery powder was simply immersed in an organic solvent "cocktail". [2]

Micron-sized copper-substituted layer oxides with a P2-like structure were produced using a simple sun-yellow method. The increase in the Cu content results in a reduction in the discharge capacity, but an increase in the reaction potential. Part of the Mn in the grid is inactive after the Cu substitution, which greatly improves the material's performance and stability. [3]

SIBs are fully investigated not only because of their abundant resources and low costs, but also because they can reduce pressure on LIBs. Polyanionic scaffolding compounds such as phosphates, pyrophosphates, sulphates, silicates, molybdates, etc. are preferred due to their long cycle strength, good thermal stability and adjustable voltage of the reactive redox pair. The current pyrophosphate cathode materials can be divided into the following categories: Na<sub>8-4x</sub>M<sub>4</sub> + 2x (P<sub>2</sub>O<sub>7</sub>)<sub>4</sub> (M = Mn, Fe, Co or Co), Na<sub>4</sub>M<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and sodium pyrophosphates. Due to the restriction of electrochemical activity, there are relatively few single-way phosphate studies. Compared to Fe-based pyrophosphates, Mn, Co and Ni-based phosphates have low electrochemical activity and actual specific capacity. The cost-effectiveness of the synthetic strategy, the variety of construction and the conductivity of the final product need to be further evaluated. In addition to half cells, studies on prototypes of whole cells based on pyrophosphates for SIBs should also be taken seriously. Finally, this is the only way for electrode materials to be put into practice. [4]

SIBs are increasingly attracting attention to the next generation of high-energy batteries. In recent years a large number of V-based electrode materials have been developed, which can be easily categorized into vanadium oxides (e.g. V<sub>2</sub>O<sub>5</sub>, VO<sub>x</sub> and VO<sub>2</sub>) and vanadium bronzes. The theoretical calculation is an effective tool for predicting novel or optimized structures of V-based materials as high-performance calculators for SIBs. As expected, it is highly desirable to explore new materials with the help of theoretical computation along with experiments. The theoretical calculation is a useful tool for predicting novel structures. Morphological control (e.g. reduced particle size, nanotubes, nanobelts, core shell) and hybridization with other highly conductive materials also influence the electrochemical performance of V-based electrodes for SIBs. Innovative, simple, environmentally friendly and cost-effective synthesis methods should be well developed. To achieve a high capacity and energy density, materials containing PO<sub>4</sub> and F<sup>-</sup> anion are often used at much higher voltages (compared to conventional electrolytes) that are suitable for cell systems with larger electrochemical windows and high anode voltage. The configuration of a SIB full cell, based on V-based materials as an anode and cathode for SIBs, will provide great progress in practical application in the future. Speed capability and cycle stability are still very limited, especially compared to LIB pendants. There are a number of advantages for the development of V-based materials for SIBs and LIBs. Vanadium is a "non-green" element (possibly harmful to the human body and the environment), and its relatively high costs should be carefully considered in the future. [5]

It was shown that 2 Na-Ions from the NFVP structure can be switched on with an average voltage of 3.1 V (vs. Na<sup>+</sup>/Na). Surprisingly, up to 74% of the theoretical capacity was maintained at 30 °C. [6]

As a rule of thumb for the development of high-performance multi-component cathode materials in alkali metal ion batteries, a homogeneous or defined distribution of the transition metal cations is considered. In contrast, the authors reported on a powerful sodium layer cathode material that resulted from a highly heterogeneous 3D element distribution. The examined material (CFM-Cu) had almost no fading capacity at C/10 after 100 cycles. [7]

NCM55 delivered excellent electrochemical performances, which were characterised by high capacity, good cyclic stability and excellent performance. X-ray measurements of electrodes after charging and unloading at selected voltages show that no phase transition took place during the desodation process. Further work is in progress to increase the average discharge voltage. [8]

Both a blank NVP and an NVP/graphen composite were synthesized with high crystallinity in particles in the submicron area. They provide similar discharge capacities and voltage profiles at low C-rates. However, a dramatic capacity gap between the two samples was observed at higher C-rates. [9]

For controlled production of BDT-G, a simple synthesis strategy has been developed, where graphs serve as carriers and increase electronic conductivity. The current strategy is simple and effective and could also be applied to other organic electrode materials used in sodium-ion batteries. [10]

A series of hybrid cathode materials  $\text{Na}_x\text{Li}_{1.5-x}\text{Ni}_{0.167}\text{Mn}_{0.67}\text{O}_2$  has been successfully synthesized by simple co-falling in combination with a calcination method. The layer structure P2 (space group: P63 / mmc), the  $\alpha$ -NaFeO<sub>2</sub> structure and a small amount of Li<sub>2</sub>MnO<sub>3</sub> coexist in the materials. The maximum discharge capacity compared to Na/Na + is provided by Na<sub>0.6</sub>Li<sub>0.9</sub> Ni<sub>0.0.1</sub>, which is approximately 220 mA h g<sup>-1</sup> in the first cycle. [11]

In this work the authors presented an electrochemical method for the direct extraction of O<sub>3</sub>-like materials  $\text{Na}_{1+x}\text{Li}_{0.05}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_y\text{O}_2$  - e.g. so far the authors found that the material could not be easily produced by conventional direct chemical synthesis. This material shows impressive electrochemical performance only in the first cycles. The coating of li- and mn-rich NCM precursors with an Al<sub>2</sub>O<sub>3</sub> surface layer in the ALD process produced sodium intercalation cathode materials with significantly improved performance. The surface layer of aluminium oxide and Na<sub>5</sub>AlO<sub>4</sub> forms an excellent passive SEI that transports Na-Ions very well. [12]

Na<sub>2</sub>V<sub>6</sub>O<sub>16</sub> nanobelts are synthesized with a mild, cost-effective one-stop and template-free hydrothermal method and are suitable as promising insert cathode material for NIBs with a high capacity of 194.6 mAh g<sup>-1</sup> and fast electron transferability. [13]

The NFNO electrode has been preloaded with a low voltage of 1.6 V. The ACEI layer with a thickness of 35 nm could prevent the secondary reaction and resolution of transition metals. This simple and inexpensive method of achieving reversible cathodes will provide deep insights into the development of advanced NIBs. [14]

Nb<sup>5+</sup> ions have been successfully donated to the crystal grid of the parent material P2-Na<sub>0.67</sub>Co<sub>0.25</sub>Mn<sub>0.75</sub>O<sub>2</sub> without changing the structure and the P63 / mmc space group. The dose of Nb<sup>5+</sup> has increased the c axis, the d distance of (002) peak and the Na-O binding length and thus significantly increased the rate. [15]

When used as cathode material in Na-Ion batteries,  $\beta$ -MnO<sub>2</sub> Nanorods showed a much better electrochemical performance than  $\alpha$ -NO<sub>2</sub>. After 100 cycles, the electrode maintained a capacity of 145 mA h<sup>-1</sup> after 100 cycles. [16]

Hybrid electrode shows a surprisingly high specific capacity of 194 mA h g<sup>-1</sup>. Such excellent electrochemical performance results from the synergistic effect of the three active components of CNT, NiHF nanocubes and BCP, which can trigger new electrochemical processes for the Na<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> introduction reactions. [17]

A novel electrode that can be used for sodium ion batteries was produced with FeF<sub>2</sub>-rGO nanocomposite and PAA binders. The degradation of the electrode structure by cycles could be suppressed by PAA with high stiffness and adhesion. This is the first report that PAA uses as binder in metal fluoride electrodes. [18]

Polyanion compounds are considered to be one of the most promising cathode materials for SIBs at room temperature due to their stable structure, their high energy density and their thermal stability character. In this review the authors have systematically discussed the latest progress in phosphates, fluorophosphates, pyrophosphates and mixed phosphates. Table 1: Summary of representative polyanion electrode materials. Polyanion electrode materials are polyanionic electrodes. The material are polyphenol polyphenol electrode materials with polyanion, polyphenols and polytinols, polytinophenol electrodes. Polytinols are polyion electrodes with polyion and polyion polytytinolside. Table 2 Comparison between different types of polyanion

compounds. Polyanion are polyanionic compounds that form polyphenol compounds. Table 2 compares polyanion to polyphenols that form a variety of polyphenols. Polyphenols are a kind of chemical compound that forms polyphenols, a form of formaldehyde that forms a formant form. Among the polyanion materials for SIBs, fluorphates are considered to be the most promising due to their stable structure and their higher redox potential (approximately 4 V). Further use of far-explored vanadium-based fluorphates is hampered by the toxicity of Element V. Therefore, the authors can consider replacing V with other environmentally friendly elements (such as Mn, Fe). The rapid pace of commercialisation of SIBs requires an increased exploration of entire cells. All components of the full cell, including the positive electrode, the negative electrode, the electrolyte, the binder, etc., should be equally appreciated. There are still a variety of challenges for polyanion materials; their mechanism must be further understood and investigated. [19]

In this work the authors have proposed to quantify the speed performance of sodium cathode materials in half cells based on the extremely exponential function. This enables a systematic comparison of different compounds in terms of the critical C-rate  $W$ , the inaccessible proportion of theoretical capacity  $\alpha$  and the defect concentration dependent  $\beta$ . the authors believe that our work would enable a deeper understanding of the various factors that contribute to the overall speed capability. [20]

P2-Na<sub>0.67</sub>Mn<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> has been studied as cathode materials for Na-Ion batteries. Sodium ion diffusive coefficients (D<sub>Na+</sub>) in these fixed solutions ranged from 10<sup>-11</sup> to 10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup>. Higher diffusion coefficients were observed in the range of Co<sup>3+</sup> / Co<sup>4+</sup> Redox. D<sub>Na+</sub> values increased with the increase in cobalt content of MC25 ; MC50 ; MC75. [21]

A number of high-quality nano- and ni-doped NFF cathode materials have been successfully synthesized using a scalable citrate-based controlled crystallisation co-formulation method. The influence of the ni-content on the structure and electrochemical behaviour of prepared materials has been examined in detail. [22]

A number of Na<sub>1-x</sub>Cr<sub>0.95</sub>Cr<sub>0.95</sub>Ti<sub>0.05</sub>O<sub>2</sub> cathodes were successfully synthesized by the two-stage solids reaction at 900 °C. The X-ray results of the Ti-doped samples show the same O<sub>3</sub> structure with the increased NaO<sub>2</sub> interlayer spacing. [23]

Interaction microstems could serve as an indispensable bridge to manage the design and synthesis of high-voltage SIB cathode materials with excellent cycle stability and thermal stability. A high initial reversible capacity of 142,8 mA h g<sup>-1</sup> with a high initial coulombic efficiency of 95% and a high capacity retention of 93%. [24]

A metastable sodium iron silicate phase was produced by solar thermal synthesis and studied for the first time as cathode material. Charging the sodium iron silicate to 4.1 V at 1 / 40 C resulted in 126 mAh g<sup>-1</sup>. The removal of even less than one na from the host structure led to an amorphous phase. This is a clear indication that sodium iron silicate is structurally unstable. [25]

C-NaCrO<sub>2</sub> cathodes showed excellent cyclicality and ultra-fast cyclicality up to a rate of 150 C. They were modified by carbon in such a way that they had a high electrical conductivity of about 10<sup>-1</sup> S cm<sup>-1</sup>. Heat production is relatively low due to the suppression of oxygen development during the exothermic reaction. [26]

The discharge capacity of the mo-doped cathode at 0.1 C after 100 cycles remains at about 120.7 mAh g<sup>-1</sup> and the retention rate is 91.51%; however, the capacity retention of the unrooted sample can only reach 64.59%. This is because the introduction of Mo with a large ionic radius prolongs the C axis of the material. [27]

Due to its high battery performance, LTMOS are promising cathode materials for SIBs. Ni / Mn-based materials show improved cell performance compared to other materials. Cation replacement was used to improve the structural stability of LTMOS by suppressing phase transitions. [28]



# Chapter 2

## Na-ion Anode Materials

### Contents

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### 2.1 Introduction

A major effort is being made around the world to develop high-performance electrode materials for Na-Ion batteries. This review provides a comprehensive overview of anode materials based on the Na-Storage Mechanism and discusses the problems and challenges associated with these anodes. The search for suitable anodes is still difficult, although considerable progress has been made. The authors believe that high-performance Na-Ions would be promising in the near future for practical applications in large energy storage. [29]

In recent years the development of new electrode materials with high sodium storage capacity and long service life has been given much attention. In a large number of anode material libraries, tin materials with alloy reaction mechanism show great potential for use in high-energy SIBs. [30]

Sodium ion-ion batteries develop as a substitute for lithium ion-ion batteries due to the sodium ion-richness in the earth's crust. The recent development of sodium ion-ion batteries was achieved by the use of selected carbon as an anode. The performance of selected carbon materials such as charging/discharge capacity, voltage profile and cyclic stability depends heavily on the sizes, additives, electrolytes and structures. [31]

Sodium ion batteries (SIBs) are considered as potential alternatives to LIBs due to the high availability of sodium resources, low costs and similar electrochemical properties. SIBs are also considered promising options for large-scale energy storage of the next generation. Among the carbon-containing materials, graphs have excellent physical and chemical properties for use as anodising material. [32]

The use of new energy conversion and storage technologies is urgently needed to meet the increasing energy demand. Rechargeable batteries are universal devices, among which the use of lithium-ion batteries is particularly extensive. Therefore, it is important to find suitable anode materials that are able to play a dual memory role. [33]

Na-ion batteries have emerged in recent years because of their natural wealth, low costs and environmental friendliness. In this article the authors highlight the current research progress in anode materials. The authors also discuss the failure mechanism and the problems and challenges associated with these anodes. [34]

The B7P2 monolayer has a high storage capacity of  $3117 \text{ mA h g}^{-1}$  for both LIBs and SIBs. This study offers us some good clues to develop/discover other anode materials with ultra-high capacity, and serves us as another vivid example. [35]

Metallic-organic devices (MOFs), which are composed of metal ions and organic ligands via coordination bonds themselves. Versatile nanostructures such as carbon, metal oxide, sulfide, selenide and phosphide were produced by pyrolysis or wet chemical strategies from MOFs. MOF-derived materials have excellent electrochemical properties for sodium ion batteries. [36]

AtiOPO<sub>4</sub> (A = NH<sub>4</sub>, K, Na) is introduced for SIBs for the first time, with sodium ion battery (SIBs) being widely observed. Most anodes have a low coulombic efficiency and a dendritic growth of sodium due to lower sodium voltages (below 1.0 V). [37]

In this report the authors focus on the latest research progress in the design and synthesis of anode materials based on tin sulfide and selenide (SnS, SnS<sub>2</sub>, SnSe and SnSe<sub>2</sub>) for LIBs and NIBs. [38]

Hard carbon is regarded as one of the most promising anode materials for sodium ion batteries. Now it is imperative to develop an appropriate method of preparation to maintain hard carbon anode particles with high initial coulombic efficiency and good cycle performance. The performance of PHC depends heavily on the carbonization temperature of the material. [39]

$\alpha$ -MoO<sub>3</sub> nanosheets, which were grown vertically on activated carbon fibre fabrics as superior anode materials for Li and Na-Ion batteries, were achieved by the method of controlled preparation. MoO<sub>3</sub> array electrodes have a high discharge capacity of  $4.48 \text{ mA h cm}^{-2}$  and an excellent cycle stability at  $0.5 \text{ mA cm}^{-2}$  (94% capacity retention after 200 cycles). [40]

A novel composite made of copper phosphide and Super P Carbon Black (CuP<sub>2</sub>/C) is a potential anode candidate. They offer a large capacity of over  $500 \text{ mA h g}^{-1}$ , a high performance and an acceptable short-term cycle stability. The study suggests that this transitional metal phosphate with a suitable carbon coating could offer great opportunities as anode materials for sodium ion batteries. [41]

A sea-like SbNPs @ C nanopoly made of Sb nanoparticles (NPs), which are evenly embedded in a carbon matrix, has been synthesized by a simple, cost-effective and high-energy hydrothermal method. As an anode material for SIBs, the materials obtained showed superior electrochemical properties. [42]

A series of Sn/P-based composites with plum pudding configuration was manufactured to achieve controlled crystalline/amorphous structures as well as an optimized size and distribution in a carbon stock. Quaternary Sn<sub>4</sub>P<sub>3</sub> / Sn/P/C composite material showed the best electrochemical performance with a remarkable long-cycle performance of  $382 \text{ mA h g}^{-1}$  and a capacity retention of 86% for nearly 300 cycles. [43]

A multi-layer MoS<sub>2</sub> nanostructure, limited to a hierarchical porous carbon fiber bond, has been synthesized via the nanocasting pathway. As an anode material, the compound displays excellent electrochemical properties for sodium ion-ion batteries. It offers high reversible capacities ( $491 \text{ mA h g}^{-1}$  after 50 cycles at  $0.1 \text{ A g}^{-1}$ ) and long-term cycle stability. This regulatory strategy could provide new insights into the production of high-performance anode materials. [44]

The amorphous sodium titanate, deposited on carbon nanotubes, has a high specific capacity, an excellent rate and an extremely long cycle life ( $100 \text{ mA h g}^{-1}$  after 3500 cycles). It is expected that the ALD approach developed here can be extended to the clearly defined production of other sodium-containing electrode materials. [45]

Two-dimensional (2D) materials have made great progress in recent years and serve as anode materials for NIBs. They have a unique 2D layer structure, infinite surface lengths and many exposed active sites. The authors offer an insight into the future perspectives of improving the performance of sodium storage. [46]

Compared to high-performance cathodes, anodes have an unstable performance that impedes the development of sibs. Efforts have been made to explore the optimized structure and composition of high-performance anodes and to make progress in the use of carbon-based materials. [47]

Hard carbon obtained from abundant biomass of tea waste was produced using a simple carbonisation method. The correlation between pyrolysis temperature and microstructure and the electrochemical properties of the prepared carbon materials has been examined in detail. The results indicate that the plateau

capacity of these anode materials is closely related to the carbonisation temperature. [48]

The behaviour and electrochemical charge/discharge of sn-bi-sb alloy films were investigated, as well as pure sn, bi and sb films as anodes for sodium ion batteries (SIBs). The most powerful alloy showed a composition of 10% sn, 10% Bi and 80% Sb (Sn10Bi10Sb80) and maintained 99% of their maximum capacity during the cycle ( $621 \text{ mA h g}^{-1}$ ) after 100 cycles. [49]

NaBiS<sub>2</sub> nanostructures, developed in a simple solvothermic way, were first tested as anode materials for sodium ion batteries. They are characterised by high capacity and low potential compared to Na/Na<sup>+</sup> and would be a promising anode material. [50]

Metal sulphides have been proven as prospective anode materials for SIBs on the basis of a conversion mechanism. CuS micro-flowers consist of nanoblades that can provide an increased Na<sup>+</sup> diffusion permit and a larger volume of space to take account of volumetric changes. The superior electrochemical performance is linked to the nano-microstructure and the controlled reaction mechanism. [51]

Carbon nanofibres (CNFs) obtained from cellulose nanofibres are investigated as anode material for sodium ion batteries. The CNFs have promising electrochemical properties, including a high reversible capacity ( $255 \text{ mA h g}^{-1}$  at  $40 \text{ mA g}^{-1}$ ) and excellent cycle stability. [52]

Sodium ion batteries (SIBs) are limited by their relatively low energy density. This deficiency requires the construction of anodes with high specific capacity and excellent cycle strength at low cost. At this point the authors consider one-dimensional structural/heterostructural carbon nanofibres (CNFs) to be the basis for the development of anode materials for SIBs. [53]

It was expected that hard coal will be the first commercial anode material for SIBs. Carbon plant origin is of outstanding importance due to its abundant source, low cost and excellent electrochemical properties. This report focuses on the recent progress in the development of hard carbon anodes of plant origin. The authors have summarized the microstructure and electrochemical performance of hard carbon materials that have been pyrolyzed from different parts of plants at different temperatures. [54]

## 2.2 Literature Reviews

### 2.2.1 High-performance anode materials for Na-ion batteries

Large energy storage is extremely important to modulate intermittent renewable resources and to integrate safely and smoothly into the intelligent electricity grid [2-8]. A large energy storage is extremely important to modulate intermittent renewable energy sources and integrate safely into the electricity grid. Li-ion batteries (LIBs) have been successfully used as a power source in portable electronic devices and electric vehicles, but a large-scale application of LIBs would force us to take into account the rising price, the low frequency and uneven distribution of the Li resource [9]. Na and Li belong to the same main group and have similar chemical properties. It should be noted that the energy density of NIBs will always be lower than that of LIBs. However, the energy density in the area of large energy storage is not a critical problem. The radius of Na<sup>+</sup> (0.102 nm) is about 40% greater than the radius of Li<sup>+</sup>. The biggest challenge in the development of NIBs technology lies in the search for high-performance electrode materials, including anode and cathode materials. Many materials have been developed for the cathode of Nibs, e.g. coated transitional metal oxides Na<sub>x</sub>MO<sub>2</sub> (M = Co, Mn, Ni, etc.) [12-14], phosphates (NaFePO<sub>4</sub>, Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>), fluoride [15-17] and great efforts are still being made to develop better cathode. Unlike Li, Na-Metal cannot be used directly as an anode in most organic electrolytes due to its safety risk and its unstable passivity layer. Graphite, the conventional anode for LIBs, is less active in NIBs, since the intermediate layer distance to the larger Na<sup>+</sup> radius is not accurate [21]. In recent years, nongraphic carbons [22, 23], alloys [24-26] and transition metal compounds [27-31] have been developed and have appeared as promising anode materials. Link between capacity and voltage for existing anode materials of NIBs [32] connection between capacity, voltage and voltage. link between voltage and capacity of the anode material of NIB. connection between capacity and voltage for Nibs anode materials is shown at the bottom of the page. [29]

### 2.2.2 Research progress on tin-based anode materials for sodium ion batteries

Global fossil energy consumption is rising year by year, causing serious ecological and ecological problems such as global warming, air pollution and desertification. Clean energy sources such as solar energy, wind energy and tidal energy have attracted attention. Electrochemical energy storage technology is an effective resource because of its high efficiency and long life span. Lithium-ion batteries (LIBs) are widely used in mobile phones, notebooks, digital cameras, power tools and have gradually been extended to new energy vehicles and energy storage devices. Due to the low reserves and uneven distribution of lithium on earth, it is necessary to develop a new energy storage technology with low costs and high performance. Sodium has similar physical-chemical properties to lithium. Compared to lithium, sodium has abundant reserves and low costs, as shown in Table 1. SIBs with sodium ions as load carriers have a greater application potential in large energy stores [7, 8] Compared to lithium, sodium ion has abundant reserves and low costs. A comparison of the properties of sodium and lithium was made of sodium and lithium. Lithium is a lithium-phenomenal form of sodium. It is a kind of lithium that has a number of properties that can be found in lithium, sodium, potassium, lithium and lithium. Many types of negative electrode materials for SIBs have been reported. Carbon-based materials and organic compounds with the advantages of low prices, simple preparation, low reaction platform and good cycle stability unfortunately have a low own capacity. Transitional metal oxides and sulphides have a high theoretical specific capacity, but their poor conductivity limits their development. Pure tin material was disturbed by its high theoretical specific capacity of  $847 \text{ mAh} \cdot \text{g}^{-1}$  far. However, the volume expansion of 420% in the process of salinisation / desodation causes the pure tin electrode to break rapidly, leading to the loss of electrical contact between the active material and the collector. [30]

### 2.2.3 Carbon materials and their composites with alloy metals for sodium ion battery anodes

Lithium-ion batteries (LIBs) are considered the most important technology for energy storage and conversion. LIBs are widely used in portable electronic devices, communication devices, stationary energy storage and ever larger markets for electrically operated vehicles. SIBs were originally researched in the late 1970s and early 1980s together with Li batteries. The successful use of LIBs diverted the attention and focus of the scientists of SIBs. Future alternative energy storage requires an increasing energy density. Na-iones have a much larger radius ( $1.02 \text{ \AA}$ ) than Li-Ions. In the beginning, sodium metal was used as an anode, but the high reactivity of metallic sodium with the organic electrolyte solvents and dendrite formation during the Na-metal separation were problematic, due to the low melting point of Na ( $98^\circ \text{C}$ ), which represents a significant safety risk in devices designed for use at ambient temperatures. Komabas Group and Nazars Group recently reported in detail on recent progress in the exploration of sodium ion batteries. However, only limited information was reported on the effects of nanostructures and the combination of carbon materials with alloy materials. It is also noteworthy that metal oxides, sulphides and carbon composites are not discussed in detail before the scope and limit of this review. [31]

### 2.2.4 Advanced nanocomposites as high capacity anode materials for sodium-ion batteries

Lithium-ion batteries (LIBs) have excellent properties such as high conversion efficiency, stable cyclical capability, adjustable power and energy properties for different power functions. Sony Corporation successfully marketed LIBs in 1991; after that, significant research work was carried out to establish them as the most prominent power source. LIBs are widely commercialised and used in electric vehicles and HEVs. The development of sodium ion batteries (SIBs) is an ideal alternative to LIBs. First studies on SIBs and LIBs were initiated side by side in the 1970s and 1980s. Due to the rapid and promising progress in the development and successful commercialisation of LIBs, however, Sibs' development was largely abandoned. Recent studies have proposed several metal oxides (MOs) and metal sulfide (MSs) as anode materials capable of achieving

an acceptable capacity level. SIBs consist of a positive electrode and a negative electrode made of sodium-containing materials. During the charging process, Na<sup>+</sup> migrates from the cathode to the anode, and the reverse occurs during the discharge process. The chemistry of sodium and lithium is clearly similar, which means the possibility of using similar compounds for both LIB and SIB systems. Reduced graphene oxide (RGO) has been reported for the first time in 2013 as a host of Na<sup>+</sup> ions in SIBs. It shows remarkable electrochemical properties such as good durability and performance. This is related to the presence of defects arising from the residual oxygen groups, and a higher distance between the layers in graphene (0.37 nm) than in graphite. In recent years, researchers have designed and developed various types of composites for anodes. Compositions consist of graphs in the form of GO, RGO, doped graphs or expanded graphite. The above mentioned metal forms are often subject to volume expansion during the charge/discharge process, resulting in poor cyclic stability. The macromolecular carbon atom graph has a waving structure and has an excellent load carrier and electron mobility of 20 m<sup>2</sup> V<sup>-1</sup> cm<sup>-1</sup> and 15000 m<sup>2</sup>,1 cm. The authors present the conclusions and future perspectives that researchers and manufacturers will be helpful in the development and construction of cost-effective energy storage materials. [32]

### 2.2.5 Dual anode materials for lithium-ion batteries

Fossil fuels such as coal, oil and natural gas are the basic energy sources of the modern economy. Nevertheless, these forms of energy are increasingly exhausted and inevitably lead to a serious deterioration of the environment. Currently, research to improve rechargeable batteries focuses mainly on two categories of electrochemical equipment: lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs). LIBs were proposed by British chemist M Stanley Whittingham in the 1970s and first introduced by Sony in 1991. Due to several advantages, they have gradually developed into one of the most universal sources of energy instead of conventional fossil fuels. LIBs are used for a variety of devices of daily life, such as electric vehicles and portable devices such as mobile phones, laptops and electric tools. SIBs were first investigated together with LIBs in the late 1970s and up to the 1980s. Due to their relatively low cost and higher sodium supply from the alkaline metals family, they are considered to be a cost-effective choice, especially when large-scale applications are needed, such as energy storage in the grid. The energy density of the currently existing L / SIBs is still limited and can hardly meet the increasing energy requirements of the whole world. The efficiency of rechargeable batteries depends on the thermodynamics and kinetics of the electrochemical reactions involved in the components (anode, cathode, electrolyte and separator). It is imperative to develop new dual electrode materials with better performance. [33]

### 2.2.6 Update on anode materials for Na-ion batteries

A large-scale energy storage (ESS) becomes extremely necessary to modulate intermittent renewable resources and integrate them safely and smoothly into the network. The development of renewable and clean energy sources such as wind, sun, biomass, tides and geothermal is becoming increasingly important. The large-scale use of LIBs suffers from challenges due to scarcity, misallocation and high costs of lithium resources. Na-Ion batteries (NIBs) are considered the most promising alternative to LIBs in order to achieve large-scale ESS and sustainable application. Table 1 Comparison of lithium and sodium. Table 1 compares lithium to sodium. Lithium and sodium are lithium, sodium, sodium. Sodium is sodium, potassium, lithium, potassium and lithium. Sodium and lithium are lithium. Sodium is sodium and sodium, lithium is sodium. Sodium is lithium. Stationary Na-Ion batteries with room temperature were examined parallel to LIBs before 1980. However, it is assumed that the usable energy density of the Na-System is much lower than that of the Li-System. Si-based materials should be the most promising anodes for LIBs, but not for NIB systems. Negative electrodes are a necessary component of Na-Ion batteries. Newman and Klemann reported for the first time about the high-grade reversible sodium infusion in TiS<sub>2</sub> at room temperature. NIBs achieved a significant breakthrough in 2000 by reaching a reversible sodium storage capacity of 300 mA h g<sup>-1</sup> for hard

carbon. Unlike lithium metal, sodium metal cannot be used directly as an anode in view of its safety hazard and unstable passivity layer in most organic electrolytes at room temperature. It is urgently needed to find suitable anode materials with a suitable voltage window, high reversible capacity and stable structure. Anode materials for NIBs have experienced a rapid development of anode materials. In this paper the authors offer more detailed and up-to-date research progress in the field of NIB anodes, especially in the last three years. This review discusses the Na-Storage and Failure Mechanisms of the selected anodes and shows the problems and challenges facing these anodes. [34]

### 2.2.7 Ultrahigh capacity 2D anode materials for lithium/sodium-ion batteries

Both sodium-ion batteries (SIBs) and LIBs were investigated in the 1970s. SIBs have been re-emerged as attractive candidates for medium and large stationary energy storage. LIBs are widely used in portable electronics and electric vehicles due to their high energy density. Two-dimensional (2D) materials are promising candidates for the next generation of LIB/SIB anode materials. They have a high storage capacity, excellent electrical conductivity and a lower diffusion energy barrier. Many 2D materials have been researched, such as graphs and its derivatives, metal dichalcogenides, metal oxides and transition metal carbides. Pore size, appropriate distance between adsorption sites and a fully planar topology can significantly increase Li/Na storage capacity. The B<sub>2</sub>S, BP, InP<sub>3</sub>, TiC<sub>3</sub> and NiC<sub>3</sub> monolayer have a greater distance between neighbouring locations than graphs (3.03 Å and 3.18 Å vs. 2.47 Å). A fully planar monolayer is beneficial to use more adsorbed areas on the substrate. The high capacity of boron nanomaterials is attributed to the stronger binding interaction of the B<sub>7</sub> unit (as the B<sub>6</sub> unit) with Li/Na atoms. The authors have considered the reported candidates of 2D anode materials for LIBs/SIBs. An inspiring material is the experimentally available striped boron ( $\beta$ 12 boron). The B<sub>7</sub>P<sub>2</sub> binary monolayer has a high stability and is considered the global minimum in the 2D space. Its capacity for LIBs and SIBs reaches 3117 mA hg<sup>-1</sup>, in particular its Na storage capacity is among the highest for 2D materials. [35]

### 2.2.8 Metal-organ framework-derived materials for sodium-ion battery anodes

Lithium-ion batteries are considered to be powerful EES alternatives due to their high energy density and longevity. However, with the large-scale use of LIBs in the markets for portable electronics and electric vehicles, the costs and limits of lithium resources have become increasingly worrying. SIBs, which work on the basis of a mechanism similar to LIBs, are a major research interest. Metal-organic frameworks (MOFs), which are composed of metal-containing nodes and organic links via coordination links themselves. MOFs were widely used as a major candidate in areas such as gas adsorption and removal, catalysis and energy conversion and storage. MOFs are widely regarded as an ideal model or precursor for the design and manufacture of porous nanostructured materials for batteries. During pyrolysis, metal ions and organic ligands can be translated into metal compounds or carbon without atomic migration within the MOF crystals. This leads to the formation of well-defined metallic ion nanoparticles embedded in a porous carbon matrix structure. This report summarises the recent progress in MOF derived materials for SIBs. The structure, morphology and composition of the MOFs as well as the manufacturing processes and conditions will influence the structure of the final products and thus the electrochemical performance. [36]

### 2.2.9 Novel 1.5 V anode materials, ATiOPO<sub>4</sub> (A = NH<sub>4</sub>, K, Na)

SIBs have an intercalation chemistry similar to lithium-ion batteries. The abundance of sodium resources makes the commercialization of energy storage at room temperature on a large scale. The first layer compound that can be used as anodised material is P<sub>2</sub>-Na<sub>0.66</sub>Li<sub>0.22</sub>TiO<sub>2</sub> with an average voltage of 0.75 V. Organic compounds such as chinine, imide and conjugated carboxylate are potential anode materials. Tunnel-like ATiOPO<sub>4</sub> compounds have been studied as anodising materials for SIBs. The orthorhombic structure of such

compounds consists of plates of TiO<sub>6</sub> octahedres and orthogonal PO<sub>4</sub>. This material is often used in nonlinear optics due to its excellent optical properties. [37]

### 2.2.10 Layered tin sulfide and selenide anode materials

Li-ion batteries (LIBs) are two of the most important types of energy storage, which have been fully investigated due to their benefits such as environmental friendliness, high energy/performance density and long life. LIBs have already achieved great commercial success in portable electronics. The use of LIBs as power sources for electric vehicles has attracted great attention in many countries, especially in China. Due to relatively weaker M-X (X = S, Se) ion bonds, which give the material kinetically favorable properties, are considered as promising anode materials for LIBs and NIBs. So far, a great deal of work has been published on applications of SnS, SnS<sub>2</sub>, SnSe and SnSe<sub>2</sub> in a short time. Table 1 Physical and electrical properties of historical SnS, SnS<sub>2</sub>, SnSe and SnSe<sub>2</sub> for LIBs and NIBs. Table 1 shows the physical properties of SnS and Nibs. SnS is a kind of layer that is overlaid with layers of layers. [38]

### 2.2.11 Pinecone biomass-derived hard carbon anodes for high-performance sodium-ion batteries

The researchers pay more attention to the synthesis of hard carbon through abundant biomass-based materials instead of expensive inorganic materials. The hard carbon (PHC) anode obtained from needle pins for sodium ion batteries showed a good electrochemical property. The pine cones have a moderate hardness and can be easily powdered to fine powder precipitation with the help of domestic milling machines. [39]

### 2.2.12 MoO<sub>3</sub> nanosheet arrays as superior anode materials for Li- and Na-ion batteries

Lithium-ion batteries have developed into attractive energy devices due to their high energy density and excellent reversibility. Due to the relative abundance of sodium resources, sodium ions have recently become increasingly attentive. Graphite has been used in LIBs with low theoretical capacity (372 mA h g<sup>-1</sup>) large-scale, but is not suitable for SIBs. Molybdenum trioxide (MoO<sub>3</sub>) is an environmentally friendly and cost-effective electrode material. It delivers a theoretical capacity of 1117 mA h g<sup>-1</sup> through insertion and conversion reactions. Among the three crystal phases of MoO<sub>3</sub>, orthorhombes  $\alpha$ -MoO<sub>3</sub> is best suited for the anode material due to its high thermodynamic stability. This article reports for the first time on the production of  $\alpha$ -MoO<sub>3</sub> nanosheets, which are grown vertically on activated carbon fibres (as MoO<sub>3</sub> NSA / CFC) as a novel flexible anode for high-performance LIBs and SIBs by direct oxidation of MoS<sub>2</sub> nanosheet arrays. [40]

### 2.2.13 Nanostructured CuP<sub>2</sub>/C composites as high-performance anode materials

Lithium-Ion Batteries (LIBs) are widely regarded as a demonstration technology for a wide range of applications. There are growing concerns about the availability of sufficient lithium resources to keep pace with the ever-growing global demand. The development of alternative technologies based on more sophisticated elements is urgently needed. Na<sup>+</sup> ions have many similar electrochemical properties as Li<sup>+</sup> ions, which can diffuse through switching-in, alloying or conversion mechanisms for effective charging storage in electrode materials. For example, tin phosphide (Sn<sub>4</sub>P<sub>3</sub>) has been described by several groups with some success as promising SIB anode material. The presence of the secondary ingredient dilutes the concentration of the P-species and can buffer its volume change with repeated softening and desodation. [41]

### 2.2.14 Ultrafine Sb nanoparticles embedded in amorphous carbon matrix

Sodium is the second lightest and smallest alkali metal with a large occurrence in the earth crust (2.8%), low cost and environmental friendliness. Sodium ion batteries (SIBs) are increasingly attracting interest as an

attractive candidate for LIBs. The Na<sup>+</sup> / Na redox potential (- 2.70 V vs. SHE) is only about 0.34 V higher than that of Li<sup>+</sup> / Li. Graphite has negligible Na-Ion storage capacity of 30-35 mA h g<sup>-1</sup>. Several other carbon-containing materials have relatively high specific capacities of about 300 mA g<sup>-1</sup>. The potential of sodium stored in a carbon-containing material is very close to the sodium deposition potential, which can lead to safety problems. Recently, metallic and intermetallic anodised host materials have been used for the development of Na-storage anode materials. Particular attention has been paid to Sn (Na<sub>15</sub>Sn<sub>4</sub>: 847 mA h g<sup>-1</sup>), Sb (Na<sub>3</sub>Sb) and Pb. These alloy-based anodes have large theoretical storage capacities and work with safer potentials. Due to their structure, applications of these alloy electrodes are primarily hampered by structural instability. Due to its rapid reaction kinetics, its high theoretical capacity (660 mA h g<sup>-1</sup>), its improved cycle performance and its excellent performance in connection with conductive carbons, Sb / carbon-based composites are considered to be a promising candidate for SIB anode materials. Sb / carbon-based composites fully exploit the potential of the active material due to the improvement of electrical conductivity compared to pure sb. W. Luo et al. showed a novel synthetic way to produce 1D-peep-like sb @ C structures by thermal reduction of carbon-coated Sb<sub>2</sub>O<sub>3</sub> submicrocronic wire composites. Compared to previous Sb-Carbon composites for SIBs, the hybrid has lower costs and a comparable electrochemical performance. [42]

### 2.2.15 Sn<sub>4</sub>P<sub>3</sub>-induced crystalline/amorphous composite structures

Sodium Ion Batteries (NIBs) have a great deal of attention due to the crusting frequency, wide spread and low cost of sodium resources as a promising alternative to lithium-ion batteries (LIBs). Although sodium has similar chemical properties to lithium, fundamental differences between Na and Li still lead to the restoration of material families for NIBs. Advanced anode materials with high capacity and cyclability are crucial for practical NIBs. The widely used carbon-containing materials in LIBs are either unable to accommodate Na<sup>+</sup> or have poor cycleability. In contrast, certain anodes offer high capacity to produce Na<sub>15</sub>Sn<sub>4</sub> and / or Na<sub>3</sub>P through conversion reactions with Na. Sn, P and their connection Sn<sub>4</sub>P<sub>3</sub>. Control over crystalline and amorphous domains can be largely tailored to the properties of the individual components. Size and spatial distribution of crystalline/amorphous domains significantly determine the response efficiency. Optimized size and distribution could weaken the interface resistance, avoid potential particle agglomerations and growth, and provide manageable networks. In this study, the authors used the above mentioned strategies for the production of sn / P-based composites based on plum pudding as high-performance, cost-effective anode materials. Nano-large snow and / or sn<sub>4</sub>P<sub>3</sub> crystallites are well distributed in the amorphous P-Matrix to form a plum pudding configuration. The comprehensive control of the composite structures, in particular the customized crystalline / amorphous domains, as well as their size and distribution, are a novel strategy for the exploration of superior electrode materials for NIBs. [43]

### 2.2.16 Nanocasting synthesis of a porous carbon fiber composite

Rechargeable lithium-ion batteries (LIBs) are widely used in portable electronics and electric vehicles, but the geographical distribution and high cost of lithium resources hinder the large-scale use of LIBs for a long time. MoS<sub>2</sub> has a multilayered structure with a d-distance of 6.2 Å, much larger than that of graphite, and a high theoretical capacity of 670 mA h g<sup>-1</sup>. Wang et al. observed the phase transition of MoS<sub>2</sub> from the semiconducting phase to the metallic phase at the atomic level. The few layer MoS<sub>2</sub> could improve the slow Na<sup>+</sup> diffusion kinetics, and the porous structure could effectively mitigate the volume change during the charging/discharge process. Capacitive electrodes store sodium ions on the surface of active materials based on electrical double layer capacity (EDLC) or faradaic pseudo capacity, which have better cycle stability than battery-like electrodes. It is generally accepted that microporous carbon with high specific surface area and large pore volume is compatible with capacitive electrodes. The ultra-small, low-layer MoS<sub>2</sub> nanostructure on a hierarchical porous carbon fiber bond (FM-HPCF) was produced as a template using a novel HPCF and as an anode material demonstrated an excellent electrochemical performance for SIBs. [44]

### 2.2.17 Atomically precise growth of sodium titanates as anode materials

Lithium-ion batteries (LIBs) are considered to be the most promising energy storage for the next generation of electric vehicles. The growing market for LIBs has raised concerns about the feasibility of lithium due to its low presence in the earth crust. Increasing demand for lithium-containing electrode materials will drive the price of lithium precursor materials (like  $\text{Li}_2\text{CO}_3$ ) up. The current challenge in the development of this technology is to find suitable electrode materials that allow a reversible sodium storage. NASICON-like compounds ( $\text{Na}_x\text{M}_y(\text{PO}_4)_z$ ,  $1 \leq x \leq 4$ ,  $M = \text{Ti}$  and  $\text{V}$ ) show good electrochemical activity with sodium in a reversible manner. Recently, sodium titanates were discovered as new anode materials with relatively low working potential ( $\approx 1$  V). ALD has been used to produce an all-in-one nanopore battery array, making it a promising candidate for commercial production of genuine 3D solid-body micro-battery. Lithium-free materials produced by ALD can be used directly as anode or cathode materials for SIBs. In this work, the authors developed for the first time an ALD approach to the separation of sodium titanate anode materials as a representative example of sodium-containing electrode materials for SIBs. Sodium titanates deposited as sodium titanates were amorphous, but could easily be converted into a high-crystalline structure after glowing. [45]

### 2.2.18 2D material as anode for sodium ion batteries: Recent progress and perspectives

Lithium-ion batteries (LIBs) have attracted a lot of attention due to the largest energy density and the highest output voltage among all rechargeable batteries. Great attention has been paid to the research of new alternative energy storage systems with cost-effective and high electrical power. Recently, sodium-ion ambient temperature batteries have again attracted attention and proved to be a promising alternative to LIBs. The 2D material family consists of graphs, transition metal dicalcides (TMD) and transition metal carbides. The unique 2D structure and the large surface could enlarge the contact area between active material and electrolyte, shorten the diffusion length of sodium ions and provide a more exposed surface with a large number of active  $\text{Na}^+$  storage sites. However, there are some challenges related to the complex synthesis methods, the unclear sodium ion mechanism, the heavy layer structure and aggregation. This report addresses recent progress in the synthesis and application of the 2D materials in NIBs. It focuses mainly on graphs, phosphorus,  $\text{MoS}_2$  and MXene. The link between structure and electrochemical performance has been fully illustrated. Finally, the conclusions and future perspectives of improving the performance of sodium storage are discussed. [46]

### 2.2.19 Carbon-based materials as high-rate anode for sodium ion batteries

SIBs have drawn intense attention to themselves and show great potential as batteries of the next generation. In the early phase, due to the abundant sodium reserves on earth, SIBs were intended for low-cost electrical energy storage. However, with research developments and deeper understanding, the potential application spectrum of SIBs is extended to small energy storage and electric vehicles. In accordance with the LIBs, the functional principle of the SIBs is also referred to as a "shuttle" mechanism. As a host that allows the reversible insertion/extraction of guest- $\text{Na}$  atoms, the anode exerts a significant influence on the electrochemical performance of the cell. The efficiency of anodes in SIBs can be significantly increased by the use of carbon-containing materials. The energy density of the cell benefits from the low discharge/charging plateau of the carbon anode. Carbon-containing materials exhibit a variety of controllable structures, which is conducive to the coordination of their electrochemical performance. [47]

### 2.2.20 High-performance anode material for sodium-ion batteries

Due to the abundantly existing sodium reserve and its similar chemical and physical properties as lithium, SIB's broad research interests are given as a complementary candidate for use in energy storage in the grid.

The ion radius of sodium is hardly greater than that of lithium, which leads to a slow ion termination kinetics during the Na + switch-in into the electrode. The large sodium ion can not affect graphite due to the low intermediate layer spacing. Hard carbon has outstanding electrochemical properties as the most promising anode materials. As an available natural resource, carbon materials from biomass have received intense attention due to easy processing, environmental friendliness and abundant resources [18, 19]. Biomass has essentially a desirable molecular architecture that is favourable for ion fusion and cargo storage [20]. Nevertheless, the hard carbon anode still has to contend with three serious disadvantages: low initial coulombic efficiency, low reversible specific capacity and high costs. Every year several billion tons of teas are consumed worldwide. Waste tea as typical biomass materials are promising candidates due to their abundant resources. PWT, pyrolyzed at 1400 ° C, has a promising electrochemical performance. This strategy offers an effective way to synthesis efficient biomass carbon materials when using SIBs. [48]

### 2.2.21 Sn–Bi–Sb alloys as anode materials

Lithium is unevenly distributed across the earth's surface, with the majority of known reserves in the lithium triangle of South America (Bolivia, Chile and Argentina with 44-64%). Sodium, on the other hand, is much more common and more widespread than lithium on the earth's surface. Using the excess of sodium to develop sodium ion batteries (SIBs) will lead to a diversification of battery technologies. New cathode materials such as Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> have been developed that have a long voltage plateau close to 3.5 V vs. Na / Na +. Graphite, the anode of choice for commercial LIB, also needs to be replaced, as it hardly reacts with Na. Some so-called hard coal have capacities of over 300 mA h g<sup>-1</sup>. A number of group 14 and 15 elements form with Na an alloy and have been tested as high-performance anodes for SIBs. You should theoretically be able to store 3 Na / Ge, which corresponds to 1108 mA h g<sup>-1</sup>, but this stöchiometry has never been achieved electrochemically. In practice, the capacity of the elemental ge is limited to about 370 mA. Theoretically, Sn has the highest gravimetric capacity at 847 mA g<sup>-1</sup>. However, the capacity to hold down pure sn is generally very low. Among the group of Na alloy materials Sb could be the most promising. Darwiche et al. found out that its cycle stability as SIB anode even exceeded its performance as a LIB anode. However, the performance of pure Sb powder is not always stable over 100 or more cycles. The composition varied from 33-100% of the majority element, and the proportion of minority elements was always 1:1. Sputtering deposits often lead to meta-stable materials such as saturated solid solutions. [49]

### 2.2.22 Novel sodium bismuth sulfide nanostructures for sodium-ion batteries

Sodium ion batteries are one of the most promising rechargeable batteries for their huge and cost-effective sodium resources. However, it is difficult to find some sort of anode material that can insert and remove sodium ion reversibility, as it does commercial graphite in the lithium-ion batteries. Researchers are increasingly paying attention to the electrochemical properties of various anode materials, such as carbon-graphene composites. Na<sub>x</sub>NbS<sub>2</sub> (0 < x < 1, room group = P63 / mmc) as electrode material for Na-Ion batteries. This novel material has a high specific capacity of 143.6 mA h g<sup>-1</sup> with a signature of Na / idle at x = 0,5 in the voltage range between 3.0 and 1.0 V at room temperature. With this the authors report on the controllable synthesis of hierarchical NaBiS<sub>2</sub> nanostructures via a simple solvothermic route. The electrochemical performance is assessed as anode material for sodium ion batteries. In addition, the possible mechanism for the electrochemical reaction is proposed. [50]

### 2.2.23 CuS microflower as a highly durable sodium-ion battery anode

The most common graphite anode for LIBs does not appear to work in SIBs due to the strong sodium en-drite formation during discharge. The development of a stable, cost-effective and powerful anode is one of the biggest obstacles to its practical application. Nano-microstructured materials or composite materials have been used and considered to be the most effective means in recent years. Metal sulfide has a high

electrical conductivity and theoretical capacity. FeS<sub>2</sub> nanospheres, NiS balls, CoS<sub>2</sub> micro / nanostructure, MoS<sub>2</sub>nanoflowers and few layers of SnS<sub>2</sub> are the most commonly used materials. Cu<sub>2</sub>S has a number of advantages such as high safety, cost-effectiveness and superior conductivity. So far, various CuS microstructures such as one-dimensional (1D) rods and tubes, 2D plates and plates as well as 3D balls and flowers have been prepared and applied as electrodes. Due to these methods, mass production is hardly feasible. The study of a new CuS manufacturing method can be extended to commercial use. For the production of nanomicrostructured CuS materials, a simple chemical de-alloyation method was introduced at room temperature, whose sodium ion-storage properties were investigated and the phase development associated with discharge/load was detected by ex-sodium XRD. The morphologies of the CuS material were adapted by optimizing the de-alloyation time. [51]

#### 2.2.24 Carbon nanofibers as an anode material for rechargeable sodium-ion batteries

The rarity and uneven distribution of lithium minerals makes it uneconomic to use LIBs as large-scale power sources outside peak times. Security concerns hamper their wider application. Cost-effective energy storage with good energy density and superior service life are intensively sought. Graphitic carbon materials are the most commonly used anode material in commercial LIBs due to their high reversibility, low costs and good safety features. Carbon-containing materials, ternary sodium compounds, metal nitride, metal oxides, phosphorus and alloys have proved promising due to their high capacity, frequency and safety. Hard carbon materials can be formed by pyrolysis of various starting substances such as sugar, polymers or cellulose. Cellulose substances are promising candidates for the production of hard carbon materials due to their frequency and renewability. The authors show a novel hard carbon nanofibre material obtained from cellulose nanofibres. [52]

#### 2.2.25 Electrospun carbon nanofiber structures as anode materials for sodium ion batteries

Lithium-ion batteries are incessant in many areas of daily life (carable electronics, electronic vehicles, hybrid vehicles, etc.) It is desirable to find an alternative resource for energy storage for the next generation. Sodium-ion batteries (SIBs) are increasingly being observed, especially in large energy storage applications. Graphite with high theoretical capacity (372 mA h g<sup>-1</sup>) was so far the common anode material for commercial LIBs. If graphite is applied to SIBs, it has relatively poor electrochemical properties. Reason is that the carbon layer distance (3.35 Å) of graphite does not match the size of Na<sup>+</sup> well. Carbon nanofibres (CNFs) have a relatively high sodium storage capacity. CNFs as amorphous carbon consist of randomly distributed graphite microcrystalline and distorted graphite layers. The typical one-dimensional structure offers a high surface volume ratio and a short transport route for ions. 1D CNFs are also considered as attractive support for the production of alloy materials - CNF and metal-chalcogenide-CNF heterostructures. It is generally known that due to several electronic reactions, alloy materials have high theoretical capacities above 400 mA hg<sup>-1</sup>. However, as they suffer from low electronic conductivity and enormous volume expansion during the charging/discharge process, their practical application will be limited. Electrospinning is a simple manufacturing process with low spin costs, a variety of spinable substances and controllable technology. By changing the nozzle structure and controlling the experimental conditions, it is easy to maintain nanofibres with different morphologies such as solid, hollow and mantle structures. Review focuses on electro-sponsored nanofibres or CNF-based composites for use in highly developed energy storage systems. Review briefly deals with the principles and devices of electro-spinning technology. The authors then emphasize CNFs, which have been modified by the inclusion of versatile morphologies and structural features as well as dotting with heteroatoms. [53]

### 2.2.26 Hard carbon anode materials for sodium-ion batteries

The massive consumption of fossil fuels contributes to global warming and acidification of the oceans. The development of LIBs is limited by the lack of and unequal distribution of lithium resources. The reserves of sodium resources in the earth crust amount to up to 2.09%, much richer than 0.0065% lithium. LIBs and SIBs have a higher energy density than supercondensers. Comparison of the most important performance parameters of energy storage. Energy storage can be used to store energy storage. Memory has been developed in a number of different types of storage systems. You can be found in a variety of types of devices, from storage to energy storage. The most important anode materials for SIBs are the materials used in the production of the anode material. SIB materials are the most important materials used in the SIB. Materials used include materials used in the production of SIB sibs and other types of nannasian nanosis materials. Hard carbon materials are mainly derived from the pyrolysis of synthetic organic substances and biomass. Synthetic organic substances are highly molecular polymers such as polyacrylonitrile [4], polyaniline [31, 32], polydopamine [16], phenolic resin [33] and polyimide [34]. Compared to synthetic organic matter, biomass is much better suited for carbon sources. The microstructure and electrochemical performance of hard carbon materials produced from various parts of the plant are mainly discussed. Our goal is to present a complete spectrum of hard carbon anode materials for SIBs extracted from plants. The opportunities and challenges for the future are also predicted. [54]

## 2.3 Conclusions

Hard coal is the most commonly used carbon source as SIB anodes and is proven to improve the electrochemical performance of SIBs. Carbon-based materials in combination with metal sulphides and cathode materials were briefly mentioned, based on the improvement achieved by the cathode. Among the prospects and challenges facing the carbon-based materials; Palacios Group [91] reported that not all additives can improve the sodium storage performance of carbon-based materials and their composites. Sometimes additives could promote the formation of a SEI layer, leading to a low coulombic efficiency. Research attention should also be given to the reason why such additives can be added to SIBs. The efficiency of hard carbon needs to be further improved. Carbon will be able to make a major contribution to the development of SIBs. High-performance and cost-effective SIB with carbon-based anodes will be needed more than replacement for LIBs in the near future. Recent developments in the synthesis of carbon nanostructures have been reported, but are still very limited in SIBs. More carbon nanomaterials should be produced for SIBS carbon materials. In addition to LIBs, CNT should be given attention as anodising material. Wang et al. reported on SnO<sub>2</sub> and CNTs composites as anode materials with high capacity for sodium ion batteries. The number of reports studied on the mixing of activated carbon with other materials, as mentioned above, is increasing rapidly. However, the method used in the synthesis of these composites is mainly ball grinding. Many reports on the structure of such a mixture are not nanostructures and the obstacles associated with a poor sodium diffusion path, low speed and volume expansion still exist. SIB cathode materials have attracted considerable attention in recent years, but have recently been less considered. Carbon coatings have been reduced by carbon coating on the surface of the cathode material. Yu et al. have synthesized a carbon-coated NVP embedded in a porous carbon matrix. The combination of red phosphorus and graphene stacks shows a relative improvement in the cyclic performance of the anode. Such an approach can be applied to other environmentally friendly alloy materials that could create opportunities for the development of much more SIB anodes such as graphenes. There are still many research areas that need further progress. The focus should be on carbon-based materials to improve storage capacity, cyclic stability and improve performance. Demonstrations of SIB filling cells to increase their energy and performance density for practical application in order to meet the current challenges of the well-known mature LIBs. [31]

Due to the availability and lower cost of sodium compared to lithium, SIBs gained great attention as an energy storage medium. Various carbon-based materials with different structures and textures have been

investigated as potential anode material for the SIB. The production of porous 3D graphene structures while simultaneously introducing defects and heteroatoms can effectively eliminate the above mentioned restrictions. The development of composite anodes with graphene as a conductive material is considered together with other materials to be a significantly effective method of increasing overall performance. In general, graphene in this compound can serve as a solid lubricant for dispersal of NPs in composites. [32]

This review mainly presents the application of dual anode materials to L/SIBs. Such dual materials are of different kinds, including metal oxides, carbon-based materials, alloys, metal sulphides and composite materials. Such advantages will contribute to battery technology fulfilling the strong consumer demand for portable, ultra-thin / light and flexible devices. (1) More active materials that enable rapid electron transfer should be synthesized or combined with currently available anodes in order to achieve better performance. (1) "Active materials" which can enable rapid electron transfer are synthesized, assembled or synthesized with currently available anodes. Different ways should be found to reduce powdering, accumulation and large volume changes during the Li or Na cycle. (2) Different ways to reduce powdering should be found. (3) Different methods should be used to reduce powdering. (4) Anodes should be synthesized with optimized structures to create a sufficiently large gap within the crystalline structures in which the alkali metals (Li and Na) are housed. Anodes are synthesized with optimized structures to provide sufficient space for Li and Na. (4) Simplified and green strategies should be designed to a large extent without expensive and toxic substances. Simplified strategies should also be designed without expensive or toxic substances such as toxic chemicals that can be used on a large scale. (4) Simplified, green and sustainable strategies should not be designed with toxic chemicals or large amounts of money. It is of great importance to find dual cathode materials for L / SIBs or other types of rechargeable batteries. Comparisons and similarities between the received dual anode and cathode material still leave behind many challenges. All in all, it is important to further optimize the above mentioned electrode materials in order to improve the performance of LIBs, SIBs and many other types of rechargeable batteries. This will enable their wide application in the form of improved electrode materials in the near future. [33]

NIBs are promising to be used in large energy stores, where weight does not play a decisive role. However, before the commercialization of springs, challenges remain, especially for anodes. Carbon-containing materials remain a central focus in the future, especially carbon-containing materials. The development of solid-state electrolytes is an essential aspect for the solution of safety problems. Furthermore, aqueous Na-ion batteries with safety benefits and low cost are another new direction of study. In the future, Na-Ion batteries could be a promising alternative to LIBs for cost-effective, environmentally friendly and large-scale energy storage. However, there are still many difficult challenges for commercialisation of Na-Ions, persistent efforts to explore the Na-Storage Mechanism and the Disruption Mechanism. [34]

A fully planned topology could increase Li/Na storage capacity for LIBs and SIBs. The proposed structure is the global minimum in the 2D space and has the essential properties as promising LIB/SIB material with ultra-high capacity. It has superior thermodynamic, kinetic, thermal and mechanical stability. The authors strongly encourage further studies of purely planar 2D materials with a large abundance of relatively well separated pores of suitable size. These are promising candidates for ultra-high capacitive LIB / SIB anode materials. The authors believe that the discovery of trends / rules in the extensive literature that can be implicit or hidden will greatly accelerate our material discovery process. [35]

MOFs have been used extensively as precursors or models for the design and manufacture of colorful nanostructures. Materials produced from MOFs typically show nanoscale particle size, well-developed porosity, and designable microstructure and morphology. The recent progress in MoF-based materials, including carbon, metal oxides, as anode materials for SIBs are summarized. The development of MOF-based electrode materials for SIBs has shown that many challenges remain and hinder the application of these materials in practice. Future developments should focus primarily on materials with low input potential such as carbon, TiO<sub>2</sub> and metal phosphate. [36]

NTP with a one-dimensional tunnel structure for ion conduction can be used as an anode material for Na-Ion batteries. KTP and NaTP, which are synthesized by ion exchange with NTP, are also suitable for the

na-switching. This is the first report of such a series of materials (ATiOPO<sub>4</sub>) with a suitable redox voltage above 1.0 V. [37]

In this review, the authors have summarized the latest research progress in tin sulfides and selenides as promising anode materials for LIBs and NIBs. Also the coordination of kinetics, mass ratio, conductivity, etc. between anode and cathode materials is crucial for powerful, fast and long-lasting full cells with optimized performance. [38]

The PHC carbonised at 1400 °C shows the best electrochemical performance with a reversible capacity of 370 mA h g<sup>-1</sup> at a current density of 30 mA g<sup>-1</sup> and 334 mA. After 120 cycles, the PHC showed a high initial coulombic efficiency of 85.4%. These excellent properties indicate that PHC is one of the most promising anode materials for large-scale sodium ion batteries. [39]

MoO<sub>3</sub>-based nanosheet array anodes have been successfully produced in a two-stage process that includes the solar thermal process and thermal oxidation under air. By controlling the glow temperature, a dense and vertical MoO<sub>3</sub> sheet array on the FCKW can be produced by the simple conversion of MoS<sub>2</sub>. [40]

Nanostructured cup<sub>2</sub> / C composite materials were manufactured using a simple method of milling balls with high energy. The coating layer of soot improved the electrical conductivity of composite materials. Composite materials showed a large specific capacity of  $\approx$  500 mA h g<sup>-1</sup> and a good performance. [41]

The authors synthesized a SbNPs @ C Nanocomposite using a simple hydrothermal method, followed by an incandescent process. Sb nanoparticles that were homogeneously embedded in the carbon matrix represented a structurally stable host for the Na-Ion alloy and de-alloyation. [42]

The structural design, which includes various components, crystalline / amorphous domains and size / distribution of the domains, has been realized to produce a number of Sn / P-based composites as anode materials for sodium ion batteries. A simple and cost-effective ball milling method has been used to control the decomposition of Sn<sub>4</sub>P<sub>3</sub> in Sn and P in carbon-containing devices. [43]

The FM-HPCF shows one of the best previously reported long-term cycle properties of anode materials on a MoS<sub>2</sub> basis for SIBs. The authors believe that the work could open up an effective way to produce an advanced, few-layer metal-dicalcium-carbon composite for energy applications. [44]

The thin layers of sodium titanate were well controlled with respect to growth rate, layer thickness and composition. Amorphous sodium titanates deposited on CNTs showed exceptional battery performance as anodising materials for SIBs, including high energy density, excellent permeability and extremely long service life. [45]

In this review, the authors have summarized the progress of 2D layer materials such as graphs, phosphorus, MoS<sub>2</sub> and MXen as anode materials for NIBs. The authors illustrate the relationship between structure and sodium storage performance of these 2D materials. The storage capacity of sodium is mainly limited by the much lower specific capacity and the tendency to re-storage and aggregation, leading to the decrease of active sites for sodium ions. Despite the outstanding intrinsic chemical/physical properties, such as large specific surfaces, superior mechanical properties, good conductivity and fast electron transfer. The construction of graphenodes with unique structures, including a 3D networked porous architecture, the introduction of defects or heterogeneity into the GO layer proved to be effective methods. In addition, the anode materials based on graphs have attracted great attention in order to take advantage of the advantages of graphs such as large specific surfaces, superior mechanical properties, good conductivity and fast electron transfer. In the case of the 2D phosphor, which is used as anodising material for NIBs, the biggest obstacle is the lack of a perfect method for the industrial production of single crystal BP with layer structure. The synthesis process is as follows: The reaction conditions are expensive, toxic and easily flammable in an environment. The sodium storage performance of MoS<sub>2</sub> anode material has been fully investigated and promising progress has been made. The biggest limitations are poor electronic conductivity, repositioning and aggregation, and the enormous volume fluctuations during the sodium / desodation process. The construction of multi-layer or single-layer MoS<sub>2</sub>, the expansion of the intermediate layer spacing and the combination of conductors have proved to be effective strategies. MXene was used as an anode material for NIBs due to the low diffusion barrier, but the low specific capacity and the strong repositioning and aggregation of the MXen plates would

impede their development. An extension of the intermediate layer spacing and the impairment of stacking of MXen layers could improve their electrochemical behaviour as electrodes. In the future, more efforts should be made to use the newly born 2D materials for NIBs that could further resolve the current environmental and future energy crisis, and more efforts should be made to exploit the material that could be used to resolve the current and future crisis. [46]

The exploitation of high-performance electrode materials for SIBs is still facing new challenges due to the large ion radius of Na<sup>+</sup> and structural instability during the fast desodation / desodation process. Multidesign strategies can improve the kinetics of electrode materials. Hard coal is considered to be the most promising anode material for practical SIBs. By expanding the intermediate layer spacing of graphene layers, the diffusion of Na<sup>+</sup> increases due to the simple insertion/extraction process. The introduction of heteroatoms such as N, S and P in hard charcoal can not only provide active sites for the adsorption of Na<sup>+</sup>. Some elements and metal-based compounds are another category of SIB anode materials. The main problem with these materials is the enormous changes in volume during the sodium and desodation process. This problem can be alleviated by nanocrystalline and the introduction of carbon-containing materials. Unique nanostructure and morphology designs can increase anode stability and promote carrier transport. In addition to anode materials, the other components of batteries can significantly influence the electrochemical performance of SIBs. As an integrated system, the electrode material does not work well when paired with an unoptimized binder or electrolyte. For example, alloy and conversion anodes show better performance with CMC binders than with PVDF. [47]

The finished PWT-1400 has a high reversible capacity, excellent performance and superior cycle performance. These excellent properties, the simple preparation process and the low costs make the PWT a promising anode in SIBs for large-scale energy storage applications. [48]

The Sn<sub>10</sub>Bi<sub>10</sub>Sb<sub>80</sub> alloy was unique in terms of its outstanding capacity retention (minimum retention at 100 cycles) and the single phased, as a separate microstructure. It is assumed that the excellent performance is due to two factors: the first is the solidification by substitutional resolution of bi and sn in the sb grid, leading to a higher resistance to internal tensions. The second, also associated with the resolution of the chemical SB potential, leads to a higher number of different sodification processes, each of which has a much lower material expansion compared to pure sb. [49]

NaBiS<sub>2</sub> nanostructures have been produced on a large scale with cheap reagents. The unsatisfactory electrode performance is attributed to the formation of bi, which leads to irreversible electrode reaction. Anode material is anode material for sodium ion batteries. [50]

The de-alloying method simplifies the manufacturing process, reduces the total cost and avoids the emission of the harmful gas H<sub>2</sub>S, which usually occurs in the conventional production process of transition metal sulphides. The 3D nanoblume CuS (S48) was obtained after 48 h emptying and had the largest specific surface area and the smallest pore size. Used as an anode for SIBs, S48 showed a high discharge capacity (325.6 mA h g<sup>-1</sup>) and an excellent cycle stability. [51]

Carbon nanofibres were first examined as anodising material for SIBs. The CNFs provided not only a high reversible capacity of 255 mA h g<sup>-1</sup> at a current density of 40 mA g<sup>-1</sup> but also excellent cycle stability. Given their low cost, simple synthesis and high performance, they are a promising material for future applications. [52]

CNFs are one of the most promising anodes for SIBs in terms of high electronic conductivity, high layer spacing and excellent structural stability. Electrochemical properties can be significantly improved by developing networking structures, porous structures and heteroatomical doping. CNFs offer not only a highly conductive network, but also buffer the enormous volume expansion of active materials when constructing heterostructures. Large surfaces and rich defects in CNFs can increase the number of active sites for sodium storage. However, during the electrochemical reactions several side reactions, such as the removal of the electrolyte, could occur. More attention should be paid to how secondary reactions can be minimized without sacrificing the additional sodium storage capacity. The heterostructures of metal phosphide CNFs have been investigated less, the integration of metallic-organic equipment into electro-sponsored CNFs with

certain structures (porous structure, multi-channel structure, etc. etc.) has been further explored. Recent progress has been made with electro-sponsored flexible cathode and anode materials for flexible SIBs. Compared to conventional rigid batteries, flexible batteries are theoretically characterized by high energy density, high safety, fast charging/discharge and low costs. Electro-spins provide technical support for the further development of flexible batteries. [53]

SIBs are the ideal replacement for LIBs as energy resources for slow electric vehicles and energy storage on the grid scale. Like graphite anodes for commercial LIBs, hard coal is the most promising anode. The natural, compact porous morphology of vegetable precursor substances could be maintained during pyrolysis in hard carbon. The layer spacing of carbon layers could be cut to an optimal value of 0.38-0.40 nm. This unique microstructure would shorten the diffusion path of Na<sup>+</sup> and benefit from the extraction and insertion of Na<sup>+</sup>. [54]

# Chapter 3

## Na-ion Electrolytes

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### 3.1 Introduction

Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> (NASICON) Solid Electrolyte is a material that is sufficient to replace a liquid electrolyte, as it has a high ion conductivity as well as high thermal and electrochemical stability. However, since the NASICON powder has a high interface resistance, the beneficial effects of ceramics itself in combination with a polymer electrode are not to be easily demonstrated. [55]

The novel bifunctional methyl phosphonate combines the good polymerisation capability of acrylates with the adjustable flexibility of the ethylene oxy group. The corresponding ternary gel polymer electrolyte is produced by radical networking copolymerization. The gel polymer electrolyte has good thermal stability at the starting temperature of 250 °C. [56]

For use in Na-Ion batteries, a free-standing transparent film for sodium ion conductivity was produced in PET-based solid polymer electrolyte, whose ionic conductivity is investigated by impedance analysis from 1 MHz to 1 Hz in the temperature range 303-363 K. [57]

The anode properties of Nb-doped rutil-tiO<sub>2</sub> electrodes were investigated in an ionic liquid electrolyte consisting of N-methyl-N-propylpyrrolidinium cation and bis-fluorsulfonyl-amide anion for use in a safe na-ion battery. The conductivity of the electrolyte was lower at 30°C than that of a conventional organic electrolyte. [58]

The best TiO<sub>2</sub> electrode showed a high specific capacity of 248 mA h g<sup>-1</sup> at 25 A power density, a 100% coulombic efficiency, superior pseudocapacitive Na-ion storage and a good capacity retention for extended charging cycles. [59]

Hard coal, due to its low cost and high capacity, is a promising anode material for sodium ion batteries. However, its practical application was largely hampered by poor performance and long-term cycle degradation. At this point the authors propose a simple strategy for oxygen plasma treatment to modify the surface of hard carbon to stabilise the SEI. This method significantly increased the specific capacity of 225 mA hg<sup>-1</sup> (for the raw carbon sample) to 325 mA. [60]

Anode materials with superior electrochemical performance are urgently needed for the development of sodium (Na) ion batteries. Ternary phosphates can provide a better electrochemical performance than binary counterparts due to the synergistic effect of their multinal components. As an anode used for NIBs, the as-synthetic P<sub>4</sub>S<sub>5</sub>e<sub>2</sub> provides a reversible specific capacity of 1038 mA h g<sup>-1</sup>. [61]

$\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$  is a promising cathode material for sodium ion batteries. After 100 cycles, IL-based electrolytes combine a capacity reserve of about 80% with high specific capacities (approximately 200 mAh g<sup>-1</sup>). [62]

The performance of a graphite electrode for lithium-ion batteries has been successfully and easily improved by solving sodium ions in an electrolyte solution. An irreversible capacity in the initial cycle has obviously been reduced, and reversible discharge capacities have increased with better capacity retention. Measurements of the alternating current impedance show that the graphite electrodes in the sodium ion electrolyte have a much lower interface resistance than that in the sodium ion-free electrolyte. [63]

Rechargeable Na / NaFePO<sub>4</sub> cells with a sodium bis (trifluoromethanesulfonyl) -Imid (NaTFSI) -incorporated butylmethylpyrrolidinium (BMP) -TFSI-Ion liquid (IL) -Electrolyte is tested with an operating voltage of 3 V. NaTFSI concentration (0.1-1.0 M) to cell power at 25 °C and 50 °C. [64]

The sodium ion half / full cells have superior performance and impressive capacity retention with bacterial cellulose yellow polymer electrolytes. Sodium ion half cells are able to maintain capacity retention. They can be used in many ways to maintain capacity. The cells can also be used to store the capacity of a single cell. [65]

The basic physical-chemical properties such as ion conductivity, viscosity, wettability and thermochemical stability of the electrolytes using NaPF<sub>6</sub> as a solvent and the mixing solvent with various components of EMV, DMC or DEC in PC or EC have been systematically measured. An optimised electrolyte can effectively promote the formation of a protective surface layer on two electrodes that slows down not only the parasitic reactions between electrodes and electrolytes. [66]

Li-Na-Co deposition / stripping reactions to replace the reactions of Li-Single in organic electrolyte are an effective method to inhibit Li-Dendrite growth and improve the cycle performance of Li-Anode in Li-Metal Batteries. The results show that Li-N +Co deposition and co-Stripping processes take place during cycles. [67]

Watery Na-Ion batteries with highly concentrated NaClO<sub>4</sub>aq. Electrolytes attract attention as candidates for high-volume high-level batteries. However, the detailed mechanism by which the potential window was expanded in 17 m NaCl O<sub>4</sub>Aq. The authors examined the local structure by a Na<sup>+</sup> ion or a ClO<sub>4</sub><sup>-</sup> ion by X-ray and Raman spectroscopy. [68]

This work aims to demonstrate a novel electrochemical energy storage device, a hybrid Na-Ion capacitor with organic electrolyte. Sodium manganese oxide with the formula Na<sub>0.4</sub>MnO<sub>2</sub> was selected and synthesized as the most suitable battery-like positive electrode. Activated carbon (AC) was used as a negative capacitor electrode. The maximum safe operating voltage of the device was set to 2.7 V, resulting in a specific capacity of 17.4 FG - 1. [69]

The strong electrostatic interaction between Na<sup>+</sup> and FSA<sup>-</sup> in electrolytes leads to high viscosity and low conductivity. The ether-substituted ionic fluid 1-methoxymethyl-1-methylpyrrolidinium (PYMOM) -FSA demonstrated a higher conductivity than Py13-FSA and the Sn4P3 electrodes. [70]

The thermal behaviour of completely lithified and natriified Sn electrodes was investigated by differential scanning calorimetry (DSC). The NaPF<sub>6</sub>-based electrolyte showed during the first exothermic reaction corresponding to the thermal decomposition reaction of the solid electrolyte boundary layer (SEI), a thermal reaction with much greater heat generation (1719.4 J g<sup>-1</sup>). [71]

The functional electrolyte consists of 1 M NaPF<sub>6</sub> dissolved in a 1:1 (v/v) mixture solvent of propylene carbonate (PC) and ethylene-ethyl carbonate. The cell capacity retention increases after 1000 cycles to 84.4% and 92.2% respectively for electrolytes with FEC-PST-Bi additive. [72]

Aqueous electrolyte based on NaClO<sub>4</sub> solution with a high concentration of 17 m is shown to increase the practical stability window to approximately 2.75 V. The lack of free water molecules in high salt concentration contributes to their inactivity. Rapid reaction kinetics and structural insensitivity of PI to the ion radius are responsible for the excellent sodium storage properties. [73]

Sodium ion-ion batteries (SIBs) are considered as high-performance energy storage for the next generation. The conventionally used fiber-glass separators (GF) for SIBs do not meet the necessary standards due to

their randomly distributed pore structure. This introduces a strategy to control GF's inner nanostructure by means of solvent-free induced phase separation (NIPS). [74]

A sodium ion conductive gel electrolyte based on a porous membrane made of poly (Vinylidene difluoride co-hexafluoropropylene) has a high safety, good mechanical properties and good electrochemical stability. The temperature dependence of the ionic conductivity of 25 to 75 °C is consistent with an Arrhenius behavior. [75]

Gelcopolymers are considered as an optimal solution for the solution of bottlenecks in liquid electrolytes such as decomposition and sodium dendrite problems. Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>-cells with gel polymer electrolytes offer better long-term cycle stability than the corresponding liquid electrolyte. [76]

Sodium vanadium phosphate (NVP) is a potential cathode material for sodium ion batteries, but its speed capability requires improvements. The electrode-electrolyte border area with dimethylether (DME) electrolyte is modified so that the porous NVP cathode leads to ultrafast kinetics and ultralong cycle life. The Na / NVP half cell with DME offers a good capacity (44 mA h g<sup>-1</sup> at 100 A g<sup>-1</sup>; 854C) and a stable ultralong cycle life for 95000 cycles. After 5000 cycles, the energy density is 217 W h kg<sup>-1</sup> and the power density 30. [77]

Na<sub>0.67</sub>Mn<sub>0.8</sub>Cu<sub>0.1</sub>Mg<sub>0.1</sub>O<sub>2</sub> of type P2 has been synthesized as cathode material for sodium ion batteries. By using the synergistic effects of the substitution of Cu and Mg, the processed material delivers a discharge capacity of 84 mAh g<sup>-1</sup>. [78]

Rubidium and caesium ions are investigated as electrolyte additives for sodium ion batteries. It has been shown that the addition of small amounts of Rb<sup>+</sup> and Cs<sup>+</sup> in the electrolyte significantly alters the chemical composition of solid electrolyte interphase (SEI) on hard carbon surfaces (HC). [79]

Iron (III) fluoride (FeF<sub>3</sub>) is regarded as a potential cathode for sodium ion batteries due to its high capacity and low cost. However, particle powderisation during the cycle usually leads to a rapid degradation of its structure and capacity. At this point the authors present a free-standing nanolimited FeF<sub>3</sub> cathode and a novel electrolyte salt, sodium difluorate (oxylato) borate (NaDFOB) for SIBs. The composite cells have a high discharge capacity of up to 230 mA h g<sup>-1</sup> and a capacity reduction of up to 70% after 100 cycles. [80]

## 3.2 Literature Reviews

### 3.2.1 Solid electrolyte for solid state Na-ion batteries

Na-Ion Batteries (NIBs) are rapidly developing into a potential technology to replace lithium in the energy storage market. NIBs have significant advantages due to the cost-effective and abundant resources available from Na compared to lithium. In view of the recent increase in renewable energy production and the high demand for energy storage (ESS), NIBs are promising systems. Inorganic solids with high ionic conductivity, electrochemical and thermally stable are being studied. Until recently, Na-β-Aluminium oxide materials have been used in solid-state batteries. Another stable oxide-based material is Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub> (Na super-ionic conductor) NASICON-solid electrolytes, which are promising. Polymer materials have flexible physical properties and are suitable to compensate for the disadvantages of oxide-based solid ceramic electrolytes. Table 1 summarises the previous studies and current trends of ceramic polymer composite electrolytes for use in NIBs. According to a current report, the ion conductivity of the above composite electrolytes is primarily due to the polymer electrolyte, and the contribution of ceramics is negligible. Table 1 Collected research data and trends on ceramic polymer composite electrolytes in Na-Ion solid batteries. Table 1 shows the trends and trends of ceramic polymer composites in Na-Ion batteries. For more information, see [www.cnn.org / cnn](http://www.cnn.org/cnn). The influence of the solid electrolyte is not readily recognizable when the oxide ceramic is in powder state. Further research is needed in the environment of methods aimed at increasing the ceramic content and enabling the ion transport by ceramic. In particular for the ion pipeline by ceramic, the ion transport channel must be formed separately in the composite electrolyte. A top-down method to combine a polymer with a ceramic that previously formed an ion transfer channel. This can lead the main ion transport channel through the ceramic, while the polymer material can be used to improve the physical properties of the solid

electrolyte. Since the proportion of ceramics in the composite electrolyte is more than 50 % by weight, a thermal and electrochemically more stable. To increase physical strength, the authors used a method in which a high-porous solid-electrolyte is partially sintered and its inner pores are filled with a polymer material. The ion conduction effect can be transferred to a highly stable solid-ceramic electrolyte through the sintered NASICON full-ceramics, which results in ion conductivity of  $1.45 \times 10^{-4} \text{ S cm}^{-1}$ . [55]

### 3.2.2 Stable cross-linked gel terpolymer electrolyte containing methyl

The electrochemical secondary battery is a promising method for large-scale storage of electricity. The sodium ion battery (SIB) is an alternative to lithium ion battery. In recent years, due to its suitable redox potential, its good electrochemical performance and its abundant reserves, it has attracted considerable research attention. Due to their high ion conductivity, good thermal stability, their wide electrochemical window and their good compatibility with electrodes, GPEs are increasingly attracting attention [15-17] GPEs are diffused like liquid electrolytes and cohesive like polymers and have a higher ion conductivity, better processability and good mechanical strength. So far, there are only a few GPE systems for SIBs. Poly (ethylene oxide) (PEO) and its derivatives are the most intensively studied polymer wirts under solid polymer electrolytes and GPEs for LIBs and SIBs. The Na / GPE /  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) cell provided excellent cycle stability, especially a long-term cycle life at 1 C. [56]

### 3.2.3 Solid-state polymer nanocomposite electrolyte of $\text{TiO}_2/\text{PEO}$

The search for alternative energy storage devices that can complement existing Li-Ion technology is urgently needed. Solid polymer electrolytes (SPEs) are an attractive alternative to replacing liquid electrolyte systems. The rich sodium richness of the planet would make Na-Ion batteries (SIBs) considerably cheaper. Polymer electrolytes have been widely studied due to their low mechanical properties, their simple manufacturing and handling in thin layers, their modularity and reliability in various electrochemical devices and their ability to create an effective electrode-electrolyte contact [3-7]. The most widely studied host for solid polymer electrolytic applications is PET. This is due to its high electrochemical stability compared to other polyethers, copolymers or PEO-branched polymers. PEO is a polymer-salt complex based on poly (ethylene oxide) and polyvinyl alcohol (PVA). The semi-crystalline nature of PEO leads to both amorphous and crystalline phases at room temperature. The suppression of the crystallinity of the polymers improves their mobility and thus leads to a better ion conductivity. PEO is a polytinomeric polymeric with low ionic conductivity. In order to reduce crystallinity and increase ion conductivity, composite or nano-combined polymer electrolytes are introduced into a sodium ion polymer electrolyte [14.15]. The addition of an inorganic filler in the micro-area leads to improvements in the amorphous phase of the polymer by slowing down the recrystallisation rate, thus improving the interface stability and sodium ion conductivity. In this work, the hydrothermal synthesis of  $\text{TiO}_2$  was modified by adding PET at a suitable time to inhibit particle growth. The smaller the particle size of the filler, the stronger the interface interaction between  $\text{TiO}_2$  and PEO [17]. X-ray (XRD), Fourier-transformed infrared spectroscopy (FTIR) and Differential Scanning Calorimeter (DSC) were used to characterise the physical and chemical properties of the polymer electrolyte. [57]

### 3.2.4 Niobium-doped titanium oxide anode and ionic liquid electrolytes

Na-ion batteries (NIBs) are the most promising candidates for the short-term replacement of batteries in stationary storage. Unlike batteries in portable electronic devices, stationary storage requires long-term cycle stability and high security instead of high energy density. With large stationary batteries it has been shown that a sodium-sulphur battery offers the advantages of low costs and a long life cycle. This battery requires a high operating temperature of more than  $300^\circ\text{C}$  to achieve an ionic conductivity for its fixed electrolytes. The electrolyte has a strong influence on many of the performance characteristics of batteries. Compared to conventional organic electrolytes, ionic liquid electrolytes have many interesting properties such as a larger

electrochemical potential window, a better thermal stability, non-volatility and hence non-combustibility. Few studies have investigated the combination of cathode materials and ionic liquids for use in a Na-ion battery [7,10-13]. Rutile type TiO<sub>2</sub> is a potential anode material for use in NIBs. Niob (Nb) doping increased its electronic conductivity by a thousand times and improved NIB anode performance. As regards battery safety, its performance in an ionic liquid electrolyte would be very interesting. [58]

### 3.2.5 TiO<sub>2</sub> sodium-ion battery anodes in diglyme-based electrolytes

Sodium ion batteries have recently proven to be promising energy storage technology due to their low cost (165 dollars per tonne of Na<sub>2</sub>CO<sub>3</sub>) and their excess sodium (2.3% of the earth's crust). Despite the similar electrochemical and redox potential, the power of Na-Ion is reduced by the slow Na-Ion diffusion resulting from its 40% volume (1.02 Å in the radius) compared to Li-Ion. TiO<sub>2</sub> has good chemical stability, easy processing, environmentally friendly, negligible load during dilution and low cost. Despite its numerous advantages, commercialisation is hampered by low electronic conductivity and low Na-ion storage capacity (100-150 mA h g<sup>-1</sup>). In order to improve the Na-Ion storage performance of TiO<sub>2</sub> anodes, nanostructure design, composition optimization, hetero-atomization and addition of carbon-conducting additives have been demonstrated [30-32]. Many unknown parameters such as electrolyte composition have to be investigated in order to improve electrochemical performance. The selection of electrolyte solutions is of great importance due to the increased reactivity of high surfaces. Nanosheets are selected as the desired TiO<sub>2</sub> morphology to improve the electrode-electrolyte contact and thus improve the effect of electrolyte composition on SEI formation and electrochemical performance. Carbon-coated TiO<sub>2</sub> sheets showed excellent performance in diglyme-based electrolyte compositions compared to carbonate-based compositions with and without SEI-producing additives. [59]

### 3.2.6 Solid electrolyte interface stabilization via surface oxygen species functionalization in hard carbon

Lithium-ion batteries have played an important role in electrochemical energy storage in the last two decades. However, the challenges of limited lithium resources have to be solved within a few years. Sodium-based materials have similar physical-chemical and electrochemical properties to lithium-based. The modified hard carbon materials have improved battery performance with a reversible high capacity of 325 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>. The authors believe that the current encouraging results will shed more light on the design of other advanced electrode materials such as hard carbon. [60]

### 3.2.7 Amorphous P<sub>4</sub>S<sub>3</sub>Se<sub>2</sub> compound as an advanced anode

The development of environmentally friendly and cost-effective sustainable energy technologies is in full swing. The practical use of NIBs continues to be hampered by the lack of suitable anode materials. Graphite, the traditional LIB anode, has proved unsuitable for direct NIB applications due to the poor integration of NAB in it. Sulphur (S) and selenium (Se) have a lower electronegativity than oxygen (O), leading to a higher reversible capacity for sulphide and selenide than oxides, as Na<sup>+</sup> from Na<sub>2</sub>S and Na<sub>2</sub>Se can be reduced more easily than Na<sub>2</sub>O due to the weaker Na-S and Na-Se bonds compared to the Na-O bonds. Compared to the above mentioned binary compounds, ternary materials have a higher reversible capacity, better cycle performance and superior rating. Amorphous materials have unique advantages due to their intrinsic structures. However, ternary phosphoric halogenides are difficult to synthesize, as they require complex synthesis methods such as melting and detouring that are costly, dangerous, time consuming and energy intensive. Identification and optimization of amorphous phosphates with low costs, high capacity, excellent throughput performance and cycle stability for NIB anode materials remains an urgent problem. A-P<sub>4</sub>S<sub>3</sub>Se<sub>2</sub> Compound as an anode material for NIBs was developed using a high-energy ball milling method (HEBM). The resulting electrode has several structural properties that are beneficial for high electrochemical performance.

An alternative sodium electrolyte (1 M NaCF<sub>3</sub>SO<sub>3</sub> dissolved in diglym) was used to support the production of hierarchical solid electrolyte interphases (SEI). [61]

### 3.2.8 Unexpected performance of sodium-ion cathode material in ionic liquid

Lithium-ion technology is proposed as the most promising battery chemistry for large applications, but there are serious concerns about the availability and price stability of lithium resources. The low costs, the high frequency and the simple degradation of sodium minerals, and the practical use of aluminium as an anode stream separator and aqueous electrolytes. Lithium and sodium share neighboring positions in the periodic table. The basic principles of systems based on sodium and lithium are actually very similar. On the other hand, sodium has a larger ion radius than lithium, it is about three times heavier and its redox potential is 300 mV above that of lithium. Due to its excellent electrochemical properties, coated LiMO<sub>2</sub> materials (M = transition metal) have been studied in detail for lithium-ion batteries. Similar coated NaMO<sub>2</sub> cathode materials were considered promising for sodium-ion batteries [4,5] and some examples are presented below. An initial capacity of 150 mAh g<sup>-1</sup> vs. Li, but only a capacity retention of 50% after 24 cycles could be achieved. Kim et al. [11] reported the electrochemical performance of historical Na<sub>0.85</sub>Li<sub>0.17</sub>Ni<sub>0.21</sub>Mn<sub>0.64</sub>O<sub>2</sub> with an average voltage of 3.4 V vs. Na / Na<sup>+</sup> in 1M NaClO<sub>4</sub> as an electrolyte solution. Kim et al. [8] presented a sodium-ion battery that used the coated NaNi<sub>1/3</sub>Fe<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> as a cathode material and hard carbon as an anode (NayC) with 1M NaClO<sub>4</sub> in the PC as an electrolyte. The cell showed a specific capacity of about 100 mAh g<sup>-1</sup> with high coulombic efficiency for 150 cycles. This connection delivered 190 mAh g<sup>-1</sup> at the first discharge with an average voltage of 2.75 V. Unfortunately, it was accompanied by a low capacity retention of only 75% after 30 cycles. Na<sub>x</sub>[Fe<sub>0.5</sub>Mn<sub>0.5</sub>]O<sub>2</sub> was developed using earth-rich elements. All of these materials were electrochemically characterised in typical electrolytes based on organic carbonates, which can favour the manganese resolution in electrolytes as a result of the Jahn plate distortion [13]. In this work the authors investigate the effect of alternative electrolytes on the basis of ionic liquids and their influence on the reversibility of Na<sup>+</sup> ions in a layer material. [62]

### 3.2.9 Enhance Li-ion battery performance of graphite anode

Carbon materials have been used as an anode of lithium-ion batteries that are now widely used. Among the various carbon materials that are electrically active as intercalates, a graphite electrode is preferred for battery application because they have a high specific capacity, a low operating voltage in lithium-metal seams and a superior cycle behaviour. The surface treatment of metal oxides [8,9], polymers [10,11] and chemically binding iodine [12] improved the electrochemical properties of graphite compared to the lithium-intercalation deintercalation reaction. In order to facilitate modification of the influence of the SEI film on the kinetic rate during the first cycle and the irreversible loss of capacity, several additives that have been dissolved in an electrolyte solution have proved to be effective: HF [13], CO<sub>2</sub> [14,15] and vinyl carbonate [16]. These additives suppress initial irreversibility and improve battery life. A new approach to improving graphite anode performance based on the addition of a small amount of sodium salt to the electrolyte solution was investigated. The electrochemical properties of graphite in Na<sup>+</sup> free and Na<sup>+</sup> containing electrolytes were compared by chronopotentiometric and impedance measurements. [63]

### 3.2.10 Electrochemical performance of Na/NaFePO<sub>4</sub> sodium-ion batteries

Lithium (Li) -ion batteries are promising for the next generation of large-scale charging tanks due to their excellent energy and power density. It is a concern that the global Li supply is not enough to satisfy the increasing demand for LIBs. Alternatives to LIBs have therefore attracted much attention. Inorganic NaFSI / KFSI (FSI = bis (fluorosulfonyl) imid) -Intermediate temperature IL-electrolytes were first proposed by Hagiwara et al. for NIBs. ILs are characterized by intrinsic ionic conductivity, large electrochemical windows, excellent thermal stability, non-volatility and non-flammability. The high discharge performance of NIBs

is unsatisfactory at room temperature mainly due to the large size of Na<sup>+</sup> (compared to Li<sup>+</sup>), which is unfavourable for the transport in electrodes. A slight increase in operating temperature effectively improves battery kinetics and is feasible in electric vehicles and stationary storage applications. Therefore, it is important to find a more stable electrolyte that allows a high NIB performance at increased temperature. NaFePO<sub>4</sub> is considered to be one of the most promising NIB cathodes due to its high operational potential, its high thermal stability and its great theoretical capacity. NaTFSI salt is dissolved in the IL to provide it with Na<sup>+</sup> transport capability. The load-discharge properties of cells with different ILs are assessed at 25°C and 50 °C. [64]

### 3.2.11 Gelation of organic liquid electrolyte to achieve superior sodium-ion full-cell

Sodium Ion Half Cells (SIHCs) with metallic sodium as an anode, also known as sodium metal batteries (SMBs), have always been a common configuration for humans to evaluate certain objects such as electrode materials, electrolytes, etc. In view of the potential safety risks such as sodium dendrite, more and more attention was focused on the development and research of sodium ions full cells in the development of SMEs. In SIFCs, irreversible consumption of active sodium from the electrolyte level should be one of the most direct and long-term methods to reduce these losses. The appropriate electrolyte is to form the stable interface to avoid gradually corroding the electrode and maintaining stability in the circulatory process. A cellular-based bacterial gel electrolyte (BC-GPE) was produced using an un toxic and cost-effective method and evaluated its sodium storage kinetics. It is expected that this economical and practical electrolyte will promote the development of the SIBs industry. [65]

### 3.2.12 Engineering optimization approach of nonaqueous electrolyte for sodium ion battery

SIBs are one of the most promising candidates for large-scale electrochemical energy storage due to the abundance of resources and the cost-efficiency of sodium. Many research work has been dedicated to the development of cathode and anode materials in the last decades. Prussian blue tones with an open and zeolite-like structure [13,14], historical transitional metal oxides and polyanion compounds. The understanding of the (electro-) chemical reactions at the electrode-electrolyte border area (EEI) is crucial to promote the cycle life of cells. Compared to aqueous cells, the cells that use organic electrolytes are more promising due to the high energy density. Also, the effect of electrolyte salts NaPF<sub>6</sub>, NaClO<sub>4</sub>, NaTFSI, NaFSI and NaFTFSI on the formation of solid electrolyte interphases in SIBs has been recently investigated. It has been reported that several electrolytes are suitable for SIBs to stabilise the interface and minimise interface reactions between electrodes and electrolytes. The oxidation state of iron ions is influenced by the upper load voltage limit. An electrolyte of NaClO<sub>4</sub> in the mixture of ethylene sulphonate (EMS) and fluoroethylene carbonate (FEC) has been shown to improve the electrochemical properties and thermal stability. In this study, the authors aim to optimize electrolytes taking into account technical aspects. NaNi<sub>1</sub> / 3Fe / 3Mn / 3O<sub>2</sub> / HC bag cells have been used to optimize the composition of non-hydraulic electrolytes in terms of ionic conductivity, viscosity and wettability of electrolytes. [66]

### 3.2.13 Enhanced cycleability and dendrite-free lithium deposition

Li-Metal is a promising way to achieve a high energy density in order to meet the requirements of electronics and automotive applications. However, dendrite formation on Li-Metal anodes remains the most important problem that leads to capacity failure and internal short circuits, hindering the practical application of metallic Li-Akkus [3.4]. Research on Li-Metalanodes focused on slowing down the growth of Li-Dendrites by various countermeasures. Inhomogeneous Li-Dissemination on substrates is the key factor for the Li-Dendrite problem. Scientists have used Li-containing alloys (e.g. Li-Zn and Li-Sn alloys) instead of pure metallic Li as anodising material. Another approach is the modification of the electrolyte system by optimising solvents

[11], Li + salts [12] and electrolyte additives [13,14] The addition of a small amount of Na + to Li + salt, which contains ionic liquid electrolytes, should effectively suppress the formation of li-denrites. Li + salt is the core of the raw materials for electrolytes. Traditional inorganic li + salts include lithium perchlorate (LiClO<sub>4</sub>), lithium hexafluoroarsenate (LiAsF<sub>6</sub>), lithium tetrafluoroborate (LiBF<sub>4</sub>), etc. Lithium + salt should have good stability, high solubility in organic solvents, simple preparation, non-toxic and environmentally friendly. In this work, the effects of the addition of Na + ions in organic electrolyte on the cyclability with conventional organic solvents and without other organic additives were investigated. In addition, the co-deposition / stripping of Na with Li was investigated with our newly developed Li<sub>22</sub>Sn<sub>5</sub> substrate [10]. [67]

### 3.2.14 NaClO<sub>4</sub> electrolyte local structure

Watery Na-Ion batteries have limited the benefits of high cost efficiency, high ion conductivity and non-flammability. However, their energy density is limited due to the low operational potential of aqueous electrolytes (1.23 V for pure water). In order to overcome this limitation, several groups have proposed to use highly concentrated electrolytes to which free water molecules are missing as novel electrolytes. 17 m NaClO<sub>4</sub> aq. Electrolyte simultaneously realizes a high cost performance and a larger stable potential window. Lee et al. reports that a Na<sub>4</sub>Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>) / / NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>-cell with 17 m electrolyte had a better cyclicity and better coulombic efficiency than the one with 9.26 m NaOTf aq. Electrodeum [Fe(CN)<sub>6</sub>] / / KMn [Cr(CN)<sub>6</sub>] achieved 1.7 V. [68]

### 3.2.15 Sodium-ion hybrid electrochemical capacitor with organic electrolyte

Hybrid electrochemical capacitors have recently established themselves as a new class of electrochemical energy storage. Hybrid capacitors form a subset of asymmetric capacitors that can be either hybrid or purely capacitive. As regards organic electrolyte-based components, several authors have recently claimed to have introduced a hybrid Na-ion capacitor. Few authors have suggested a reliable approach for hybrid Na-Ion capacitors with non-hydraulic electrolytes. The advantages of using Na<sub>x</sub>MnO<sub>2</sub> as electrode material are the non-toxicity of Mn, low cost and simple synthesis methods. The stabarian morphology of crystals allows work on higher C-rates. The work describes one of the first practical realizations of a Na-Ion capacitor with organic electrolyte in the narrowest sense. For the first time in this type of electrochemical memory, Na<sub>0.4</sub>MnO<sub>2</sub> was used as redox-like, sodium-rich positive electrode. [69]

### 3.2.16 Electrochemical performance of Sn<sub>4</sub>P<sub>3</sub> negative electrode for Na-ion batteries

Na-ion batteries (NIBs) have attracted as much attention as Na-resources in sea water and earth crusts are present. As a negative electrode material for NIBs, hard carbon is a promising active material that can store Na + in its nanopores and intermediate layers [1] A negative carbon electrode has reported a reversible capacity of about 350 mA h g<sup>-1</sup> on [2] On the other hand, Na-Ion capacitors (NICs) are also potential energy storage. P.P. [12-14], G.P [12], Ge [12], Ge. Ge [13] and Ge [14]. Ge. P.S. Ge. is Ge. G.P. Ge. is Ge. It's Ge. P.P. Si, Si, P.I.P., Si. Si. P. Si was born in New York City, New York, New Jersey. Si is an American born in the state of New Jersey. Si is a Grammy-winning actor and author of a novel. P.P.P.P., Cu, Cu is a Cu Cu, Cu Cu is the Cu Cu of Cu Cu Cu of Cu Cu. P.C. Cu is a Cu Cu with a Cu Cu Cu. Cu was born in Cu, and Cu was Cu Cu. P.P.P., In, P.A. "In" is a popular video game. P.I.P is a member of the US House of Representatives. The UN is a national television network focused on women in the United States. P.P.P., La. P.A. is award-winning author and author of the novel "La La", first published in New York, New York and Washington DC. La La P.I.P is the most famous author of the book "L.P.", "P.A." The Sn<sub>4</sub>P<sub>3</sub> electrode showed the best cycle performance with a high capacity of 750 mA h g<sup>-1</sup> which was maintained over 200 cycles [13] As a result, the Sn<sub>4</sub>-P<sub>3</sub> electrode proved to be the best in the cycle. Li et al. applied an ionic liquid electrolyte of sodium bis (fluorsulfonyl) amide (NaFSA) to a Sb<sub>2</sub>S<sub>3</sub> / graphene electrode. They reported a reversible capacity of approximately 600 mA h g<sup>-1</sup> over 100 cycles. Furthermore, they showed by tests with an electric burner that the electrolyte was not

flammable. Na<sup>+</sup> is coordinated by solvent molecules in the electrolyte and is incorporated into the negative electrode material by means of a desolvation process during charging. The load density of Na<sup>+</sup> is smaller than that of Li<sup>+</sup>, which leads to a simpler desolvation process for Na<sup>+</sup>. However, the strong electrostatic interaction of Na<sup>+</sup> with FSA<sup>-</sup> in the ionic liquid electrolyte prevents the Na<sup>+</sup> transport not only from the electrode-electrolyte border area, but also in the electrolyte mass. [70]

### 3.2.17 Thermal stability of Sn anode material with non-aqueous electrolytes

Lithium-ion batteries (LIBs) are primary candidates for the next generation of electric vehicles. LIBs offer the highest energy density and output voltage of all rechargeable battery technologies. Sodium-ion batteries are considered an alternative to LIBs, since sodium is the fourth most common element in the earth's crust. SIB anode materials are mainly limited to non-graphic hard carbon, where sodium ions adsorb/desorb at the surface of hard carbon nanoscopic pores. However, these materials have relatively low specific capacities of  $< 300 \text{ mA h g}^{-1}$ . Metallic Sn has attracted great attention as SIB anode material due to its high Na storage capacity of  $847 \text{ mA h g}^{-1}$ . However, alloy anodes are usually subject to a large volume change during Na<sup>+</sup> extraction that leads to cracking and powdering of the particles. To solve these problems, considerable efforts have been made. The safety problems of SIB anode materials represent major technological challenges, especially for large-scale applications. The risk of thermal reactions associated with charged anodes is probably higher in SIBs than in LIBs. The study of the thermal properties of Sn sodium electrodes is important for the development and practical application of batteries. So far, there has been no comprehensive research focusing on the thermal properties of sodium-containing Sn electrodes. Sn electrodes are considered promising candidates for next generation battery systems such as SIBs. The authors propose an effective strategy to limit the likelihood and damage of a thermal exhaust event during SIB operation. [71]

### 3.2.18 Long cycle life of sodium-ion pouch cell achieved by using multiple electrolyte additive

For SIBs, numerous cathode materials have been reported, including Prussian blue analogues, layer-structured sodium metal oxides and polyanion materials. Most materials are assessed by the semi-moon cell using Na-Metal as an anode and an unoptimized electrolyte. The sodium ion whole cell, reported by Barker et al. at the earliest, was based on a NaVPO<sub>4</sub>F / Hard Carbon System and 1 M NaClO<sub>4</sub> / EC + DMC (2: 1 by weight) electrolyte; such a cell lost more than 50% capacity only after 30 cycles. Fluorethylene carbonate (FEC) was widely used as an electrolyte additive for lithium and sodium ion-ion batteries. Fluorocarbonate solvents were found to play an important role in the formation of stable solid electrolyte interphase (SEI) at the anode. Prop-1-en-1,3-sulfone (PST) and ethylene sulphate (DTD) are able to suppress the impedance growth of lithium-ion batteries. Rubidium and caesium salts are reported to be able to alter the chemical composition of SEI on hard carbon surfaces. Some technical problems such as battery power, electrode power gridability and performance deterioration cannot be understood well. This article characterises and discusses the effects of PST and DTD on the cycle performance of SIB and the surface chemistry of anode and cathode by X-ray electron spectroscopy (XPS) and XPS. [72]

### 3.2.19 High energy aqueous sodium-ion capacitor enabled by polyimide electrode

SICs have the potential to bridge the gap between sodium-ion batteries and supercapacitors by combining the properties of high energy density, power density and long life span. The concerns about safety, costs and environmental impacts usually remain in the shopping cart. In order to eliminate the above mentioned problems, it is imperative to develop a kind of electrolyte with the characteristics of high thermodynamic tension, no flammability and environmental friendliness. The electrochemical stability window of the aqueous electrolyte is too narrow to carry most of the electrochemical redox pairs used in SICs, leading to an insufficient energy density. Suo et al. examined "water-in-salt" electrolyte (21 m lithium bis (trifluoromethanesulfonyl) (LiTFSI),

molarity [m] = solvent/weight [mol kg<sup>-1</sup>] The process and production of the battery can be carried out at room temperature without strict moisture requirements. Organic materials including electroactive carbonyl groups could be the best choice. The structures of organic materials are very insensitive to the association and dissociation process of alkali metallion. Flexible polymer backbone could ensure a higher mobility of large-format na<sup>+</sup>. Sodium enolate, which is formed in such systems, is stabilized by the conjugation of nuclear  $\pi$  electrons. The mechanism of relatively large cation activity has been studied in detail. Fluid SICs based on PNCDA anodes and porous carbon-microsphere cathodes (PCMS) have been produced in an ambient atmosphere where the practical operating voltage is 2.0 V by using highly concentrated electrolytes. [73]

### 3.2.20 Design of a porous gel polymer electrolyte for sodium ion batteries

Lithium-Ion Batteries (LIBs) have advantages of a long service life and a large range for operation. LIBs can facilitate the minimization of cell size due to their high energy and power density. SIBs have electrochemical processes that are almost identical to those of LIBs, since the chemistry of sodium is similar to that of lithium. SIBs usually use a system consisting of an organic liquid electrolyte with a separator between cathode and anode. Polymer-based porous separators are considered to be the most suitable separator in LIBs despite their weak thermal stability. Fiberglasses (GF) are widely used, but the thickness of GF is very far from the standard. The loose woven hollow structure of GF can lead to a thermal outburst and an explosion due to a direct connection between the electrodes. Well-organized pores inside the GF can improve electrolyte uptake and promote a smooth ion flow between cathode and anode. Thin PVdF-HFP layers on both sides of the GF improve the interface adhesion to improve the ion transport between electrolyte and electrode. Accordingly, the above mentioned gel polymer electrolyt design enabled the improvement of the properties of the C-rate and the long cycle capacity of SIBs. [74]

### 3.2.21 A sodium ion conducting gel polymer electrolyte

Lithium-ion batteries, due to their high voltage and energy density, can capture the market for portable electronics [1-6] Lithium-ion batteries could restrict the use of lithium-ion batteries in large energy storage systems. Clean and renewable energy sources, which are urgently needed due to air pollution and emissions of warming gases from the combustion of fossil fuels. Sodium is the most promising alternative to lithium for energy storage applications due to its high abundance, low cost and appropriate redox potential. Despite the low output voltage and lower energy density of sodium ion batteries compared to lithium ion batteries, the abundance and lower raw material costs in large energy storage systems where the weight requirement is lower are more critical [1,8]. High-temperature Na/S and Na/NiCl<sub>2</sub> cells have been tested for applications in energy storage systems. They are operated at elevated temperatures (300-350 °C) where complex materials and technologies are needed to ensure their durability and safety. The interest in non-hydraulic sodium ion batteries increases with ambient temperature [10-20]. The use of solid electrolytes as a replacement for organic electrolytes can be a solution to improve the safety of sodium ion-ion batteries. Gel polymer electrolytes (GPEs) are gaining increasing attention due to their good ionic conductivity, their wide electrochemical window, their good compatibility with electrodes and their good thermal stability. Due to its attractive properties, Poly (Vinylidendifluoride), PVDF, has been selected as a polymeric host substance for lithium-ion battery applications. PVDF-based GPEs are highly electrochemically stable due to the presence of a strong electron-reducing functional group (-C-F). Bellcore technology for lithium-ion yellow electrolytes is based on an extraction process. The extraction process requires a large amount of organic solvent, which is not practical for a large-scale application. Furthermore, it is difficult to completely remove the softener by extraction and drying, which would lead to poor electrochemical behaviour. The authors used a simple phase separation process to produce a high-porous polymer membrane based on P (VDF-HFP) for sodium ion conductive gel electrolytes. Water as a solvent and pore inducer instead of the extraction step that requires volatile solvents

is very promising from an economic point of view. [75]

### 3.2.22 Spirocyclic biphosphate based copolymer gel electrolytes

SIBs have attracted considerable attention in the development of large stationary energy storage systems due to the abundant natural reserves and the relatively low cost of sodium salts. However, they suffer from high volatility, inflammatory conditions, poor thermal stability and leakage risks and even encounter serious safety risks and unavoidable sodium dendrite problems. Various strategies have been implemented and other electrolyte variants have also been studied to solve SIB's safety problems. Inorganic solid electrolytes have poor processability and lower interface compatibility with electrodes. Solid polymer electrolytes have remarkable properties, such as leaks of liquids and excellent processability, but have low ionic conductivity at room temperature. Gel polymer electrolytes (GPEs) serve as a scaffold for the immobilisation of liquid electrolytes and show excellent electrochemical properties in SIB systems. The networked polymer structure is an efficient strategy for improving the mechanical properties of GPEs and can be further enhanced by commercial membranes such as fiber optics. The safe and non-flammable phosphoric electrolytes were developed and used in lithium batteries while they were rarely used in SIBs. The higher the phosphorus content, the better the flame-retardant effect, the authors design a monomer with two phosphate groups and a rigid spirocyclic structure. The corresponding GPEs for sodium ion batteries were produced by thermal polymerisation in situ. [76]

### 3.2.23 Enhanced rate and cyclability of a porous Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>

Sodium ion batteries (SIBs) are considered good candidates for large batteries due to the abundance of sodium resources and the associated low costs. It is therefore essential to achieve a high power density, a high energy density and a long service life in order to market cost-effective SIBs. Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>; NVP is a promising candidate for SIB cathodes due to its fast sodium diffusion and stable cycle life. The low electrical conductivity of NVP ( $1.63 \times 10^{-6} \text{ S cm}^{-1}$ ) prevents a high performance that can be achieved by the installation of conductive materials such as carbon and graphs. Alloy type of anode materials such as Bi and Sn showed excellent performance and long cycle life when pairing with ether-based electrolytes. In particular, Bi / NVP full cells with DME electrolyte showed good performance of up to 10 A g<sup>-1</sup> and a stable cycle life of up to 500 cycles at 1 A g<sup>-1</sup> (related to the anode). Porous high-surface NVP nanoparticles are produced using a solar-gel method. The interface between NVP cathode and electrolyte is modified by various electrolytes (e.g. electrolytes on aether or carbonate basis). The DME electrolyte can effectively alter the interface, which drastically reduces the overpotential and charge transfer resistance. [77]

### 3.2.24 Synergetic effects of multi-metal substitution and electrolyte optimization

Sodium layer oxide Na<sub>x</sub>TMO<sub>2</sub> (TM: transition metal) is one of the most promising cathode materials. They generally have empty layers, which, in addition to their simple synthesis, allow a two-dimensional Na-Ion diffusion [6-10]. In principle, the Na<sub>x</sub>TMO<sub>2</sub> materials consist of stacked TMO<sub>6</sub> layers inserted between the Na-Ions. Low energy density and poor cycle performance are the main obstacles to the development of SIBs. The main application for SIBs is the large-scale electrical energy storage, where costs are in the foreground. The selection of transitional metals in the cathode materials should also focus on soil-rich, cost-efficient elements such as Mn, Fe, etc. P<sub>2</sub>-Na<sub>x</sub>MnO<sub>2</sub> cathodes allow faster diffusion of Na<sup>+</sup> ions and show more stable structures [3,16]. However, the cycle and performance of these materials for practical applications is still too low [10,14,17,18]. The combined structural modulation is used to improve the electrochemical performance of P<sub>2</sub>. P<sub>2</sub> is a combined structural modulation that improves the electrochemistry of the chemical compound P<sub>2</sub>. The combined structural modulations are used to improve the electronic performance of P<sub>2</sub> and P<sub>2</sub>. It is expected that Cu<sup>2+</sup> / Cu<sup>3+</sup> has a high redox potential of 3.6 V (vs. Na / Na<sup>+</sup>) and inactive Mg ions can stabilise the crystal structure. Na<sub>0.67</sub>MnO<sub>2</sub> via Cu and Mg co-substitution. In Na<sub>0.67</sub>Mn<sub>0.8</sub>Cu<sub>0.1</sub>Mg<sub>0.1</sub>O<sub>2</sub> / Na

cells, four electrolyte formulations were used. The effect of the electrolyte on cell performance was also investigated. Fluoroethylene carbonate (FEC) enabled a long-term cycle on both anode and cathode performance. [78]

### 3.2.25 Rubidium and cesium ions as electrolyte additive for improving performance

CsPF<sub>6</sub> was first proposed by Zhang et al. to eliminate the formation of Li-Dendrites in Li-Ion Batteries by a self-healing electrostatic protection mechanism. Furthermore, it was found that Cs<sup>+</sup>-Ions and Ethylene Carbonate (EC) promoted the formation of a robust, ultra-thin and compact SEI layer on the surface of graphite, which enabled the operation of a graphite anode in PC-rich electrolyte. Sodium Ion Batteries (SIBs) have been studied due to the abundant resources and low cost of sodium. For SIBs, HC has been recognised as beneficial anode material due to its relatively high reversible capacity (300 mAh g<sup>-1</sup>) and its low sodium ion insertion potential. In order to use HC, a suitable electrolyte has to be formulated to enable the formation of a robust and protective SEI layer on the surfaces of HC. This layer is necessary to protect the solvents from continuous reduction, but also to provide the pathway of ion transfer for stable and fast soiling and desodation cycles of Na<sup>+</sup> ions. [79]

### 3.2.26 Nanoconfined iron fluoride cathode in NaDFOB electrolyte

Lithium-ion batteries have long been a research interest in the storage of electrical energy due to their energy/performance density and long service life. The high price and scarcity of electrode materials could restrict their application, especially for more cost-sensitive applications such as the mass market for electric vehicles and energy storage in the grid. SIBs have attracted great attention due to the much lower cost and greater abundance of sodium compounds. Iron trifluoride (FeF<sub>3</sub>) is considered one of the most attractive candidates for intercalation cathodes for SIBs. FeF<sub>3</sub> is needed to pass a three-electron transfer that eventually converts it into NaF and metallic Fe. Such a transformation reaction could also reduce the stability of the electrode cycle. Fe<sup>3+</sup> can dissolve during the conversion reaction in electrolytes, resulting in a "Fe loss". NaClO<sub>4</sub> and NaPF<sub>6</sub> have been frequently used in previous studies to improve the stability of cells. However, the notorious difficulties in drying and the potential production of corrosive HF from these salts limit the use of these two salts. Noble helmet and his employees showed that using 0.5 M NaPF<sub>6</sub> in EC: DMC can induce a protective thin film. Electrolyte salts can have a profound effect on the stability of anodes in SIBs. Propylene carbonate (PC), for example, resulted in much better cycle stability than other solvents such as Dimethyl carbonate. Despite these promising observations in cells with some selected anode and cathode chemicals, the influence of the electrolyte composition of SIB has not been studied in detail. NaDFOB has excellent properties such as a large electrochemical window and a lower viscosity. In SIBs it has been shown that improved cycle stability is achieved by creating an improved solid electrolyte interphase (SEI) on the anode surface. FeF<sub>3</sub>-C Nanocomposite cathode in combination with advanced ternary electrolyte based on sodium difluoro (Oxalato) board (NaDFOB) for SIBs. The nano-sized FeF<sub>3</sub> is included in the composite to improve structural stability in a carbon nanofibre (NF) matrix. [80]

## 3.3 Conclusions

In a ceramic polymer composite electrolyte, ion transfer with ceramic powder is difficult. The authors have proposed a top-down procedure in which a polymer on a ceramic has a pre-formed ion transport channel. The authors used a method of partial sintering on a NASICON ceramic with high porosity. [55]

A novel ternary networked GPE cell on a methylphosphonate basis has been synthesized and the corresponding Na / GPE / NVP cell has been assembled. Compared to the conventional LE cell, the GPE cell improves the performance of the sodium ion cells, especially at increased temperature. [56]

Nanocomposite polymer electrolyte (nCPE) with the ratio of EO: Na = 20 and 5 W. % TiO<sub>2</sub> additive results in a maximum ion conductivity of approximately  $2.62 \times 10^{-4} \text{ S cm}^{-1}$  at 60 °C. XRD studies showed the amorphous nature of polymeric salts complexes. [57]

The conductivity of an Nb-doped TiO<sub>2</sub> electrode and the ionic liquid NaFSA / Py13-FSA has been studied for use as an anode and electrolyte in a highly safe Na-Ion battery. The conductivity at 30 °C showed that the potential performance of a TiO<sub>2</sub> anode with a temperature increase to 60 °C has been successfully exercised. [58]

Carbon-coated TiO<sub>2</sub> nanosheets showed the highest specific capacity of 224 mA h g<sup>-1</sup> at a current density of 25 mA g<sup>-1</sup>. These works suggest that the synergy of protective carbon coating and electrolyte composition plays a crucial role in improving the performance of the current generation of sodium ion batteries. [59]

Oxygen function groups on hard carbon by oxygen-plasma treatment to reduce overpotential by stabilising the solid-electrolyte border area. After low costs and simple modifications to low-grade hard carbon, high capacities, excellent cycle stability and good performance have been achieved. [60]

If used as an anode for NIBs, it provides a charging/discharge capacity of 1038 / 1193 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>. This study suggests that a novel anode material a-P4S<sub>2</sub> could stimulate the development of amorphous phosphor-based materials for high-performance batteries. [61]

The layer cathode material Na<sub>0.45</sub>Ni<sub>0.22</sub>Co<sub>0.11</sub>Mn<sub>0.66</sub>O<sub>2</sub> was electrochemically characterised in two different electrolytic solutions: the electrochemical (de-) sodium process shows a higher reversibility for the ionic fluid than for the organic carbonate-containing system. Post-mortem electro-characterisation showed the formation of a thin and uniform SEI layer only in IL-based electrolyte. The effect of the incandescent temperature during synthesis has been studied for materials produced at 750 °C and 800 °C. The material synthesized at lower temperature has the best electrochemical performance. Na<sub>0.45</sub>Ni<sub>0.22</sub>Co<sub>0.11</sub>Mn<sub>0.66</sub>O<sub>2</sub> is a promising cathode material for use in Na-Ion batteries. [62]

Sodium ion addition can improve the electrochemical performance of a graphite anode. The resistance of the SEI layer, which forms during the first loading cycle on the graphite surface, decreases significantly if the electrolyte contains a small amount of Na<sup>+</sup>. [63]

BMP-TFSI-based ILs, which have a high decomposition temperature and are non-flammable, are promising electrolytes for use in high-security NIBs. The NaTFSI concentration in the IL-electrolyte influences the electrochemical performance of the NaFePO<sub>4</sub> electrode. IL is better suited for applications at elevated temperatures than the organic electrolyte. [64]

GSSIHs on a BC-GPE basis delivered a high capacity of 106.3 mA h g<sup>-1</sup> and cycle stability after 900 cycles. They also showed impressive performance, while those with conventional liquid electrolytes can only have a capacity of 68.1 mA h g<sup>-1</sup>. [65]

Carbonate based electrolytes for NFM / HC-SIBs exceed their performance in terms of capacity maintenance and safety. PC / EMC-Electrolyte also promotes the formation of a protective interface layer that softens parasitic reactions between electrodes and electrolytes. The authors could show that a second-generation NaPF<sub>6</sub> / PC-EMV optimised by additions not only enables the NFM / HC bag cell to cycle over 2500 cycles reversibly but also makes the cell safer. [66]

The effects of the additive Na<sup>+</sup> in LiODFB / EC + DMC (1: 1 v / v) -electrolyte on the cycle behaviour of Li-separation on the surface of the Li<sub>22</sub>Sn<sub>5</sub> substrate electrode have been investigated. An optimized Na<sup>+</sup> concentration is 0.13 mol L<sup>-1</sup>, since the Li<sup>+</sup> salt concentration is 1 mol L<sup>-1</sup>. [67]

The highly concentrated NaClO<sub>4</sub> aq. Electrolyte was examined by means of Raman spectroscopy and X-ray bending in combination with EPSR modelling. The stable potential window was not modified as the concentration increased from 10 m to 17 m, which corresponds to a residual free water in the aqueous electrolyte. [68]

This is the first demonstration of this kind of cell configuration and one of the very rare reports in which both electrodes are tested against their real counter electrodes. The device itself has the potential to replace current state-of-the-art electrochemical capacitors by providing a much higher energy density. This approach seems to be more sustainable in terms of cost and availability of components than Li-ion capacitors, using

much more sodium than charge carrier. [69]

Ether-substituted ionic liquid electrolytes NaFSA / Py1MOM-FSA successfully improved the efficiency of the electrode. In these electrolytes, the electrochemical reaction of Na + and Sn / P was promoted compared to the Py13-based electrolyte without aether-humidity, which contributed to a higher capacity. [70]

The safety risk of a fully-sedated Sn electrode was assessed by a DSC instrument in a temperature range of 20 to 400 °C. The NaPF6-based electrolyte produced a thicker surface film on the Sn electrode, resulting in an intensive thermal decomposition reaction of the SEI layer. [71]

Up to 1000 cycles of 1 Ah sodium ion bag cells were demonstrated by the use of several additives that combine fluoroethylene carbonate (FEC) with prop-1-en-1,3-sultone (PST) or with PST and DTD (DTD). The bag cell held a capacity retention of up to 92.2% after 1000 cycles at 1 °C between 2.0 V and 3.8 V. [72]

High viscosity and low ion conductivity of the electrolyte have no significant influence on the electrochemical properties of electrode materials due to the high ion activity of highly concentrated electrolytes. Rapid kinetics and structural stability of PNTCDA compared to inorganic materials enable a high power density of 20 kW kg<sup>-1</sup> and excellent cycle stability. [73]

DI-water and methanol in a binary system without solvents act as a pore inducer or positioner during the phase-in version of PVdF-HFP. The electrochemical performance of SIBs in a harsh environment such as long cycles and high current density has been improved. [74]

A sodium ion conductive gel electrolyte has been successfully produced by a simple phase separation process using water as a solvent and pore producer. It has a higher ion conductivity of 0.60 mS cm<sup>-1</sup> at room temperature than the commercial separator (Celgard 2730). It has high safety, good mechanical properties and good electrochemical stability. [75]

The rigid, less combustible spirocyclic pentaerythritol diphosphate-based networked gel electrolytes were produced by thermal in-situ polymerization and the corresponding sodium ion-ion batteries assembled. The gel copolymer electrolyte has excellent thermal stability, good electrochemical stability, high ionic conductivity, high sodium ion transfer rate and good interface properties. [76]

In this study, porous NVP nanoparticles were synthesized using a simple sol-gel method and their electrochemical performance was investigated using carbonate and ether-based electrolytes. The low load transfer resistance and the high ion conductivity of the electrolyte were mainly responsible for the high rate and long-term cycle behaviour. [77]

The novel P2 is published in P2 in a novel about a young couple. P2 was published in 2007 and was published in 2009. The novel is published in April 2015 and is published in October 2015. The novel's author is currently working on a novel called P2. Na<sub>0.67</sub>Mn<sub>0.8</sub>Cu<sub>0.1</sub>Mg<sub>1.0</sub>O<sub>2</sub> SIB cathode material has been designed to use the synergistic effects of Cu and Mg ions. It can deliver a maximum capacity of 84 mAh g<sup>-1</sup> at 1 C with 93% capacity retention after 500 cycles. [78]

The addition of small amounts of Rb + and Cs + ions in electrolyte significantly improves the cycle performance of the hard carbon anode in sodium-ion batteries. This improvement is attributed to the participation of Rb + and Cs + ions in the formation of a higher-conducting and more stable SEI, resulting in a lower cell response resistance. [79]

A carbonization temperature of 600 °C proved to be optimal to achieve the best electrochemical performance. The use of NaDFOB salt in the ternary electrolyte (EC: DEC: DMC) enabled the development of a thin and compliant CEI protective film on the cathode. [80]

**Part II**

**Li-S Batteries**



# Chapter 4

## Li-S Cathode Materials

### Contents

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### 4.1 Introduction

Nanostructured Li<sub>2</sub>S-based cathodes containing 20 % by weight of MWCNT showed promising discharge capacities of up to 1050 mA h g<sup>-1</sup>S at a slow rate of C/20 and 800 mA g<sup>-1</sup> at a C/2 rate. Without electrolyte additives (such as polysulphide or lithium nitrate) Li<sub>2</sub>S-cathodes showed a capacity reduction of up to 90% after 100 cycles. [81]

Lithium-Sulphur-Akkus (Li-S) offers a better alternative to the current commercial lithium-ion battery due to its high energy density, low costs and satisfactory safety. During battery operation, the shuttle effect seriously destroys the battery life and leads to severe capacity degeneration. Copolymerisation strategy, where elementary sulphur melts into linear polysulphate and then is co-polymerised with polymerised left monomers to stable organic sulfur polymers. [82]

Lithium-Sulphur Batteries (Li-S) with a high theoretical capacity are considered to be one of the most promising candidates. For the flexible Li-S batteries, the interpretation of the foldable electrodes including anode and cathode is crucial. The flexible sulfur cathode could be obtained by integrating the electroactive sulfur with a flexible substrate in general. [83]

Molybdenum sulphide (MoS<sub>2</sub>) with a two-dimensional layer structure can effectively inhibit the pendulum effect of lithium-sulphur batteries (Li-S batteries). MoS<sub>2</sub>'s structure and properties are briefly presented in this essay. The existing problems and possible future research directions are shown. [84]

Lithium-Sulphur Batteries (LSBs) are a promising next-generation energy storage system that goes beyond state-of-the-art lithium-ion batteries. However, liquid LSBs on an electrolyte basis suffer from a "polysulfide shuttle" and safety concerns created by the use of combustible organic electrolytes. [85]

A clear trend in entropy and the decrease in dQ/dV peak amplitude with excess Li content has been observed. The effect is partly due to the presence of attached Li ions that interfere with the formation of the ordered phase. All the Li-Li rejection parameters in the model increased in value when the defect rate  $\gamma$  increased. [86]

Carbon aerogels have great potential as a host for lithium-sulphur batteries. The production of carbon aerogels usually requires special drying techniques to maintain their porous structure. The authors develop a simple method to adapt the flexible structure of carbon aerogels by simple use of NaCl, leading to a more stable porous structure that resists the collapse of the pores during the conventional drying process. [87]

Lithium-Sulphur-Akkus (Li-S) is one of the most promising energy storage systems due to its high energy density of 2560 Wh kg<sup>-1</sup>. But the strong pendulum effect of polysulphide-intermediate products, the poor conductivity of S and large volume changes during the cycle leads to rapid capacity loss and poor cycle performance. The authors show S-Nanodots impregnated microporous carbon-capsulated conductive vanadium nitride nanowires as powerful S-cathode materials for Li-S-Akkus. [88]

The S @ MnO<sub>2</sub> @ GO showed excellent performance and long service life. The extreme GO was built together to block the open pores of MnO<sub>2</sub> and thus minimize the possibility of polysulphide to drain into the electrolytes. The GO significantly improved the electrical conductivity of the sulfur cathode. [89]

Li-S battery cathodes with a hierarchically structured Janus-Wirt consisting of multiwall carbon nanotubes (MWCNTs) and Polyethyleneimin (PEI) The MWCNTs act as a conductive skeleton for the physical containment of S and the PEI can chemically immobilize the S/Lithium polysulfide. [90]

## 4.2 Literature Reviews

### 4.2.1 Nanoporous Li<sub>2</sub>S and MWCNT-linked Li<sub>2</sub>S powder cathode

Lithium (Li)-based battery chemistry has proved to be a viable solution when it comes to integrating renewable energy sources into an intelligent power grid. Rechargeable Li-Ion batteries have already developed into a solution for the choice of portable electronics, telecommunications devices, power tools and electric vehicles. Elementary sulfur (S) could be a promising candidate for cathodes due to its high theoretical capacity of 1672 mA h g<sup>-1</sup>. However, the isolation properties of S, the dissolution of lithium polysulphides (which occur in the course of the S-lithion) in electrolytes during the cycle and the resulting cathode dissolution. The need to use Li-containing anodes (usually Li-folies) currently prevents the commercialisation of S-based cathodes. Inorganic metal oxide and organic polymer shells around porous S- and S-containing composites show promising results in reducing polysulphide dissolution. However, such methods have not yet shown complete prevention of unwanted lithium sulfide deposits at the surface of the Li-metal anode. Li<sub>2</sub>S is compatible with safer Li-free anodes (e.g. graphite or Si/Sn-based composites). The use of anodes that are subject to small volume changes during the cycle (e.g. graphite) facilitates the formation of a stable electrically insulating SEI. The high melting point of the commercial Li<sub>2</sub>S (- 940 ° C) makes it difficult to infiltrate it into conductive carbon economy. The ball grinding does not allow the formation of uniform particles with controlled morphology or strong bonding between Li<sub>2</sub>s and carbon. H<sub>2</sub>S is a fairly toxic gas that is harmful to the environment. Due to volume changes and poor mechanical properties of the usually used PVDF binders. This method is fast, simple and environmentally friendly, as it does not release dangerous gases. Compared to commercial Li<sub>2</sub>S, this novel method improved the use of nanoscale Li<sub>2</sub>s in cells due to the significantly improved electrical conductivity of the proposed cathodes. [81]

### 4.2.2 Organosulfur polymers as cathode materials

The world's population and ever-increasing energy demand require energy storage, which has a high energy density and low cost of long service life. So far, the lithium-ion battery (LIB) is the most mature technology and enabled the wireless revolution of portable electronic devices. However, it cannot meet the requirements of advanced electric and hybrid vehicles because its energy density is at its limits. The Li-S battery is one of the most promising candidates due to its low cost and the high theoretical energy density. It consists of metallic lithium as an anode and elementary sulphur as a cathode. Due to the combination of the low molecular weight of sulphur and the net weight of two electrons produced by the electrochemical transformation of elementary sulphur into lithium sulfide (Li<sub>2</sub>S), the sulphur cathode could have a high theoretical capacity of 1675 mA h g<sup>-1</sup>. The biggest challenge for the practical application of the Li-s battery is the unwanted electrochemical use of sulfur cathode. Previous strategies focused on the physical encapsulation of sulphur within various

conductive matrices, including carbon-containing nanomaterials [23-26], polymers [27-29], metal oxides [30-32] These small sulphur-allotropes were of great interest in new energy fields. Such copolymers were able to effectively improve the properties of the Li-S battery as cathode material. Recent advances in copolymers, which are obtained from elementary sulphur and various binding monomers, including alken / alkin, thiol and nitrile, as active cathodes for Li-S batteries. Some novel polymeric sulfur materials by donating other elements are also presented in this review. [82]

### 4.2.3 Recent progress of flexible sulfur cathode

The so-called flexible batteries refer to the fact that the battery can withstand deformations such as bending, twisting, stretching and even folding. While these processes take place, the battery can be completely restored in its original state and the performance does not change. Flexible electronic technologies will bring a new round of electronic technology revolution and also have revolutionary effects on the social lifestyle. Lithium-Sulphur Batteries (Li-S) with a high theoretical capacity are considered to be one of the most promising candidates for the next generation of energy storage [7-11] Compared to conventional lithium-ion batteries, Li-S batteries can offer a higher energy density of 2500 Wh kg<sup>-1</sup> or 2800 Wh L<sup>-1</sup>. The reaction principle of the Li-S battery is simple, it is actually a complex reaction process, which incorporates soluble or insoluble lithium polysulfide intermediate products [19,20]. On the image you can see two obvious discharge plates, which are around 2.3 V and 2.1 V during the discharge process. The complex electrochemical processes of Li-S batteries present a series of enormous challenges. The obstacles that stand in the way of their commercial application are described below: First of all, the sulphur is not a good conductor for electrons (the electronic conductivity of sulphur is  $5 \times 10^{-30}$  S cm<sup>-1</sup>) and the discharge products (Li<sub>2</sub>S or Li<sub>2</sub>S<sub>2</sub>) are almost an insulator. A large volume expansion of the active material would cause problems, such as damage to the structure of electrode materials, rapid drop in capacity and security problems [24-28]. Most positive sulfur electrodes are inorganic brittle materials with extremely low elastic stretching values. There are some safety risks such as leaks or short circuits when deformation is used when the liquid electrolytes are used. Metal Li is usually used as a negative electrode, while Li is very susceptible to fatigue fractures when repeated deformation occurs. [83]

### 4.2.4 MoS<sub>2</sub> in the cathode of lithium sulfur batteries

Traditional energy generation and consumption cause global warming and environmental degradation. At the same time, global fossil energy will be exhausted according to current energy consumption patterns in the future. Energy storage and conversion are the key to coping with the climate crisis and to sustainable development of human society. Li-S batteries are rechargeable and usually consist of a sulphur-based cathode, a binder, a separator, an organic liquid electrolyte, a lithium anode and a pantograph. The function principle of Li-S batteries is in Fig. 2. During the discharge process, sulphur is first dissolved in the electrolyte in the solid phase (S<sub>8</sub>(s)) and then converted to S<sub>8</sub>(l). The solid phase is then reduced to high-quality lithium polysulphides (Li<sub>2</sub>S<sub>n</sub>, 4 ≤ n ≤ 8). Element Sulphur has a theoretical specific capacity of 1675 mA h g<sup>-1</sup>. Li-S batteries can achieve a high theoretical gravimetric and volumetric energy density of 2500 W h h kg<sup>-1</sup> and 2800 W h h l<sup>-1</sup>. Lithium-air batteries have a greater marketing potential than lithium-air batteries. [84]

### 4.2.5 Flexible electrolyte-cathode bilayer framework with stabilized interface

Lithium-sulphur batteries (Li-S batteries) have gained attention as a promising energy storage system for electric vehicles. However, the practical use of Li-S batteries is severely impeded by the continuous capacity decline due to the shuttle effect of soluble discharge intermediate "polysulfides" in liquid electrolytes. The replacement of liquid electrolytes by solid electrolytes has been considered as an alternative approach to solving these problems. In order to enable the operation of Li-S batteries at room temperature with fixed electrolytes, it is essential to provide an electronically conductive skeleton for the S-load within the cathode. S-cathodes with reduced graphene oxide and soot have been researched to improve electrical conductivity in

ASSLSBs. A composite frame consisting of two layers, consisting of a one-dimensional (1D)  $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$  (LLTO) ceramic nanofibre/poly (ethylene oxide) (PEO) composite electrolyte coupled to a 3D flexible carbon nanofibre/sulphur (CNF/S) cathode. This two-layer structure can be placed on the top of the anode surface to form a complete Li-S cell without the use of additional electrolytes or separation layer. [85]

#### 4.2.6 Quantifying structure dependent responses in Li-ion cells with excess Li spinel cathode

Increasing demand for rechargeable batteries in electric vehicles and stationary storage. A cause of power waste in Li-Ion cells is the structural change of electrode materials during cell operation. A number of in situ methods have been developed to diagnose changes in electrode structure by thermal (calender) aging or longer charging/discharge cycles in real time. A class of promising techniques is based on thermodynamic measurements, such as entropy profiling (EP). This technique is based on the principle that the partial molar entropy change is proportional to the temperature response of the emptiness voltage (OCV) of a cell through a cell. While EOCV is the idle voltage,  $T$  is the absolute temperature,  $p$  the pressure,  $x$  is the proportion of Li that is displayed in the electrode ( $0 \leq x \leq 1$ )  $n$  is the number of electrons that are transmitted per extractable Li atom in the anode or cathode.  $F$  is the Faraday constant and  $S$  is the entropy per mole of extracted Li. Selman et al. conducted electrochemical-calorimetric measurements of  $\text{Li}_x\text{Mn}_2\text{O}_4$  and commercial Li-Ion cells. Reynier et al. investigated the entropy change during entropy storage in graphite and disorderly carbons. The entropy change during li storage in graphite was recently studied theoretically and later also the entropy change in cathode materials, including  $\text{Li}_x\text{CoO}_2$ ,  $\text{Li}_x + y\text{Mn}_2 - y\text{O}_4$  Spinell and nickel-manganese cobalt (NMC)-based layer materials. Entropy profiles of the stoichiometric compound,  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $0 \leq x \leq 1$ ), show two clearly defined peaks. Peaks are created by the formation of an ordered phase in the intermediate state of the charge and the transition to an disorderly fixed phase of solution on both sides. More fixed positions indicate that the ordered phase is gradually disrupted, leading to a reduction of EP and  $dQ/dV$  peak amplitudes. Two approaches have already been applied to open-circuit voltage profiles (OCV) to understand entropy profiles on a more quantitative level. Ab-initio approaches based on effective cluster interactions (ECIs) could be applied within a framework of density functional theory (DFT). Parametric models can be adapted directly to experimental OCV profiles. The current work seeks an atomic interpretation of OCV and entropy profiles. The authors focus on the systematically different cathode compositions  $\text{Li}_{1+y}\text{Mn}_2 - y\text{O}_4$ . This work sheds a new light on the microscopic origins of peaks observed in  $dQ/dV$  and EP. [86]

#### 4.2.7 Graphene/carbon aerogel for high areal capacity sulfur cathode

Lithium-Sulphur Batteries (LSBs) have attracted tremendous attention in recent years. They are considered to be the most promising candidate to replace the commercial lithium-Ion batteries in the near future. However, the low utilisation of sulphur and poor cycle stability still hinder the practical use of LSBs.  $\text{LiNO}_3$  is proposed as an efficient electrolyte additive that reduces the pendulum effect of polysulphides and could significantly increase the coulomb efficiency of LSBs. Porous carbon materials, transitional metal oxides and conductive polymers were also used to encapsulate sulphur to promote the use of active materials. As a result, the reversible capacity could be reached with a continuous cycle power of more than 800 mA g/h. One-dimensional carbon nanotubes (CNTs) and graphene nanosheets (GNSs) are the ideal candidates for the production of thick sulphur cathodes due to their high electrical conductivity. The high costs of these materials and the complex manufacturing processes hinder their large-scale application. The three-dimensional carbon aerogel is another attractive porous carbon material with permeable three-dimensional hierarchical structure. Carbon aerogels are used in the areas of absorption agents, sensors, catalysts, super capacitors, [34-36] and rechargeable batteries. A hierarchically porous graphene carbon aerogel (HPGCA) has been developed by NaCl-supported hydrothermal self-assembly. This HPGCA contains rich mesopores and macropores, inherited from the interconnected GO-plates and provides sufficient space for absorbing sulphur, which allows a

high gravimetric/spherical sulfur load. [87]

#### 4.2.8 Carbon encapsulated mesoporous vanadium nitride

Lithium-Sulphur Batteries (Li-S) are considered one of the most promising energy storage systems. Carbon-C materials such as carbon nanotubes, graphs, activated carbon- and carbon-coal bullets are widely used as S-whites in Li-S batteries. Carbon-C composites have an improved life span by physically including the Li<sub>2</sub>S in the pores or carbon-host layers. Leading UN nanowires, coated with conductive C (MVN @ CNW), are described as high-performance S-host materials for advanced S-cathodes of Li-S batteries. UN is considered the most promising candidate for SCs because it has a high electrical conductivity ( $\sigma_{\text{bulk}} = 1.67 \cdot 10^6 \Omega^{-1} \text{m}^{-1}$ ). [88]

#### 4.2.9 MnO<sub>2</sub>-GO double-shelled sulfur (S@MnO<sub>2</sub>@GO)

Sulphur as a cathode material for lithium batteries has a theoretical capacity of 1675 mAh g<sup>-1</sup> [1-3], about ten times more than conventional cathode materials (e.g. LiCoO<sub>2</sub> and LiNixMnyCo<sub>1-x-y</sub>O<sub>2</sub>) for lithium-ion batteries. In the last ten years, considerable efforts have been made to improve Li-S batteries by developing efficient electrolytes and nano-carbon compounds. Wang et al. [14] reported an S / C compound cathode by heating an active carbon with elementary sulphur. In another work, a high capacity of 1320 mAh g<sup>-1</sup> and a stable cyclic performance was achieved by impregnation of sulphur in a highly ordered mesoporous carbon. In contrast, sulphur-metal oxide composites have rarely been reported, and there are few reports of S / TiO<sub>2</sub>-based composites than cathodes for Li-S batteries. This is most likely because Oxide typically has a lower electrical conductivity and is heavier (larger molecules) than carbon. Some of the oxides (like MnO<sub>2</sub> and TiO<sub>2</sub>) can complement the resulting composites with capacity. The S @ MnO<sub>2</sub> @ GO has good performance (175 mAh g<sup>-1</sup> at 6000 mA g<sup>-1</sup>, based on the composite) and a long cyclic life (40% capacity within 400 cycles). In addition, both the MnO<sub>2</sub> and the GO can improve electrical conductivity (10<sup>-5</sup> - 10<sup>-6</sup> S cm<sup>-1</sup> for MnOO<sub>2</sub> [36] and 85 S cm<sup>-1</sup> for reduced GO [37]). [89]

#### 4.2.10 High-performance Li-S battery cathode enabled by immobilizing sulfur

The Li-S battery is due to its relatively higher theoretical specific capacity one of the promising candidates for the next generation of lithium batteries. The main disadvantages of the S-electrodes are low conductivity, large volume changes during the cycle and the resolution of high-quality lithium polysulfide (LPS) in liquid electrolytes. Carbon nanotubes, a commercial carbon nanomaterial, were widely investigated as host for S due to its unique nanostructure for the immobilization of S. The authors propose an effective strategy for constructing a unique Janus-S-Bet by combining MWCNTs with branched polyethylene (PEI). The PEI was selected due to its plentiful amine and imin groups for LPS chemical absorption barriers. PMP was produced by a layer-by-layer method of Langmuir-Blodgett-Scoping (LBS), which was then separated with sulphur solution to produce a binding-free Li-S battery. [90]

### 4.3 Conclusions

X-rays showed the lack of crystalline impurities in the samples produced, while electron microscopy (REM and TEM) in combination with N<sub>2</sub> sorption measurements showed the influence of the preparation conditions on the morphology and porosity of the samples. Furthermore, the authors showed the effects of the CNT content and the salt concentration of the electrolytes on the utilization of cathode capacity, speed performance and cycle stability. [81]

Sulphur-rich copolymers in Li-S batteries have attracted a lot of attention due to their excellent processingability, flexibility and large electrochemical stability windows. The reverse vulcanisation method has

been significantly developed for the production of sulfur-rich copolymer. The authors investigated the copolymer synthesis and its use as active cathode materials in LiS cells. Recent studies on sulfur-rich copolymers have achieved a major breakthrough in the field of Li-S batteries. However, there are still some obstacles when it comes to the practical application of higher sulphur loading. Future research can focus on the following directions: The development of more stable and long-term controllable polysulfane, bound in polymers, so that polysulfide can form low order directly during discharge. [82]

The main advantages of the flexible sulfur cathode for Li-S batteries are the following: The construction of the flexible conductive network could not only improve the conductivity of the entire cathode but also exhaust the volume expansion of the sulfur during the reaction. The intentionally introduced heteroatom and polarity connections could slow the shuttle effect by chemical adsorption. In order to maintain the advantage of Li-S batteries, it is necessary to increase the sulphur content and the degree of utilisation of the flexible cathode. Although these flexible cathode are free-standing and binding-free, they always have a low sulphur load in order to achieve excellent mechanical flexibility. It is urgently necessary to develop a more useful 3D network to load more sulphur. The existing research on flexible cathodes of Li-S batteries continues to focus on the design, but neglects the research and characterisation of "flexible" properties. These associated research needs to further investigate their mechanical properties, including intrinsic strength properties and structural stability in dynamic bending. Most characteristics (especially electrochemical performance) of flexible electrodes are based on static and button cell tests, so that the results obtained cannot fully reflect the actual behaviour of electrodes under operating conditions. The volatility and flammability of ether electrolytes poses great safety risks, so flame retardant electrolytes and solid electrolytes have to develop further. The development of flexible solid-li-S batteries is still in the early stages, but fortunately, the LIBs have gathered many experiences that are worth being used and studied. To achieve flexible Li-S batteries, the anode of the metal Li plays another key role, but there are few related studies. Compared to flexible sulphur cathodes, the flexibility of the Li-Metal anode is more difficult and challenging. The design and application of flexible cathodes are based on the continuous development of flexible skeletons. Future work focuses on improving electrochemical performance and improving the mechanical properties of electrode materials. Meanwhile, the development of stretchable Li-S batteries should be adapted to various complex stress applications. [83]

MoS<sub>2</sub> can accelerate redox reaction kinetics during the discharge/charging process through strong adsorption of polysulphides. It has great potential benefits for Li-S batteries, such as the cathode material of Li-S batteries. It can accelerate redox reactions in the discharge and charging process. MoS<sub>2</sub> has a strong adsorption for sulfur-containing groups and thus prevents the resolution of polysulphides. It can ensure better cycle stability over several thousand charging/discharge cycles. It has a great advantage in reducing the "Shuttle effect", which has seriously hindered its commercialization. MoS<sub>2</sub> is a kind of typical graphene-like two-dimensional transition metal sulfide. Each layer of Mo is bonded between two layers of S atoms and the layers are connected by weak van-der-Waals forces. This special structure makes the interaction forces within the layer strong, while the interactions between the layers are relatively weak. MoS<sub>2</sub> has a high theoretical storage capacity of 670 mA h g<sup>-1</sup>, when it reacts with Li<sup>+</sup>. This capacity is much higher than that of Graphen (372 mA g<sup>-1</sup>). The Mo atom has an oxidation state from 2 Valenz to 6 Valenz. These properties determine its high theoretical lithium storage capacity. Many methods for the synthesis of MoS<sub>2</sub> nanocongeners have been developed. Hydrothermal methods can synthesize nanomaterials in different dimensions in one step. Template methods are more conducive to the synthesis of core envelope structures. The progress of these methods has made a major contribution to the development of Li-S batteries. [84]

For RT-ASSLSBs, a novel two-layer array of 1D-LLTO ceramic nanofibres was developed, which after 50 cycles has a stable cycle performance with a high coulombic efficiency of over 99%. This two-layer structure design opens ASSLSB an alternative way to work at room temperature constantly by dealing with several challenges. [85]

The authors investigated the effect of excess Li,  $y$  ( $0 \leq y \leq 0.2$ ) in  $\text{Li}_{1+y}\text{Mn}_2 - y\text{O}_4$  on entropy, voltage and  $dQ / dV$  profiles. By numerical optimization the authors compared the results of a midfield model with experimental results. The following findings can be drawn from this work: The author provides insights into

the development of the first language of the world. The work was published in 1998 and is published in 2000, with a number of publications being published worldwide, including the National Geographic Institute of the United States. Entropy profiles showed a systematic suppression of the transition between order and disorder in the Li / emptiness structure depending on the amount of excess Li,  $y$  in the grid. The grid structure was suppressed by a systematic process of order and disorder. In all compositions  $dQ / dV$  showed two peaks of uneven size and shape. In accordance with previous works, these peaks were also suppressed by excess Li. For example, these peaks were suppressed by excess Li by being suppressed by excess Li to reduce their size. An inherent problem in conventional models based on pair-wise interactions is the profile symmetry on both sides of  $x = 0.5$ , in contrast to the experimental profiles. In order to model the observed peak symmetry, a single correction term was used in simulations that allowed the interaction parameters to vary linearly over the intercalation range. The adjustment of both profiles by numerical optimization showed that tinted li positions, proportional to the defect rate  $x_{pin} = 3y$ , led to an overestimation of peak magnitude suppression. (5) The optimized interaction parameters indicated an increased Li-Li rejection with increasing Li,  $y$ . (5) An increased Li-Gitter attraction (point term) with increased Li-Li surplus was found as a point term for Li-Gitter attraction. The same trend was shown in the separate optimization of simulated fits to  $dQ / dV$  and entropy profiles or in the adjustment of a weighted sum of both profiles. Quantitative differences between the parameter values of individually optimized fit indicate restrictions in the approximation of the mean field for high Li-surplus spindles. The work provides insights into the physical origins of the peak values in electrochemical and thermodynamic profiles of Li-ion cells. It could lead to a better understanding of the changes observed in aging cells. The authors stress the importance of taking into account interaction parameter changes during intercalation. [86]

NaCl is used to adjust the viscosity of the hydrothermal media, to minimize the carbon nanosphere by products and to modify the flexibility of the hydrogel. The HPGCA produced in this work is a promising host for lithium-sulphur batteries with high energy density. [87]

The authors have demonstrated the synthesis of the S-Nanodots embedded in the core shell of the MVN @ C NWs through a melt diffusion process. This freestanding flexible film electrode has a high reversible capacity of 636 mAh g<sup>-1</sup> after 200 cycles at a current density of 1 C. [88]

A new cathode material S @ MnO<sub>2</sub> @ GO was produced by coating S particles on site. The reaction between KMnO<sub>4</sub> and S was used to separate the material on site and mount GO on the surface of MnO<sub>2</sub>. The resulting material has a stable capacity of approximately 350 mAh g<sup>-1</sup>. The good cyclical performance goes along with our deliberately constructed two-scale structure: the wave-like MnO<sub>2</sub> shells of the S @ MnO<sub>2</sub> @ GO serve as a protective layer to prevent the polysulphide from entering the electrolytes, and to create rich hollow spaces for the S-expansion after the lithion. The cyclical performance should be further improved before the practical application of the S @ MnO<sub>2</sub> @ GO, which can be achieved by reducing the size of S particles. Nevertheless, our coating from MnO<sub>2</sub> to S in situ offers a new approach to producing S-cathodes for Li-S batteries with easily controllable S-content. [89]

In PMP-S Composite, the Amine/Imin groups in PEI have a strong chemical adsorption capability that can effectively immobilise LPSs, and the MWCNT skeleton can physically limit S/LPSs due to its networking structure at the same time. PMP cathode with more than 65 WW% S has a high reversible specific capacity and an excellent cycle stability. [90]



# Chapter 5

## Li-S Anode Materials

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### 5.1 Introduction

The resolution and diffusion of Li-Polysulfide (LiPS) intermediate products is considered one of the most serious problems for the loss of capacity and the cell failure of lithium-sulphur batteries (Li-S). Hereafter the authors have proposed a failure mechanism of the Li-Metal anode in Li-S cells, based on the mechanistic investigation of the complex interactions between LiPSs and Li-Metal. [91]

Sericin, which is equipped with numerous lithiophiles and anionophiles functional groups on its polypeptide chain, is proposed as a compliant protective layer both on copper and on li-metal anodes. Long cycle life (335 cycles) and a high coulombic efficiency (98%) are achieved in serially decorated Li/Cu cells. [92]

A Li-S battery with safety configuration has been designed with electrochemically-precised Si/C microballs as anodised, S/C composites as cathode and ionic liquid at room temperature of the Li-S battery. [93]

### 5.2 Literature Reviews

#### 5.2.1 Lithium metal protection through in-situ formed solid electrolyte interphase

Lithium-sulphur batteries (Li-S batteries) with a high theoretical energy density of  $2600 \text{ W h h kg}^{-1}$  are considered an attractive alternative. Li-S batteries also have the outstanding advantages of high natural frequency, low cost and non-toxicity of sulphur for mass applications. The intrinsic insulating effect of sulphur and the final discharge product (Li<sub>2</sub>S) leads to a low use of active materials in electrochemical reactions. The shuttle effect and the parasitic reaction of Li-polysulfide (LiPS) between anode and cathode lead to a severe loss of capacity and a poor life of a complete Li-S cell. The formation of Li-Dendrites causes low energy efficiency and dangerous safety problems. Most tests were carried out with a sulphur load of less than 70% and an area density of less than  $2.0 \text{ mg cm}^{-2}$ . A dramatic increase in the lipid concentration in the electrolyte results in rapid capacity reduction and a low coulombic efficiency. If the defective cell is adjusted, the glossy Li-metal anode becomes dark and the cell is almost dry. Problems with dendrites in Li-S batteries are more serious and more complicated due to the LiPS-based chemistry of electron transformation [61]

Lips-intermediate products are considered a two-edged sword. The study of the positive role of LiPSs in the Li-Metal anode is crucial to suppress dendrite growth on the anodised side. In a functioning Li-S cell there is always continuous composition and concentration fluctuations of the LiPSs during the charging/discharge cycle. The role of polysulphide on the Li-Metal anode is very difficult to identify in a real battery. The authors found that the electrolyte with a sulphur concentration of 0.10 M produced an unprecedented dendrite-free morphology, exceptional coulomb efficiency and superior long-term stability. [91]

### 5.2.2 Sericin protein as conformal protective layer for Li metal anodes

The use of Li-Metal as anodising material can significantly increase the energy density of batteries and meet the requirements for transport and stationary energy storage. The use of Li-Metal anodes is two-edged, as the simple separation of dendritic Li on metal substrates during repeated coating and strip operations. Li-Dendrites will grow rapidly and uncontrollably under the influence of complex mechanisms. The enormous impedance of the interface between electrolyte and electrode strongly affects the electrochemical performance of Li-whole body batteries. A change in the liquid electrolyte composition by additions could facilitate the favorable SEI formation with better stability [12.1]. Alternatively, the uptake of Li in a porous, electrically conductive, chemically and mechanically stable matrix can minimize volume development when considering the enormous volume change of Li-metal anodes during the cycle. Sericin is a natural adhesive protein macromolecule with rich polar functional groups. Serin, aspartic acid, glycine and threonin are four important amino groups. It is electrochemically inert in a large voltage window, allowing it to act as a stable decorative layer on the electrode surface. Sericin coating with rich polar function groups as an efficient artificial SEI for effective suppression of Li-Dendrites. By using this natural biological material, the cycle performance of Li-Metal-Anodes is significantly improved. The protected Li-Metals allow a high CE ( $\leq 98\%$ ) for 335 cycles at 1 mA cm<sup>-2</sup> based on a high surface capacity of 2 mAh cm<sup>2</sup> per cycle. [92]

### 5.2.3 Lithium-sulfur battery with prelithiated Si/C anode

The lithium-sulphur battery (Li-S) is one of the most promising candidates for high energy because of the high theoretical capacity of the sulphur cathode (approx. 1672 mA h g<sup>-1</sup>) and the lithium anode. The practical use of Li-S batteries is still hampered by the poor safety aspects resulting from the use of lithium-metal anodes and combustible organic liquid electrolytes. The safety problem created by the lithium metal anode is attributed to the formation of Li-dendrites on its surface during repeated Li-coating that could penetrate the separator and lead to an internal short circuit [22]. Therefore, the construction of a rechargeable cell with lithium-containing electrode materials instead of lithium-metal attracts great attention. Li-S batteries are commonly used organic liquid electrolytes with combustible and volatile properties such as ethylene carbonate, dimethylcarbonate and electrolyte on a glyme basis. RTILs have attracted more attention because they are not flammable, have a negligible vapour pressure, have a high conductivity of lithium ions, have a large electrochemical window and prevent the formation of Li-Dendrites [27,31,32]. Nn.n.n.n. was born in New York City, New York, New Jersey in 1996 and currently lives in the U.S. state of New Jersey. She has been married for more than 20 years and has been born into a four-member family with one mother and two daughters. -Methylmethylmethylmethylamine is a form of compound. The compound is a kind of substance that can be found in the form of methylmethylamineamine. In the United States it has been used for more than 1,000 years. Nn.n.n.n. was born in New York City, New York, New Jersey in 1996 and currently lives in the U.S. state of New Jersey. She has been married for more than 20 years and has been born into a four-member family with one mother and two daughters. Imidazolium-based ionic liquids have also been studied as electrolytes in Li-S batteries with improved performance compared to conventional organic solvent electrolytes [28]. The electrolyte could contribute to suppressed polysulphide resolution in the electrolyte. The Li-S battery can effectively avoid the above-mentioned safety concerns by using electrochemically-precised Si/C microsphere as an anode, S/C composite materials as a cathode and an ionic liquid of ionic liquid at room

temperature. Nn.n.n.n. was born in New York City, New York, New Jersey in 1996 and currently lives in the U.S. state of New Jersey.n. She has been married for more than 20 years and has been born into a four-member family with one mother and two daughters. -Methyl-methyl-phenomena is a form of drug used to treat cancer.-Methamine is a form known as a precursor to life saving drugs.-Required drugs are available in the USA and Europe. Nn.n.n.n. was born in New York City, New York, New Jersey in 1996 and currently lives in the U.S. state of New Jersey.n. She has been married for more than 20 years and has been born into a four-member family with one mother and two daughters. -Allylpyrrolidinium up to (trifluoromethanesulfonyl) imide (RTIL P1A3TFSI) as electrolyte. The ready-assembled Li-S battery has superior electrochemical properties regarding specific capacity and cycle stability. [93]

### 5.3 Conclusions

LiPSs are involved in the formation of inorganic layers in the SEIs on Li-Metal in a widely accepted ether-based electrolyte. Li-Metal-Anode with LiF-Li<sub>2</sub>S<sub>x</sub>-rich SEI results in a stable coulombic efficiency of 95% after 233 cycles for a Li-Cu half cell. [91]

Rich polar function groups in the sericin polypeptide chain can interact with mobile ions in the electrolyte, whereby the lithium groups (such as -OH, -COOH and -CO-NH-) can regulate the Li-ion flow near the electrolyte-electrode border area. Anionophile groups (such as -NH<sub>2</sub>) would bind the anions (TFSI -), so that the formation of dendrite Li induced by space can be prevented. This functional li was also used successfully in Li/S batteries. [92]

This innovative system effectively avoids the safety problems associated with the use of metallic lithium anodes and combustible organic liquid electrolytes. The results of the galvanostatic discharge indicate that the initial discharge capacity is 1457 mA h g<sup>-1</sup> at a rate of 0.1 C. [93]



# Chapter 6

## Li-S Electrolytes

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### 6.1 Introduction

Due to its high theoretical capacity (1672 mAh g<sup>-1</sup>), its high energy density (2600 Wh kg<sup>-1</sup>), lithium-sulphur battery could be one of the most promising candidates in the field of modern electrochemistry. However, the deactivation of active substances and the polarization of electrodes by the "shuttle effect" hindered the commercial use of lithium-sulphur batteries. [94]

The Lithium-Sulphur Battery (Li-S) is a promising energy storage technology to replace lithium-ion batteries, leading to a higher energy density and lower cost. The resolution of lithium-polysulfide intermediate products in conventional Li-S-Electrolytes is considered one of the most important technical barriers in the development of the battery. [95]

Li-S batteries are considered promising candidates for the next generation of energy storage devices. However, the formation/resolution of Li-Dendrites and the transport of high-quality polysulphides prevent their practical application. The authors show a highly concentrated electrolyte, 12 M lithium-Bis-Imid (Fluorosulfonyl) salt (LiFSI) in DME solvents. [96]

High-performance solid polymer electrolyte (SPE) has long been sought for the next generation of lithium batteries with high energy density and safe rechargeability. An SPE, consisting of 80% lithium bis-imide (trifluoromethanesulfonyl), 20% poly (ethylene carbonate) (PEC) and a polyamide (PA) fibre membrane backbone, has been produced by solvent casting processes. [97]

LiF-rich SEI layer is formed on Li-Anode to suppress side reactions under the synergistic effect of LiFSI and FEC. Li S @ pPAN cell, which was assembled with the new electrolyte, has relatively low lithium ion transfer resistance, excellent long-term stability and performance. [98]

The sleek redox kinetics of polysulfide intermediates exacerbate the inevitable "shuttle effect", which leads to low sulphur release, rapid capacity loss and anode corrosion. Biological reagents Dithiothreitol (DTT) can be stabilized in the original electrolyte system at room temperature and selectively cut the -S-S-bonds of poly'sulphides. As a result, the hierarchical porous carbon/S-cathode, which uses the electrolyte with 10 g L<sup>-1</sup> DTT, has a high performance and superior cyclic stability. [99]

Lithium hexafluorophosphate (LiPF<sub>6</sub>) and lithium bis (Trifluoromethanesulfonyl) Imid (LiTFSI) are used as li-salt in butyl methylpyrrolidinium bis (BMP-TFSI), ionic liquid electrolyte (IL) for Li / LiFePO<sub>4</sub> cells.

IL-electrolyte is characterised by high thermal stability and non-flammability and is ideal for high safety applications. [100]

LiNO<sub>3</sub> is selected as an electrolyte additive for the Li/S battery. The EFF reaches more than 90% in the 0.4 M LiNO<sub>3</sub> modified electrolyte. The LiS battery has an increased Columbian efficiency, where LiNO<sub>3</sub> electrolyte is added. [101]

A lithium-sulphur battery that combines alternative cathode design and relatively safe, high-conducting electrolyte in a suitable way. The composite cathode is produced by infiltration of sulphur in an N-doped 3D-graphene scaffold. One of the main reasons for the high performance is the low resistance of the electrode/electrolyte interphase, driven by an improved electrode design and a suitable electrolyte. [102]

LiNO<sub>3</sub> is known to improve performance by suppressing the lithium anode by creating an optimized solid electrolyte interphase (SEI) and the associated lithium polysulfide-shuttle effect during the cycle. The authors have found that an electrolyte with 0.1 mol kg<sup>-1</sup> lithiumNO<sub>3</sub> shows the best performance because this electrolyte has the highest conductivity, the lowest viscosity and the lowest glass transition temperature (T<sub>g</sub>). [103]

A novel, high-quality MoS<sub>2</sub>-doped glass ceramic electrolyte Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> (Li<sub>7</sub>P<sub>2.9</sub>S<sub>10.85</sub>Mo<sub>0.01</sub>) was manufactured using a simple combined method of high-energy ball milling and incandescent and has a high ionic conductivity of 4.8 mS cm<sup>-1</sup> at room temperature and a stable wide electrochemical window up to 5 V (v. Li / Li<sup>+</sup>). [104]

Solid-Lithium Battery is considered a next-generation energy storage with high security and energy density, but its low lithium-ion conductivity severely limits its practical application. To solve the above-mentioned problems, the authors report a new superhionic conductive gel electrolyte (SHGP) (2.2 x 10<sup>-3</sup> S cm<sup>-1</sup> at 60 °C) and 0.75 x 10<sup>-3</sup> S cm at 30 °C. Such a highly ionic polymer electrolyte allows a significantly improved specific capacity of 950 mAh g<sup>-1</sup> at 0.2 C. [105]

Solid polymer electrolytes (SPEs) are highly desirable due to their low volatility, high safety and the ability to suppress shuttle effects, for high energy-density lithium-sulphur batteries. A polysiloxane polysiloxane SPE was produced with double-prepared polysulfan copolymer, lithium-bis (trifluoromethanesulfonyl) imid and poly (vinylidene fluoride). [106]

The lithium-sulphur battery is one of the most promising alternative sources of energy. The polysulfide shuttle between anode and cathode induces a low coulombic efficiency, a low sulfur cathode load and a strong reduction in cycle life. Using the appropriate sulphur-electrolyte load in Li-S batteries is an easy method to adjust the shuttle. [107]

Lithium-Sulphur Batteries (LSBs) are a promising next-generation energy storage system that goes beyond state-of-the-art lithium-ion batteries. However, liquid LSBs on an electrolyte basis suffer from a "polysulfide shuttle" and safety concerns created by the use of combustible organic electrolytes. [108]

Low Coulombic Efficiency (CE) during repeated Li-Metal Coating/Stripping greatly limits the practical application of rechargeable Li-S batteries. A new electrolyte system is developed based on a high concentration of LiNO<sub>3</sub> in diglyme (G2) solvent. [109]

LiNO<sub>3</sub> could effectively solve the shuttle problem with polysulfide (PS) in the Li-S battery, but it causes explosive hazards due to the cathode composition such as cannon powder (KNO<sub>3</sub>, sulphur and carbon). A LiNO<sub>3</sub>-free electrolyte was developed to inhibit the PS-Shuttle and lithium-dendrite problem with pure 1,3-dioxolane as a solvent. [110]

Lithium coating/ stripping was investigated under constant current operation with a copper powder electrode in a superconcentrated electrolyte of lithium bis (fluorosulfonyl) amide (LiFSA) with methylphenylamino-di (trifluoroethyl) phosphate (PNMePh) and vinyl carbonate (VC) as additives. The typical Li coating of Cu electrodes in organic electrolytes of conventional lithium batteries is carried out with potentials of several millivolts compared to a Li-metal analogue. [111]

The resolution and diffusion of Li-Polysulfide (LiPS) intermediate products is considered one of the most serious problems for the loss of capacity and the cell failure of lithium-sulphur batteries (Li-S). Hereafter the authors have proposed a failure mechanism of the Li-Metal anode in Li-S cells, based on the mechanistic

investigation of the complex interactions between LiPSs and Li-Metal. [112]

A modified solution method was used to synthesize cubic pomegranate-solid electrolytes  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) and  $\text{Li}_{6.45}\text{Ca}_{0.05}\text{La}_{2.95}\text{Ta}_{0.6}\text{Zr}_{1.4}\text{O}_{12}$ . The synergistic dosing of Ca and Ta induces the formation of cubic LCLZTO with high ionic conductivity. Cells with LCLZTO showed a better cycle performance at 0.2 C and an extremely high coulombic efficiency. [113]

Li-S batteries have recently experienced a significant improvement in gravimetric capacity and cycle performance. However, maintaining a high energy density of batteries depends on the high surface load and high use of active material on the electrode. New problems such as electron and ion transport in thick cathodes, the exhaustion of electrolyte and lithium dendrite growth must be addressed. [114]

Lithium-sulphur batteries are a promising energy storage beyond conventional lithium-ion batteries. The "shuttle-effect" soluble polysulfide is an important barrier between electrodes and leads to rapid loss of capacity. If added to the electrolyte Pyrrol, a protective layer of polypyrrole can be formed at the sulphur cathode. [115]

Li-S cells with a tetraglym (G4) and Li [TFSA] (TFSA: up to (trifluoromethane sulfonyl) amide electrolyte (SIL)) The sulphur cathode (S-cathode) consists of sulphur, carbon powder and a polymer binder. Poly (ethylene oxide) and poly (vinyl alcohol) (PVA-x) are used as binders for composite cathodes with different densities (x%). [116]

The advantages of fluoroethylene carbonate (FEC)-based electrolyte solution (1 M LiPF<sub>6</sub> in FEC/dimethylcarbonate) compared to ethylene carbonate. The formation of solid electrolyte interphase (SEI) on the surface of the cyclic S/C electrodes was demonstrated by scanning electron microscopy. [117]

However, the low ionic conductivity of the existing SPE limits battery power at room temperature. A novel SPE film was produced that uses strength in food quality as a host. [118]

The operation of a lithium-sulphur battery (Li-S) includes the transport of Li<sup>+</sup> ions and soluble sulphides mostly in the form of dissolved ions. The authors present molecular simulations to determine the resolution parameters of electrolytes and sulphides in two different electrolyte systems: LiTFSI in DOL / DME and LiPF<sub>6</sub>. [119]

The coulombic efficiency of lithium coating/de-insulation approaches 98.1%. The excellent electrochemical properties are attributed to the elastic and robust solid electrolyte intermediate phases both at the sulphur composite cathode and at the lithium-metal anode. [120]

The discharge and charging mechanisms of the Li-S battery include the formation of soluble lithium polysulfide species that can diffuse through the battery and cause problems related to capacity loss and poor coulombic efficiency. The BPD additive increases the capacity reserve of lithium-sulphur batteries. [121]

The main components that give rise to safety concerns are the volatile organic electrolytes and the dendrites forming lithium-metal electrodes. The essential understanding of the lithiation/delimitation process as well as the SEI layer formation of alloy anodes in combination with IL-electrolytes at room temperature is considered an approach for safer Li batteries. [122]

## 6.2 Literature Reviews

### 6.2.1 Electrolytes for lithium sulfur batteries

LiSBs have a theoretical capacity of 1672 mAh g<sup>-1</sup> and a six times higher specific energy density than conventional lithium-ion batteries. LiSBs are abundant in nature, cheap, non-toxic and environmentally friendly, making them one of the most promising rechargeable batteries currently being developed [11]. The commercial use of lithium-ion batteries is still hampered by several intrinsic problems arising from the sulphur and complex chemical reaction. Electrolyte is an important component of the battery and influences the boundary reaction and the safety of the cell. In recent years, two basic types of electrolyte systems have been investigated: due to the reaction nucleophilic addition and substitution between reduced sulphur species and

carbonate esters, conventional carbonate solvent in lithium-ion batteries is usually not suitable for LiSBs. Recent research on LiSBs in recent years has promoted the dynamic development of electrolytes. The authors focus on the comprehensive review of the latest electrolytic research. The authors highlight the ion transfer mechanism and the electrode-electrolyte border surface architecture as well as the synergy effect between and between the solvents, lithium salts and additives in the liquid electrolyte. [94]

### 6.2.2 High capacity lithium-sulfur batteries at low electrolyte/sulfur ratio

Li-S batteries are considered to be promising energy storage for the next generation. Due to their high theoretical energy density and the use of cost-effective, naturally abundant and non-toxic sulfur cathodes, they have gained increasing attention in recent years. Despite their advantages, applications remain hampered by critical performance losses such as low practical energy density, low coulombic efficiency and rapid capacity reduction. Highly developed carbon-sulphur composite cathodes (C-S) help to capture the active materials within the porous carbon matrix. However, this approach does not solve the problems per se, especially in the resolution and diffusion of lithium polysulphides from the cathode, which is inevitable in liquid electrolytes. Parallel to the development of highly developed sulfur cathodes, further approaches have been developed to reduce the loss of polyethyl sulfide effectively and lead to improved cycle performance. Li-S batteries can be significantly influenced by many parameters such as sulphur content / surface load in the cathode, electrolyte quantity, lithium excess and cycle rate. In order to achieve a high energy density, both the sulphur loads and the solubility use should be as high as possible [26] Unfortunately, compared to conventional LIBs, much more electrolyte is needed, which significantly reduces their practical energy density. Recently, the authors reported on a novel functioning electrolyte system that uses dimethyl disulfide as a co-solvent to promote an alternative electrochemical reaction pathway for sulfur cathodes by forming dimethyl polysulfide (DMPS) and lithium organosulfide as new redox intermediates and increasing the capacity of Li-S cells. [95]

### 6.2.3 Li-S battery interphase - a new generation of Li-S batteries

Highly developed energy storage with high energy density, long lifetime and low cost are key solutions for our future energy needs. Li-S batteries with much higher energy density due to the conversion reaction of Li-Metal and S have attracted great attention. However, two essential barriers associated with the nature of Li-S chemistry still hamper their practical application: (1) Li-Dendrite growth, which not only triggers irreversible electrolyte consumption but also raises safety concerns. Due to the relatively lower reactivity of ether on Li-Metal, ether-based electrolytes with high salt concentration have been studied extensively for Li-S batteries. However, a high CE and / or free Li-Dendrite can only be achieved with low power density. Innovative electrolytes based on lithium bis (trifluoromethanesulfonyl) -Imid (LiTFSI) with high ion strength should effectively suppress the resolution and migration of polysulphide species. It remains a great challenge to identify an electrolyte that can overcome the polysulphide-shuttle reaction on the cathode side and Li-dendrite on the anode side without sacrificing the capacity utilization of the S-cathode [13] Compared to strategies of nanostructure development, rational design and optimization of electrolytes offer a more economical and practical approach. The authors formulate a simple electrolyte system that uses a high concentration of LiFSI in dimethoxyether (DME) without additives such as LiNO<sub>3</sub> and/or other co-solvents. [96]

### 6.2.4 Poly(ethylene carbonate)-based electrolytes with high concentration Li salt

Lithium-ion batteries with increased energy density have great commercial success as a leading power source for mobile electronic devices, electric vehicles and intelligent power grids. There are challenging problems such as the expansion of silicon volume, the formation of Li-Dendrites and the dissolution of transition metals from cathode. The use of solid electrolytes is considered one of the most promising methods for solving the above-mentioned problems. Solid polymer electrolytes (SPE) attracted a lot of attention. The vast majority of the Li-ion leading SPE is based on polyethylene, in particular poly (ethylene oxide) (PEO). These challenges

have so far restricted the practical use of SPE. Researchers have recently begun to investigate polyethylene carbonate (PEC) as an alternative host material. The highly concentrated LiTFSI-PEC electrolyte with good wetting capacity compared to porous electrodes allows for an even distribution of the Li<sup>+</sup> flow, thus having a positive effect on the suppression of lithium dendrite growth and the improvement of battery cycle performance. LiFePO<sub>4</sub> Li-solid batteries with the optimized solid-state electrolytes showed an excellent cycle performance. Remarkable performance is due to the high  $\kappa$  and the excellent ability to wet porous electrodes (20PEC-80LiTFSI). [97]

### 6.2.5 Carbonate electrolyte with lithium anode for high performance lithium sulfur battery

The rapid development of electric vehicles, unmanned aircraft and others urgently requires rechargeable batteries with high energy density. The state-of-the-art lithium (Li) ion batteries (LIBs) can only have volumetric and gravimetric energy densities of up to 770 Wh L<sup>-1</sup> and 260 Wh kg<sup>-1</sup>. Li-metal batteries (LMBs) are considered a promising choice due to the extremely high theoretical specific capacity of the Li-Anode (3860 mAh g<sup>-1</sup>) and the very low potential (3.040 V vs. SHE). Efforts have been made to address these problems, including the use of solid-state electrolytes [8,9], Li-surface modification [10,11] and electrolyte optimization by special additives [6,12] and ionic liquid [15]. The protection of the lithium metal electrode on site by the improved electrolyte systems is making continuous progress. Li[N(SO<sub>2</sub>F)<sub>2</sub>] (LiFSI) is a promising alternative to lithium salt due to its good compatibility with Li-Metal. FEC has been extensively studied as an effective electrolyte additive to facilitate the formation of a stable SEI layer on Li-Metal and silicon-containing anodes [6,27-29]. FEC-based organic carbonate solution with LiPF<sub>6</sub> has been investigated at Li/Li-cells and LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub> (NMC) cells. A new 1 M LiFSI electrolyte has been developed, which is dissolved in the carbonate solvents EMC / FEC (70 / 30, v / v) for LMBs. It is confirmed that it can suppress lithium dendrites and effectively improve coulombic efficiency. [98]

### 6.2.6 Dithiothreitol as a promising electrolyte additive

Recently, rechargeable lithium-sulphur batteries (Li-S) were considered one of the most promising candidates in the field of lithium-ion batteries. The practical application of Li-S batteries still has to deal with a number of challenges, especially: slow conductivity of S and discharge products (Li<sub>2</sub>S<sub>2</sub> and Li<sub>2</sub>S). Li-S batteries are based on a multi-stage fixed reaction ( $16\text{Li} + \text{S}_8 \rightarrow 8\text{Li}_2\text{S}$ ) via LiPSs as intermediate products. The flow of polysulphides is not only due to the thermodynamical unavoidable diffusion in the electrolytes, but also to the slow reaction kinetics. Therefore, the increase of the conversion rate of LiPSs will become solid Li<sub>2</sub>S<sub>2</sub>/LiS and vice versa to a fashionable strategy to suppress the "Shuttle effect" in Li-S batteries fields. Biological reagents such as vitamin C (VC), glutathione (G-SH) and dithiothreitol (DTT) are often used as effective reducing agents to cut the -S-S- bonds at room temperature quickly and effectively into disulfides. Compared to conventional materials, biological reagents may be an ideal candidate for resolving the problem of chemical bonding due to their superior performance under mild reaction conditions. The DTT introduced in the electrolyte can quickly eliminate the accumulation of LiPSs by the reaction of cutting the -S-S-bonds. Due to the special functionality, the electrolyte with DTT allows the hierarchical porous carbon (HPC) / S-cathode to have a high initial discharge capacity of 808 and 594 mAh g<sup>-1</sup>. [99]

### 6.2.7 Electrochemical performance of rechargeable Li/LiFePO<sub>4</sub> cells

Lithium (Li) batteries are the most promising option for next-generation hybrid and electric vehicles. They are considered for the net second energy storage of renewable wind and solar energy. Organic electrolytes, which are typically used in Li batteries, are responsible for the major safety problems, as they have poor thermal stability, high flammability and low heat capacity. Due to their volatility and toxicity, these electrolytes are also potential environmental hazards. Ionic liquids (ILs) are promising for use as electrolytes for Li batteries.

ILs are characterized as task-specific electrolytes that can give Li batteries the desired functionality. The limitation of the IL-electrolyte is the relatively high viscosity compared to conventional organic electrolyte. Recently Castiglione et al. [17] found a significant improvement in Li<sup>+</sup> mobility in IL at rising temperatures. Li / LiFePO<sub>4</sub> cells are evaluated with BMP-TFSI-based IL-electrolytes. Two types of Li-Salts, LiPF<sub>6</sub> and LiTFSI, are used and the resulting battery properties are compared, varying the concentration of the latter salt from 0.1 M to 1.0 M to modify the physical and chemical properties of the IL-electrolyte. [100]

### 6.2.8 Improved cycling performance of lithium sulfur batteries with LiNO<sub>3</sub>-modified electrolyte

Lithium-sulphur redox pair is one of the most promising candidates for the high theoretical capacity of sulphur and lithium, which corresponds to 1675 [1] and 3680 mAh g<sup>-1</sup> [2]. Despite these advantages, there are still many problems to overcome for practical applications. The use of Li-electrode is still difficult due to its low cycle efficiency and harmful dendritic morphology of the deposited Li. In this study, the electrolyte was added as a supplement to LiNO<sub>3</sub>. In the modified electrolyte, an improved cycle performance of the lithium-sulphur battery was achieved. The composition of the lithium protection film was analyzed by X-ray photon spectroscopy (XPS). [101]

### 6.2.9 Lithium sulfur battery using material design and electrolyte chemistry

The lithium-sulphur battery has a theoretical energy density of about 3600 Wh kg<sup>-1</sup>. However, this interesting system has several disadvantages, such as the insulator character of sulphur. The installation of sulphur in conductive carbon-containing matrices has been fully investigated to ensure high current rates and to reduce the resolution of polysulfide during the cycle. The nitrogen storage in graphene foam has been proven to limit the shuttle effect due to the adsorption of polysulfides via the carbon surface by pyridinic and pyrrole function groups. A composite cathode consisting of elementary sulphur in a 3D matrix of N-doped graphene (3DNG-S) [39,40] and electrolyte solution that combines DEGDME solvent with LiTFSI and LiNO<sub>3</sub> salts, both in concentration of 1 mol kg<sup>-1</sup>. [102]

### 6.2.10 Optimising the concentration of LiNO<sub>3</sub> additive in C<sub>4</sub>mpyr-TFS

The solubility of polysulfide intermediates leads to a permanent loss of sulphur as an active redox species from the cathode during the cycle. In addition, the formation of dendrites during the secretion of lithium, which depends on the electrolyte composition, leads to safety problems in lithium batteries. Mikhaylik of Sion Power Corp. has patented a process that uses N-O bonds containing additives in the electrolyte to suppress the PS-Shuttle effect. Kim et al. [1] showed that while LiNO<sub>3</sub> suppresses the polysulfide-shuttle effect, the ion conductivity of the electrolyte decreases due to increased viscosity, indicating an optimal amount of 0.2 M LiNO<sub>3</sub> in a tetraethylene glycol-dimethylether electrolyte solution. LiNO<sub>3</sub> can suppress the redox skin of lithium polysulfides and stabilise lithium metal surfaces against harmful morphological changes during the cycle. The authors have investigated the SEI layer properties of lithium metal anode and the performance of Li-S batteries containing electrolytes based on the ionic liquid 1-butyl-1-methylpyrrolidinium to (trifluoromethanesulfonyl) imide (C<sub>4</sub>mpyr-TFSI). [103]

### 6.2.11 Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> glass-ceramic electrolyte

Lithium-ion batteries (LIBs) are becoming "king" in the field of electrochemical energy storage. However, a cloud hangs over the prosperity of the LIB business. Full-body lithium-ion batteries are one of the most promising candidates for LIBs of the next generation. Inorganic sulfide solid electrolytes have a high ion conductivity of more than 1 mS cm<sup>-1</sup> at room temperature and a large electrochemical window of up to 5 V compared to Li/Li<sup>+</sup>. Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> as metastatic phase has a high conductivity of up to

3.2 mScm<sup>-1</sup>. Kato et al. recently reported a superior conductor with exceptionally high ion conductivity (25 mScm<sup>-1</sup> for Li<sub>9.54</sub>Si<sub>1.74</sub>P<sub>1.44</sub>S<sub>11.3</sub>). The ionic conductivity of sulfide electrolytes can be improved by substitution. Huang et al. reported a 70Li<sub>2</sub>S-30P<sub>2</sub>S<sub>5</sub> system with Li<sub>3</sub>PO<sub>4</sub> substitution. Your glass ceramic with 1 mol% Li<sub>3</sub>PO<sub>4</sub> substitution showed a high conductivity. Li<sub>3</sub>PS<sub>4</sub> with LiI dosage was increased to 0.63 mS cm<sup>-1</sup>. The study provides a reference for the construction of high-performance electrolytes for solid Li-S batteries. High ion conductivity and good chemical stability compared to lithium metal are demonstrated in this Li<sub>7</sub>P<sub>2.9</sub>S<sub>10.85</sub>Mo<sub>0.01</sub> system. [104]

### 6.2.12 High ionic conductive gel polymer electrolyte

Solid-Lithium batteries are considered energy storage for the next generation due to their high safety, high energy density and excellent stability. Liquid organic electrolytes are often used for lithium-ion batteries (LIBs), however, LIBs that are operated with liquid electrolyte are faced with serious security concerns, such as material defects, electrolyte discharges and combustion due to intrinsic liquidity, inflammatoriness and electrochemical instability. Solid-Ceramics / Polymer Electrolyte [8] is recognised as a rational replacement to offer one of the most promising approaches to resist Li-Metal leaks and improve safety. Gel polymer electrolyte consisting of polymer matrix, where the liquid electrolyte is trapped, has a high ion conductivity and easy manufacturing capacity. Some common polymers such as poly (ethylene oxide) (PEO) and poly (acrylonitrile) could be used as matrices for GPE. PETO polymers as linear homopolymer is a host material for the production of GPEs promising. "Quasi-solids" -Li-S batteries (such as gel batteries) have been developed, whose electrolytes have hybrid properties and combine polymers with liquid electrolytes. Liquid electrolytes could well be encapsulated into the GPE, which resulted in a high ionic conductivity and a good affinity for electrodes. Furthermore, the polymer matrix could effectively prevent the discharge of liquid electrolytes and thus improve the safety of the battery. [105]

### 6.2.13 Dendrite-free Li metal deposition in all-solid-state lithium sulfur batteries

A lithium-sulphur battery (Li-S) has a high theoretical capacity (1672 mAh g<sup>-1</sup>) and energy density (2600 Wh kg<sup>-1</sup>), with additional advantages such as natural abundance, low cost and non-toxicity. Despite its advantages, practical applications were limited by the low electrical conductivity of sulphur, the notorious shuttle effect and safety problems due to the resolution of polysulphides in liquid electrolytes and the formation of lithium-dendrites. Polysiloxane electrolyte has superior thermal and electrochemical stability, but low ion conductivity and poor mechanical properties at ambient temperature. The ion conductivity of polysiloxane electrolytes can be improved by the molecular structure design of the polymer matrix. The Si-H bond has a high reactivity with C = C double bonding, allowing the cyclic propylene carbonate or ethylene oxide chain segment to be conveniently linked by block copolymerisation [20] with polymer molecules, whereby processes can be refined [21,22]. In this work the authors have produced a polymer-in-salt SPE membrane with the electrolyte polysiloxane (BPSO), lithium bis (trifluoromethanesulfonyl) imid (LiTFSI) and poly (Vinylidene fluoride) (PVDF). The CPE membranes have satisfactory ionic conductivity and mechanical properties, but can also block the growth of lithium dendrites and the resolution of polysulphides. [106]

### 6.2.14 Polysulfide shuttle control

The enormous consumption of fossil fuels leads to a rapid reduction of their durability and increasing pollution. High-capacity energy storage is highly desirable to meet the needs of electric vehicles and the use of renewable energies such as solar or wind energy. Li-S batteries have a gravimetric energy density equal to or 2-3 times as high as Li-Ion batteries. The practical use of Li/S batteries is severely hampered by some persistent problems, including (1) sulphur and discharge products (Li<sub>2</sub>S<sub>2</sub> and / or Li<sub>2</sub>S), which have a low electrical conductivity and impair the battery's reaction speed. (2) LiS and other insoluble compounds are produced during the cycle and cover the active compounds, thereby inhibiting the access of lithium ions and

degrading the conductive network. (3) The highly soluble polysulfide can penetrate through the separator to the negative lithium electrode where it is reduced to insoluble  $\text{LiS}_2$ . Highly developed composite cathodes with excellent conductivity, robust electron/ion signal path as well as superior reversible discharge capacity and cycle performance are emerging from conductive nanocarbons. So far, the question of how to stop the shuttle from polysulphides is still a key theme to maintain Li-S cells with superior Li-storage performance. This article examined the fit between CNT @ S cathode and electrolyte. The reason why the authors have selected the cathode with excellent Li-ion storage power is that the CNTs were produced in series with relatively high electrical conductivity, adjustable pore size distribution and robust equipment by chemical vortex vapour deposition. [107]

### 6.2.15 Flexible electrolyte-cathode bilayer framework with stabilized interface

Lithium-sulphur batteries (Li-S batteries) have gained attention as a promising energy storage system for electric vehicles. However, the practical use of Li-S batteries is severely impeded by the continuous capacity decline due to the shuttle effect of soluble discharge intermediate "polysulfides" in liquid electrolytes. The replacement of liquid electrolytes by solid electrolytes has been considered as an alternative approach to solving these problems. In order to enable the operation of Li-S batteries at room temperature with fixed electrolytes, it is essential to provide an electronically conductive skeleton for the S-load within the cathode. S-cathodes with reduced graphene oxide and soot have been researched to improve electrical conductivity in ASSLSBs. A composite frame consisting of two layers, consisting of a one-dimensional (1D)  $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$  (LLTO) ceramic nanofibre/poly (ethylene oxide) (PEO) composite electrolyte coupled to a 3D flexible carbon nanofibre/sulphur (CNF/S) cathode. This two-layer structure can be placed on the top of the anode surface to form a complete Li-S cell without the use of additional electrolytes or separation layer. [108]

### 6.2.16 Long term stability of Li-S batteries using high concentration lithium nitrate electrolytes

The surface layer (passivation layer) is formed by reactions between Li-Metal and Electrolyte. An ideal SEI should limit or prevent further reactions of the electrolyte and Li-Metal-Dendrite growth at the Li-Top. SEIs, which are formed in most liquid electrolytes, tend to break during repeated electrochemical cycles.  $\text{LiNO}_3$  is essential for preventing the polysulphide shell in Li-metal anodes and Li-S batteries. The use of electrolytes with high salt concentrations is a promising means of significantly extending the life of Li-S batteries. Electrolytes without  $\text{LiNO}_3$  do not contain  $\text{Li}_2\text{O}$  as a SEI component. [109]

### 6.2.17 $\text{LiNO}_3$ -free electrolyte for Li-S battery

The renewed interest in lithium-sulphur batteries (Li-S) in recent years is a response to the search for battery systems with higher energy density than the conventional Li-Ion batteries. The Li-S battery could theoretically deliver an energy density of  $2600 \text{ Wh kg}^{-1}$  and achieve in reality at extremely low material costs over  $500 \text{ Wh}^{-1}$ . A major disadvantage is the solubility of the long-chain polysulphide ( $\text{S}_n$ ,  $n \geq 4$ ), which forms at the cathode by reducing the pure sulphur or oxidation of short-chain polysulphide. The drowning of polysulfide causes adverse side reactions with Li-Anodes and commutes between anode and cathode, resulting in low current efficiency and battery failure. Various ways have been studied to suppress the shuttle of polysulfide, such as including sulphur in porous carbon [2-9], to use new binders [10-14] or to add a Li + leading layer to the separators [15,16] or cathode [17,18]. Such approaches generally increase the complexity and cost of cell production, however, did not yet lead to satisfactory performance improvements. The PS-Shuttle effect is closely related to the composition of the electrolyte used. The ideal Li-S-Electrolyte should have good Li + conductivity, low PS permeability and high chemical stability with lithium anode. Researchers have developed novel electrolytes with different solvents (DOL / DME, DME, THF, PC, TMS, EMS) and salts ( $\text{LiTFSI}$ ,  $\text{LiNO}_3$ ).  $\text{LiNO}_3$  could help to build a stable SEI on the lithium surface and achieve an efficiency of over 99%. However,

the NO<sub>3</sub> group would gradually become exhausted while cycling and the dangerous cathode composition would be passed along similar to the Black Gun Powder (wood charcoal, sulphur and potassium nitrate). The PSK decreases with the increase in molecular weight and the C: O ratio. However, the conductivity of the Li<sup>+</sup> ions would decrease accordingly, which is a paradox that impedes the development of Li-S-electrolytes. Pure DOL reduced the sulphur consumption by almost half compared to the DME / DOL-binary system. The DOL solvent is known for its compatibility with lithium, which inhibits the formation of lithium dendrites and can protect lithium by a thin layer of the membrane formed by ring-opening polymerisation [54,55]. The cathode-S content is  $3.0 \pm 0.1 \text{ mg cm}^{-2}$ . [110]

### 6.2.18 Lithium stripping in super-concentrated electrolyte

Lithium dendrites lead to the short-circuiting of a cell, resulting in vapour and combustion of the organic electrolyte. In order to suppress the growth of Li-Dendrite Li, many techniques have been proposed. Also, the mechanism of dendrite growth needs to be fundamentally elucidated. [111]

### 6.2.19 Lithium metal protection through in-situ formed solid electrolyte interphase

Lithium-sulphur batteries (Li-S batteries) with a high theoretical energy density of  $2600 \text{ Wh kg}^{-1}$  are considered an attractive alternative. Li-S batteries also have the outstanding advantages of high natural frequency, low cost and non-toxicity of sulphur for mass applications. The intrinsic insulating effect of sulphur and the final discharge product (Li<sub>2</sub>S) leads to a low use of active materials in electrochemical reactions. The shuttle effect and the parasitic reaction of Li-polysulfide (LiPS) between anode and cathode lead to a severe loss of capacity and a poor life of a complete Li-S cell. The formation of Li-Dendrites causes low energy efficiency and dangerous safety problems. Most tests were carried out with a sulphur load of less than 70% and an area density of less than  $2.0 \text{ mg cm}^{-2}$ . A dramatic increase in the lipid concentration in the electrolyte results in rapid capacity reduction and a low coulombic efficiency. If the defective cell is adjusted, the glossy Li-metal anode becomes dark and the cell is almost dry. Problems with dendrites in Li-S batteries are more serious and more complicated due to the LiPS-based chemistry of electron transformation [61] LiPS-intermediate products are considered a two-edged sword. The study of the positive role of LiPSs in the Li-Metal anode is crucial to suppress dendrite growth on the anodised side. In a functioning Li-S cell there is always continuous composition and concentration fluctuations of the LiPSs during the charging/discharge cycle. The role of polysulphide on the Li-Metalanode is very difficult to identify in a real battery. The authors found that the electrolyte with a sulphur concentration of 0.10 M produced an unprecedented dendrite-free morphology, exceptional coulomb efficiency and superior long-term stability. [112]

### 6.2.20 Synthesis of Ta and Ca doped Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>

The lithium-sulphur battery (Li-S) is considered to be one of the most promising rechargeable battery systems due to its high theoretical specific energy (about  $2600 \text{ Wh kg}^{-1}$ ). Sulphur elements are inexpensive, environmentally friendly and abundant in the earth's crust and have a great potential in industrial application. The shuttle effect due to long chain polysulfide is the focus of research on Li-S batteries. Two approaches are usually used to solve the problem: the other is to protect the Li-Anode by protecting layers of electrolytes from contact with polysulfide. The use of Li<sup>+</sup> conductive solid electrolytes in the Li-S system offers a promising solution to the problem of the shuttle effect. Based on the "all-solid state" concept, great efforts have been made to integrate solid electrolyte into lithium-sulfur batteries [17]. Li-S batteries with hybrid electrolytes were used. Liquid electrolytes ensure fast kinetics of ion transport, while the solid-state electrolyte serves as a rigid barrier to the separation of electrodes and block polysulphides. In numerous studies it has been reported that solid-state electrolytes of type LISICON and NASICON are imported into Li-S batteries. Among the ceramic-based solid-body electrolytes, garnet compounds based on Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) have proven to be the most promising Li<sup>+</sup> conductor due to their considerable ionic conductivity of more than  $10^{-4} \text{ S cm}^{-1}$

- 1 at room temperature. Solid body reaction and wet chemical process are two main approaches to the synthesis of LZO. Solid body reaction is due to its simple synthesis procedures the most commonly used method, but also has some drawbacks such as high sinter temperature and long heating times (e.g. 36 h). The recent report on a modified solution method offers a new way to obtain LLZO effectively without the development of toxic NO<sub>x</sub> gas from nitrogen precursors [44]. The solution method has been used successfully in the LLZO synthesis [41,44]. It is generally reported that two approaches achieve a high ion conductivity in the LZO: one approach is to obtain with the group Ia-3d a cubic phase that is much more conductive than a tetragonal phase with room I41/acd; the other approach is to partially reduce the Li content or increase the gaps in Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>. It is an effective method to reduce the Li content by replacing Zr<sup>4+</sup> with higher valence cations. The solid electrolyte is also used in Li-S cells based on the "hybrid-electrolyt" concept. The velocity and cycle performance of the cell with sulfur cathode and LCLTZO as electrolyte and "separator" was used to compare with conventional cells without LCLZO. [113]

### 6.2.21 Li-S batteries with high cathode and electrolyte reservoirs

The Li-S battery has proven to be one of the most promising candidates due to its high theoretical capacity of 1675 mA h g<sup>-1</sup> and its high sulphur content. Despite these advantages, the practical application is still hampered by the low level of solubility, the low coulombic efficiency and the strong loss of capacity when cycling. Carbon-containing materials enable Li-S batteries to have a high specific capacity (1500 mA h g<sup>-1</sup>) and long cycle stability (0.050% capacity to fade per cycle). Unfortunately, the improvement of specific capacity and cycle performance sacrifice the energy density. Also the high surface sulphur load of more than 5 mg cm<sup>-2</sup> is indispensable for the marketing of Li-S batteries. The thickness of the sulphur cathode will also be increased sufficiently. According to previous reports, the electrolytic wetting/penetration is the most important challenge in order to achieve high sulphur loss. The high costs and complex manufacturing processes will be the hurdles for their industrial production. High sulphur loading cathode with optimized microstructure and commercially available carbon materials is desirable for Li-S batteries with high energy density. Lithium metal anode shows strong reactivity with the solvent in the electrolyte under high lips concentration, which would consume electrolyte continuously, which would lead to an accelerated Li-Dendrit growth. This negligible problem in cells with low surface sulphur load was intensified under the increased surface capacity, which could end the life of the cell. Li-S batteries offer a high surface capacity and stable cycle performance. Cell components - cathode and intermediate layer - are designed to solve the chronic problems when attempting to produce practical "high-energy" cells. In the cathode MPC, SP and G, which are separated as sulfur wood, lead material or block layer, are integrated into the hierarchically porous microstructure. Glass fibre membrane, which is placed between separator and cathode as an intermediate layer, absorbs the electrolyte and remains wet during the cycle. [114]

### 6.2.22 Pyrrole as electrolyte additive to trap polysulfides

Lithium-Sulphur Batteries (LSB) are widely regarded as one of the most promising candidates for next generation energy storage (2600 Wh kg<sup>-1</sup>). The practical application of LSB is still hampered by a number of defects, including poor cycle life, enormous capacity failures and power losses [6,7]. Rapid capacity reduction at LSB is closely related to the "Shuttle effect" of soluble polysulphide intermediate products. Nanostructured cathodes [6,10-13], modified separators or intermediate layers [8,14-17], protected anodes [18-22] and highly developed electrolyte [7,23,24] could limit soluble polyasulphide. Lithium nitrate (LiNO<sub>3</sub>) was widely used as an additive in ether-based electrolyte for LSB because it reacts with metallic lithium to a surface-passive film that acts as a physical shielding for the protection of the lithium anode. However, LiNO<sub>3</sub> can be irreversibly reduced on the carbon surface with potentials less than 1.6 V. Polypyrrole (PPy) was formed during the loading/discharge process by electrochemical oxidative polymerization method as a surface protection layer on the sulphur cathode. PPy has a good conductivity and stability that can act as a directing agent, absorbent or

barrier layer. [115]

### 6.2.23 Effects of polymer binders on discharge and charge reactions of lithium-sulfur

Li-S batteries attract a lot of attention as the next generation energy storage. The theoretical energy density is very high due to the high theoretical capacity of a Li-Anode (3860 mAh g<sup>-1</sup>) and a S-cathode. One problem that prevents practical use is the dissolution of the cathode in the liquid electrolytes during discharge and charge reactions. The dissolved Li<sub>2</sub>S acts as a redox shuttle between cathode and anode in the cell, and this shuttle effect causes the low coulombic efficiency in unloading and charging. Glyce-li-salt complexes can be used as thermally stable electrolytes for lithium batteries. Glyce have a strong solvent for Li<sup>+</sup> ions and form relatively long-lived (stable) solvents with Li<sup>+</sup> ions in certain molar ratios, [Li (Glyme) x] x + [33-38] Triglyme (G3) and tetraglyme, which form low melting complexes with Li [TFSA] in a ratio of 1: 1 M. The S-cathode consists of S (active material), carbon powder (conductor) and a polymer binder. The ion transport takes place during the electrochemical reaction of S in the pores. In the porous composite cathode, the binder connects the carbon particles to an electron line network. [116]

### 6.2.24 Fluoroethylene carbonate as a component in organic carbonate electrolyte solutions

Lithium-sulphur batteries have attracted considerable attention due to a high theoretical specific capacity of sulphur cathodes (1672 mAh g<sup>-1</sup>). Most often, essential electrolyte solutions such as 1,3-dioxolane (DOX) and dimethylether (DME) are used for Li-S batteries. This high capacity is related to the ability of sulfur atoms to absorb two electrons, resulting in the conversion of elemental sulphur into lithium sulfide (Li<sub>2</sub>S). The use of FEC-based electrolyte solutions for Li-S cells can promote the development of sulphur lithium silicon batteries [20,21] FEC is a crucial component of electrolyte solutions in which Si-Anodes function very well due to the formation of more effective films on Si-Anodes [18,19] [117]

### 6.2.25 Unique starch polymer electrolyte for high capacity all-solid-state lithium sulfur batteries

Lithium batteries with high energy and long service life are the central energy source technology for new energy vehicles. The power of batteries strongly depends on the lithium-ion conductivity of the electrolyte. The best way is to construct solid electrolytes using natural products that are comparable to or exceed today's materials. Solid polymer electrolytes (SPEs) have the flexible properties that enable different designs for batteries while improving energy performance at a high level of safety. The general improvement of the ion conductivity of SPE is largely based on a modification of the polyethylene oxide electrolyte (PEO). PEO, consisting of functional groups of aether oxygen (-C-O-C), can dissolve lithium salts and provide ways for lithium ion transport. Starch, a form of energy storage in plants, is the largest percentage of carbohydrates in the human diet and is found in significant amounts in basic foods such as potatoes, wheat, maize and rice. Starch consists of repeated glucose monomers that are associated with glycosidic compounds and form a stable helix structure that would allow the reversible transport of ions. [118]

### 6.2.26 Molecular modeling of electrolyte and polysulfide ions for lithium-sulphur batteries

Lithium-Sulphur-Akkus (Li-S) promises a high theoretical capacity of 1670 mAh g<sup>-1</sup>. A typical Li-S battery consists of an anode of lithium foil and a composite cathode composed of a porous, sulphur-impregnated carbon economy. The carbon economy ensures electronic conductivity [4] and structural integrity. The pore size distribution of the porous cathode host controls the sulphur infiltration during cathode production and determines which pore sizes are filled with sulphur. It is expected that this will be repeated during the battery

cycle, during which not every type can be formed in pores that do not match its size. In Li-S batteries, the Li<sup>+</sup> ion transport is the first necessary stage for the formation of lithium sulfides during discharge. Similarly, the "shutting" of polysulfides depends on the ion concentration of the electrolyte and sulfide solution, which would affect the viscosity of the solution. For Li-S batteries, a continuous ion transport model was recommended, which takes into account pore size distribution and as input data requires the size (minimum and maximum dimensions) of electrolyte and polysulphide ions in a desolated and dissolved form and their desolating energy [8]. A common electrolyte in Li-S batteries is LiTFSI in DOL / DME solvent mixture (DOL: Dioxolan; DME: Dimethoxyethane) LiPF<sub>6</sub> in EC / DMC (EC: Ethylene carbonate; DMC: Dimethylcarbonate), in which the high dielectric content in LiPF<sub>6</sub> in EC / DMC (EC: Ethylene carbonate; DMC: Dimethylethylethylcarbonate) For polysulphide in Li-S batteries, there is no such data, and the current study is dedicated to this. EDF is based on spherical dissolved ions, which is usually not the case, especially with polysulfides. Markoulidis et al.'s continuum model showed a good consistency between predictions of the capacity of super capacitors and experimental data. It is generally known that the dissolved PF<sub>6</sub><sup>-</sup> ion in organic solvents can be easily desolated. Binding energies between Li<sup>+</sup> TFSI<sup>-</sup> and S<sub>8</sub><sup>2-</sup> with DME were determined using the polarizable continuum model with - 4.60, - 1.79 and - 5.85 eV. The study includes a series of molecular simulations to determine the number of coordinations as well as the geometrically optimized model and the dimensions. Two electrolytes were used: LiTFSI in DOL/DME and LiPF<sub>6</sub> in EC/DMC. No chemical reactions were considered in the electrolyte solution. [119]

### 6.2.27 Lithium sulfur batteries with compatible electrolyte

Lithium-Sulphur Batteries (Li-S) are considered one of the most promising candidates for next generation electrochemical energy storage. Li-S batteries have many overwhelming advantages over other competitors. The theoretical capacity of sulphur reaches 1672 mAh g<sup>-1</sup>, which in combination with lithium (Li) metal anodes leads to an energy density of 2600 Wh kg<sup>-1</sup>. The construction pattern of the sulphur cathode consists of encapsulating sulphur in a guide material by heat treatment or liquid phase coating. Complex sulphur-carbon-material synthesis and expensive cathode processes represent a major challenge for the practical application of Li-S batteries. The conductive network and absorption site are easily blocked by Lips when it comes to high-loadable and dense sulphur electrodes. Fortunately, a category of sulphur materials, including sulfurised pyrolyzed poly (Acrylonitrile) (S @ pPAN), has good compatibility with conventional carbonate solvents. Li-metal reacts with electrolytes and forms a solid electrode intermediate phase (SEI) on the Li-surface when it is immersed in liquid electrolytes. An ideal SEI would inhibit the further Li-corrosion and suppress the formation of Li-dendrites. The LiF-rich SEI layer was developed by LiF (30% LiF in electrolyte) and the in-situ lithion of fluorinated compounds. In view of the positive effect of fluorine, the conventional film-forming solvent EC was replaced by FEC to reword a new electrolyte 1 M LiPF<sub>6</sub> / FEC-DMC (1: 1, v / v). Here the authors have used this FEC-based electrolyte in Li-S cells and Li Li, Li Li Cu half cells and demonstrated its excellent compatibility with both sulphur composite cathode and Li-metal anode. [120]

### 6.2.28 Thiol-based electrolyte additives

The lithium-sulphur batteries (Li-S) have a theoretical capacity of 1672 mAh g<sup>-1</sup>, which is more than 5 times higher than LiCoO<sub>2</sub> in conventional Li-Ion batteries [3,5,6] In addition to increased energy density, elementary sulphur is readily available, environmentally friendly, naturally abundant and cheap. There are still many problems in the practical use of Li-S batteries. The problems include the stability of the cathode material and the resolution of intermediate species. High reactivity of the Li-Metalanode, which degrades electrolyte [4.11]. Dendrite formation at the Li-Anode. Many problems arise from the formation of polysulfide intermediate products during the reduction process. The electrochemical reduction of sulphur leads to a loss of capacity. The intermediate polysulfide is soluble in the solvents typical for the Li-S battery. The polysulfide anions can migrate freely between cathode and anode, causing a so-called shuttle effect that leads

to a low coulombic efficiency. In order to solve problems related to polysulphide resolution, both cell level and electrode level modifications were followed at the Li-S battery. At cell level, intermediate layers and porous power collectors were used to improve capacity conservation. In another implementation, high-connected polymers with different functional groups produced by means of thiol-en-chemical were coated on the cathode surface to increase battery power. Another method for maintaining Li-S battery capacity is the use of solvents, supporting electrolyte salts and electrolyte additives [4,7,8,32,33]. The addition of co-solvents and functional molecules to the electrolyte solution can improve battery performance. In this work the authors investigate thiol-based electrolyte additives such as Biphenyl-4,4'-dithiol (BPD) to improve the performance of Li-S batteries. The authors also provide a comprehensive understanding of the origin of the capacity conservation observed in these additives. [121]

### 6.2.29 Interfacial properties of alloy anodes in combination with room temperature ionic liquid

Lithium secondary batteries are in most cases the technology of choice as energy storage with high gravimetric and volumetric capacity and performance. The current lithium battery technology still lacks the energy and power requirements to be used for applications such as electric and hybrid vehicles and to have space for the sporadic nature of certain renewable energy sources. Lithium metal is considered to be the best anode material. However, the dendritic growth of lithium can lead to short circuits during the charging process, giving rise to serious safety concerns for lithium metal anodes. The most commonly used material for commercial secondary lithium ion battery anodes is graphite, as Yazami et al. (0.2 V vs. Li + / Li) has shown. Ionic liquids generate interest due to their exceptional properties in terms of high ionic conductivity, large electrochemical windows, low volatility and low flammability. Li-air batteries that use ILs as electrolytes have several advantages, including their higher stability compared to the superoxide anion radical, increased safety and negligible vapour pressure. The use of metallic Li as anode is the main problem in connection with all Li-ion battery technologies that could be effectively replaced by the alloy anodes. The challenges associated with the formulation of a suitable ionic liquid electrolyte are discussed in various lithium battery technologies. Special emphasis is placed on alloy anodes to develop safer Li-ion batteries. Similarly, the possibilities of using an alloy electrode / IL-electrolyte combination in the case of Li-S and Li-O<sub>2</sub> batteries are discussed. [122]

## 6.3 Conclusions

The electrolyte is an essential part of LiSBs, and in this review extensive research work has been divided into several parts. The physicochemical properties, electrochemical performance and prospects for three types of electrolytes have been summarized in the sections. The diagrams on the performance of different electrolytes are shown in Figure 11. In LiSBs the concept of electrolytes is more complicated due to the unique active material reaction than in conventional lithium-ion batteries. The strong nucleophile reaction between liquid electrolyte and sulphur, the low ion transfer rate, the high solubility of ether for polysulphide and the weak strength of gel electrolytes are still barriers for a high energy density. Inflammability, pyrolysis and discharge of liquid electrolyte are potential safety risks. For solid electrolytes and composite electrolytes, the expensive raw materials and the rough preparation conditions of inorganic ceramics lead to high costs. The commercialisation of LiSBs is also determined by the synergy between electrolytes and electrodes. [94]

A novel functional electrolyte system with Dimethyl disulfide (DMDS) as a co-solvent to promote an alternative electrochemical reaction pathway for sulfur cathodes. High-sulphurised cathodes can cycle in this electrolyte and have a stable specific capacity of about 1000 mAh g<sup>-1</sup> per sulphur. This work provides a new strategy to improve the practical energy density of Li-S batteries. [95]

The Lithium polysulfide shuttle effect and the growth of lithium dendrites in the Li-S battery were suppressed by the formation of a robust LiF-rich SEI with high interface energy and controllable lithium coating

/ stripping kinetics. Such unique electrochemical properties for highly concentrated electrolytes also inspired us to develop a more practical pseudo-high concentration electrolyte by using a "non-solvent" to lower salt costs. [96]

(20PEC-80LiTFSI) / PA-electrolyte with high-performance PA-fibre membrane as matrix and highly concentrated LiTFSI-PEC as ionic transport material can be used in a solid-state lithium battery. This flexible fixed-electrolyte membrane has a high ion conductivity of  $4.05 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$  at  $55^\circ \text{C}$ . [97]

Under the synergistic effect of LiFSI and FEC, a LiF-rich SEI layer forms on the Li-Anode to reduce side reactions and adjust the Li-deposit morphology. After 1000 cycles at  $2^\circ \text{C}$ , a capacity of 1270 mAh g<sup>-1</sup> remains for the S @ pPAN cathode, corresponding to a capacity drop of 0.0015% per cycle. [98]

Biological reagents DTT as an addition to this work are first introduced into the conventional electrolyte for Li-S batteries. DTT in the right concentration can quickly cut the disulfide bindings of polysulphides at room temperature and thus facilitate the transition from S<sub>8</sub> to Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S. [99]

The high decomposition temperature and the non-flammability of the BMP-TFSI-based IL make it a promising electrolyte for use in high-security Li batteries. IL-Electrolyte with an appropriate concentration of LiTFSI is ideal for high-temperature applications. [100]

The modified electrolyte is produced by the addition of LiNO<sub>3</sub> in 0.5 M LiCF<sub>3</sub>SO<sub>3</sub>-DOL / TEGDME. Due to the protection film produced on the lithium anode, the increased lithium cycle efficiency was achieved in the lithium sequencing and solution experiment. Polysulphide in the electrolyte was prevented from coming directly into contact with the lithium. [101]

A nitrogen-doped carbon material, consisting of a three-dimensional graphene array (3DNG), was produced using a simple microwave-based solvothermic path and used for the homogeneous absorption of crystalline sulphur. The resulting 3DNG-S compound was examined in lithium-metal cells with the electrolyte solution DEGDM-LiTFSI-LiNO<sub>3</sub>. The battery showed a very stable specific capacity of about 1000 mAh g<sup>-1</sup> with the coulombic efficiency approaching 100%. [102]

The efficiency of lithium-sulphur cells with a mixed C<sub>4</sub>mpyr IL-organic electrolyte has been studied with different concentrations of LiNO<sub>3</sub> additives. Conductivity and lithium-ion diffusivity reach peak values, while viscosity with values of 0.05-0.15 mol kg<sup>-1</sup> is lowest. [103]

All-solid-state Li-S battery with Li<sub>7</sub>P<sub>2</sub>.9S<sub>10</sub>.85Mo<sub>0.01</sub> electricity is proven to have a higher capacity and a better cycle life than the equivalent of a Li<sub>7</sub>p<sub>3</sub>S<sub>11</sub> electric battery. Our studies can provide valuable information for the synthesis of Li-superionic conductors for all-solid-state batteries. [104]

The SHGP-electrolyte showed a strong adsorption to lithium polysulfides, since the enriched polar functional groups in SHGP could produce chemical adsorption with lithium polysulfides. The original design of this super high ionic conductive polymer electrolyte, presented here, opens a new direction for high-performance quasi-solid Li-S batteries. [105]

A polymer-in-salt-electrolyte membrane has been produced with the bi-phosphate polysiloxane copolymer, LiTFSI and PVDF, which has a high ionic conductivity at ambient temperature. The CPE membrane blocks the lithium-dendrite growth and the diffusion of polysulphides during repeated loading/discharge cycles. [106]

When the loading of electrolytes with sulphur was 1.12 mol L<sup>-1</sup>, an initial discharge capacity of 1098 mAh g<sup>-1</sup> at 0.1 C and a coulombic efficiency of 97.3% at a CNT @ S cathode was shown in a LiTFSI / DOL / DME electrolyte. [107]

For RT-ASSLSBs, a novel two-layer array of 1D-LLTO ceramic nanofibres was developed, which after 50 cycles has a stable cycle performance with a high coulombic efficiency of over 99%. This two-layer structure design opens ASSLSB an alternative way to work at room temperature constantly by dealing with several challenges. [108]

The dominant electrolytes for Li-S batteries are based on the DOL: DME system with LiNO<sub>3</sub> as an addition to preventing the polysulphide-shuttle mechanism. The SEI layer formed on the Li-Anode surface is very stable and the main component is Li<sub>2</sub>O. This layer suppresses the reduction of electrolyte-co-salt, LiTFSI, and solvent (G<sub>2</sub>). LiNO<sub>3</sub> is consumed during the cycle by chemical reactivity with Li-metal. When used as

an additive (i.e. in small quantities) as is the case with state-of-the-art DOL: DME-electrolyte, the beneficial effect is limited to stabilising the SEI. Li-S batteries with a high CE value after extended cycle are activated by an electrolyte. The CE of Li-Metalloanodes is 99.9% due to the interruption of support for the SEI (i.e. the isolation of Li). The low losses (inefficiencies) per cycle are the result of the consumption of LiNO<sub>3</sub> during each coating/insulation cycle. [109]

Pure DOL low K<sub>sp</sub> of PS was chosen as an electrolyte solvent for Li-S batteries, resulting in low PS solubility, slow PS permeability, high Li<sup>+</sup> conductivity and excellent reversibility of lithium anode. As a result, 350 Wh was reported for the first time in literature – 1 secondary Li. S soft pack batteries. [110]

Li-coating tests on Cu powder electrodes were performed in a superconcentrated electrolyte from LiFSA and PNMePh with VC. A two-stage li strip was observed; the potential plates for the first and second stripping steps appeared at - 0.2 V and + 1.0 V versus the Li-Metal Counter electrode. [111]

LiPSs are involved in the formation of inorganic layers in the SEIs on Li-Metal in a widely accepted ether-based electrolyte. Li-Metal-Anode with LiF-Li<sub>2</sub>S<sub>x</sub>-rich SEI results in a stable coulombic efficiency of 95% after 233 cycles for a Li-Cu half cell. [112]

A modified solution method was used to synthesize cubic pomegranate-solid electrolyte LCLTZO. The synergistic dosing of Ca and Ta favours the formation of cubic LCLZTO with high ionic conductivity of  $4.03 \times 10^{-4} \text{ S cm}^{-1}$ , while LLZO has a tetragonal phase with low conductivity without substitution. [113]

A novel integrated approach to the practical application of Li-S batteries. For the cathode, the hierarchically porous and highly conductive sulfur host G / MPC / SP is easily prepared. The use of the GF membranes as electrolytreservoir strongly suppresses the Li-Dendrite growth. [114]

Py was oxidised during cycles and forms a surface protection layer on the sulfur cathode. The protective layer serves not only as a guide for an effective electron trail, but also as an absorption agent and barrier layer that suppresses the diffusion of polysulfide intermediates. [115]

PETO and PVA-x were used as binders to produce S-combined cathodes of a Li-S cell. PETO is soluble in electrolyte [Li (G4)] [TFSA] and forms complexes with Li<sup>+</sup>. The formation of PEO-Li<sup>+</sup> complexes in electrolytes leads to the release of free G4 molecules. The compatibility of PVA-x with [Li (G4)] [TFSA] changes depending on the degree of leakage (x) PVA 100 is insoluble in the electrolyte, but when the acetate content in PVA x (x < 100) is reduced, PVA-100 is compatible with Li (g4). This is because the interaction between PVAX and [Li<sup>+</sup> -ion transport is relatively weak. The production of uncoordinated G4 is inhibited, resulting in a low solubility of Li<sub>2</sub>S<sub>m</sub>. [116]

The electrolyte solution on a FEC basis shows an improved capacity retention during the charge discharge cycle of S/C composite electrodes. This result was achieved for two completely different electrodes produced with two types of carbon economy, namely micrometer-sized microporous carbon powder and activated carbon. The surface film, which forms at the first discharge, consists of the products of the reaction of the electrophilic organic carbonates with the nucleophilic lithium PS. The results achieved are promising for the current ongoing development of SLS batteries with FEC-based electrolyte solutions. The results of the SLS battery development were promising, the study said. The study was a step forward in the development of battery storage technology. [117]

Full-body lithium-sulphur batteries show impressive capacity, cycle, temperature and safety growth. This electrolyte is widely available and economically more beneficial than most other solid polymer electrolytes developed so far. This opens a promising way to cost-effective implementation of energy in green transport. [118]

[119]

FEC-based electrolyte system shows excellent compatibility with both S @ pPAN cathode and Li-metal anode compared to conventional EC-based electrolytes. SEI layer consists of polymer carbonate and LIF on both sulfur composites. This electrolyte is also excellent for the high capacity of Li-S batteries (up to 7.7 mAh cm<sup>-2</sup>). [120]

The use of electrolyte additives on a thiol basis such as BPD increases the capacity of Li-S batteries. The formation of BPD short-chain polysulphide complexes (Sn<sup>2-</sup>, 1 ≤ n ≤ 4) inhibits the formation of isolated

short-chain polysulphides such as S<sub>3</sub><sup>•-</sup>. BPD appears to be the most powerful electrolyte additive. [121]

Ionic liquids form a protective surface layer on the surface of alloy anodes, which in turn would improve the cyclic stability of the anode. It was found that ionic fluids formed a stable layer on the surface of the alloy anodes, which could be used to create an additive-free approach compared to organic solvents. IL-electrolytes based on quaternary ammonium salts such as tetraalkyl ammonium [R<sub>4</sub>N<sup>+</sup>] or cyclic amines are often used as electrolytes for Li secondary batteries. The latter imidazolium appears to be most effective in both SEI formation and total cell performance. The formation of the SEI on the anode surface is crucial for the correct operation of secondary lithium-ion batteries, including those that work with ionic fluids as electrolytes. In most cases, the use of a molecular supplement to ionic fluid is not necessary because the correct selection of anions could control the rapid formation. The choice of cation is another decisive factor, as the inclusion of certain functional groups reduces the number of Li coordinations, which would result in easier Li desolvation and better transport characteristics. The addition of two ether functionalities to the PP16 cation reduces the Li co-ordination numbers. Compared to commercial graphite electrodes, a thinner and more even SEI layer formation occurs in the case of alloy anodes in combination with IL electrolytes. For example, the better connection between the originally formed LiF and anode surface minimises the thickness of the SEI layers. In the case of ionic liquids, a higher coulombic efficiency is observed due to its lower dielectricity constant compared to conventional organic solvents, due to the lighter desolvation of the solvent shell when the dielectricity decreases. A stable impedance response can be observed with various alloy anode/IL electrolyte systems, which is due to their resistance to electrolytic degradation and organic film formation. A stable reaction can also be observed when anode and IL electrolyte are used in anode/IL systems. The unique combination of IL-electrolytes with alloy anodes is not limited to Li-ion batteries and is also used in modified Li-Technologies, such as Li-S- and Li-Air Batteries, which show promising results as a step towards safer batteries. [122]

## **Part III**

# **Li-O<sub>2</sub> Batteries**



# Chapter 7

## Li-O<sub>2</sub> Cathode Materials

### Contents

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### 7.1 Introduction

A hybrid air electrode consisting of a mixture of fluorocarbons (CF<sub>x</sub>) and ketchen soot (KB) activated carbon composites was prepared to improve the performance of the Li-O<sub>2</sub> battery. Four types of CF<sub>x</sub> materials were used as lithium inserts. Compared to the conventional air electricity of KB, all CF<sub>x</sub>/ KB hybrids showed a higher specific discharge capacity, especially with high current density. At a current density of 0.5 mA cm<sup>-2</sup>, the fluorinated graphite electrode showed the best. [123]

The amorphous, low-oxygen, thin-coated carbon nanotubes (CNTs) are synthesized by atomic separation and used as cathode materials for lithium-air batteries. The battery with the corresponding CNT @ TiO<sub>2</sub> / x-cathode has high discharge/charge capacity and good cycle performance. [124]

The understanding and control of the growth of the vital Li<sub>2</sub>O<sub>2</sub> product is crucial for the development of effective cathode catalysts in Li-O<sub>2</sub> batteries. The weak oxygen adsorbability on the cathode surface determines the path of the first electron transfer to O<sub>2</sub>. N-doped carbon nanocattles are cathodes that simultaneously realize a large discharge capacity and a low charge overpotential. [125]

MFe<sub>2</sub>O<sub>4</sub> @ carbon cloth (M = Co, Fe) has been prepared by electrodeposition to be an effective cathode for LOBs. This cathode can effectively prevent interference with a polymer binder during the discharge process. [126]

The EIS and ECM data are first reported for a binding-free Li-O<sub>2</sub> cell. The EIS results are consistent with the total discharge capacity results for a cell that is experiencing increased polarization due to cycles. Surface morphology is also presented for the cell and shows product formation at the cathode. [127]

The capacity limits, the local formation of Li<sub>2</sub>O<sub>2</sub>, the passive use of active surfaces and the depletion of oxygen due to mass transport properties in a composite cathode are modelled, numerically simulated and experimentally evaluated. The theoretical maximum specific energy of the Li-O<sub>2</sub> battery is known as 3458 Wh. Wh kg<sup>-1</sup> cathode. [128]

The joint cutting is a general method for increasing the performance of Li-O<sub>2</sub> cathodes. Without the catalyst, the granular gel cathode is able to perform 170 cycles with a fixed capacity of 1000 mA h gcarbon<sup>-1</sup> or maintain a specific capacity of more than 10,500 m<sup>-1</sup>. [129]

The carbon surface is unstable and highly reactive in contact with Li<sub>2</sub>O<sub>2</sub>, leading to the formation of irreversible by-products (e.g. Li<sub>2</sub>CO<sub>3</sub>). After unloading, a nanosheet-like Li<sub>2</sub>O<sub>2</sub> growth was observed on In<sub>2</sub>O<sub>3</sub>-coated CNPs, which is beneficial for longer life. [130]

This article is dedicated to improving the performance of lithium-air batteries by optimizing the cathode treatment process. Together with nickel foam, the spraying method is the best approach to high-performance cathode production, measured by the discharge capacity, the discharge voltage and the high rate discharge capability. [131]

The efficiency of cathode cells for lithium-air cells is assessed from the perspective of the automobile. New cathode structures are manufactured to improve the performance of air-powered cells. For the assessment of the performance of cathode cells, the convex air flow is used, which is crucial for automotive operation. The peak performance is measured using the standardized USABC test procedure, a benchmark for the performance assessment in the automobile. [132]

A cathode architecture made of ZnO nanoparticles, anchored on vertical carbon nanotubes (ZnO / VACNTs), suppresses LiO<sub>2</sub> disproportionation. This discharge chemistry leads to a reduced charge overpotential and extended service life. The results show that the electrochemical reaction adjusted by the cathode is a powerful tool to improve the performance of Li-O<sub>2</sub> cells. [133]

Due to its high energy density, the Li-Air Battery plays a key role in the future renewable energy and electric vehicle industry. However, it suffers from a dwindling cycle and low performance, mainly caused by the problem of the cathode. Here the authors create a nanoporous three-dimensional gas diffusion electrode that is to replace a conventional compound electrode. [134]

Li-O<sub>2</sub> batteries can be used as flexible power sources with extremely high specific energy density to meet the increasing demand for flexible and portable electronic devices. The finished flexible cathode has superior electrochemical performance, including a high specific capacity (22.4 mAh cm<sup>-2</sup> at 0.15 m<sup>-2</sup>) and excellent performance. [135]

## 7.2 Literature Reviews

### 7.2.1 Enhanced performance of Li-O<sub>2</sub> battery based on CF<sub>x</sub>/C composites

Due to its higher specific energy density compared to conventional lithium-ion batteries, Li-O<sub>2</sub> batteries generate increasing research attention. However, some significant barriers still limit their practical application. One of these barriers is that the battery's performance is usually much lower than that of the conventional Li-ion battery. This process is considered a main mechanism that leads to poor performance. The choice of electrolytes plays a key role in the performance of Li-O<sub>2</sub> batteries. Tetra (ethylene) glycol dimethyl ether (TEGDME) and dimethyl sulfoxide (DMSO) are currently identified as relatively stable liquid electrolytes. DMSO, however, has high volatility and is unstable compared to Li-metal. Zhang et al. proposed the concept of the hybrid air electrode for the Li-Air Batteries, where lithium materials were incorporated into an air cathode. Compared to the pure carbon-free air without electricity, these hybrids significantly improved their performance, especially in the CF<sub>x</sub>-based hybrid. The physical properties of CF<sub>x</sub> materials, electrocatalytic activity and electrochemical performance were investigated. [123]

### 7.2.2 Atomic layer deposition of amorphous oxygen-deficient TiO<sub>2-x</sub>

Lithium-Air Batteries are considered one of the most promising energy sources for new energy storage. It has been reported that the electrodes directly determine the battery performance, in particular the cathode catalysts used in the oxygen reduction reaction (ORR) and the oxygen development reaction (OER) during discharge/charging operations. TiO<sub>2</sub> is due to its superior catalytic properties, excellent stability and environmental friendliness one of the most frequently studied metal oxide catalysts for lithium-air batteries. TiC cathode showed a high catalytic activity for ORR/OER reactions and cycle stability during discharge/charge

operations. A thin layer of low oxygen TiO<sub>2</sub>-X on carbon nanotubes (CNTs) was synthesized by ALD. ALD is a thick controlled and layer-to-layer process that builds uniform and well controlled coatings of nanostructures. [124]

### 7.2.3 Li-O<sub>2</sub> growth in lithium batteries: Effect of oxygen adsorbability on oxygen

Lithium oxygen batteries generate enormous interest due to their extremely high energy density from about two to three times that of the state-of-the-art lithium-ion batteries. A typical Li-O<sub>2</sub> cell consists of a Li-Metalanode, a porous cathode and a Li + containing electrolyte. In discharge, O<sub>2</sub> is reduced to form a vital product of the insulating solid Li<sub>2</sub>O<sub>2</sub> at the porous cathode. Modulation of electrolyte composition can control the Li<sub>2</sub>O<sub>2</sub> growth model by the effect of LiO<sub>2</sub> solubility, e.g. by the administration of solvents with a high donor number. However, the growth mechanism on these cathode surfaces was unclear or controversial [17,18], which is due, for example, to a strong li<sub>2</sub>/O<sub>2</sub> adsorption to modified catalysts. The correlation between the Li<sub>2</sub>O<sub>2</sub> growth model and the oxygen adsorbability on the cathode surface is established. The authors realize at the same time a large capacity and a low overpotential by forming abundant thin layer Li<sub>2</sub> oxygen on the cathode of N-doped carbon nanocages with a high specific surface. [125]

### 7.2.4 MFe<sub>2</sub>O<sub>4</sub> (M=Co, Fe) on carbon cloth as air cathode

Due to its high theoretical specific energy density (3500 Wh/kg), which is almost ten times as high as the commercial Li-ion cells [5-7], Li-O<sub>2</sub> batteries (LOBs) are considered to be the best potential components for energy storage. Some critical points in the LOBs still exist, such as low specific capacity in practice, weak cycle stability and a large overpotential in charge discharge. The main reason for these restrictions is the sluggish ORR/OER kinetics. Many efforts have been devoted to the development of bifunctional oxygen electric catalysts that are effective both for the ORR and for the OER. Many studies have shown that CoFe<sub>2</sub>O<sub>4</sub> has a good bifunctional catalytic property in LOBs. In these works, polymeric binders (such as polyvinylidene fluoride) were used to connect the electrocatalyst to the electrical collectors. Polymer binders are commonly known for increasing the weight of the air cathodes, but they also inevitably react with the oxygen radical intermediate products. MFe<sub>2</sub>O<sub>4</sub> (M = Co, Fe), which is grown directly on carbon fabric, was produced using an electrodeposition method. These materials avoid the use of polymer binders, prevent the occurrence of associated side effects, but also have good flexibility. Significantly, the electrochemical performance of the material was investigated by cyclic voltammetry, discharge tests and electrochemical impedance spectroscopy. [126]

### 7.2.5 Li-O<sub>2</sub> cell with binder-free cathode

The world is heading towards a 30% higher energy consumption by 2030. Lithium-ion batteries are an evolving technology. Their operation is limited only by the amount of lithium in the anode. Although they have a theoretical energy density of 11,000 Wh - 1 which is almost ten times more than lithium-ion batteries, the energy density achieved is much lower than the theoretical [3,4]. Polarization is a key factor in why a lithium-ion battery cannot maintain its capacity and efficiency for as many cycles as a commercial Li-ion battery. There are several publications on the discharge performance of traditional Li-O<sub>2</sub> cells with binders. Some of these studies also include impedance spectroscopy data and circuit models to provide additional insights into the electrochemical kinetics that drive cell operation [5-10]. None of the publications that report on binder-free cells [11-13] deal with impedance behavior by means of impedance spectroscopy or comparable switching models (ECM). Electrochemical impedance spectroscopy data and an ECM are presented that accurately describe the cell behaviour of a binding-free Li-O<sub>2</sub> cell. Joint performance results such as discharge capacity and cathode surface morphology are also presented for the cell. These new results can form a basis for future comparisons of impedance studies and ECM. [127]



dimethoxyethane (DME) and lithium nitrate (LiNO<sub>3</sub>) can partially eliminate CO<sub>2</sub> evolution from CNT electrodes by disabling defects. Lee et al. used a surface modification method to cover entire carbon surfaces. A porous carbon nanopaper (CNp) coated by In<sub>2</sub>O<sub>3</sub> thin layer and catalytic RuO<sub>x</sub> nanoparticles (NPs) can be used as a highly efficient Li-O<sub>2</sub> cathode. An amorphous coating layer, which is not reactive for superoxide and peroxide species, can be formed on CNp by the use of atomic layer separation (ALD) that prevents direct contact between CNp and electrolyte. [130]

### 7.2.9 Cathode process on lithium-air batteries performance

Lithium-air batteries with an energy density of 11140 Wh/kg without oxygen have been considered the most promising candidate in recent years. The concept of Li-Air Chemistry in the aqueous system was first proposed by Littauer and Tsai in 1976. Among the Li-Air batteries, the water-free system achieved more encouraging results due to better performance and relatively simple structure than the others. Jung et al. operated a battery stable up to 100 cycles without significant reduction of discharge capacity and voltage [11]. Bruce and Bruce produced a battery that had a capacity reserve of 95% after 100 cycles, using nanoporous gold electrodes (NPG). In literature, nickel foam [22,23] and carbon paper [24] are usually used as a cathode substrate. In recent years, several new methods have also been developed to improve battery performance. However, a comparative study of the effects of the cathode process has not yet been reported. The main objective of this article is to optimize the cathode process in order to improve the performance of Li-Air batteries. Due to the great power generated by rolling, a substrate with a certain mechanical strength should be used for rolling, and a flat substrate in the surface is required for the coating process. [131]

### 7.2.10 Electrochemical analyses of cathodes for lithium-air batteries

The latest lithium-ion technology (SOA) with graphic carbon and inorganic oxides delivers 180 Wh kg<sup>-1</sup>. Lithium-Air Batteries are an attractive alternative and use the energy generated by the reaction of a lithium-metal anode and an oxygen-accessible porous cathode. In order to develop a lithium-air cell that simultaneously meets the energy, performance and cost goals required for use in an electric vehicle, many challenges have to be solved. Three specific technical challenges still need to be solved before lithium-air batteries can be considered for commercial automotive applications. Cell designs on the laboratory scale used for research are not suitable for automotive applications because they are not suitable for mass production and do not minimise mass and volume to maximize energy and power density. Experience with the proton exchange membrane (PEM) in fuel cells has shown that air is the only technically feasible option for an oxidation source in vehicles. Pure oxygen is difficult to store efficiently on board the vehicle and makes tanking difficult. Regardless of the cell design, the performance density in operation must be improved with air, not with pure oxygen. The behaviour of porous air cathodes and the EIS analysis techniques used for their investigation are not yet fully established for lithium-air cells. The operating regime (kinetic, ionic and / or mass transfer) for lithium-air cells has not yet been identified, but has been documented for PEM fuel cell cathodes using stationary polarization data. This article describes efforts to evaluate and improve the performance of lithium-air batteries for automotive applications. Using existing materials, various cathode production techniques are used to construct the cathode structure in such a way that improved performance is achieved by convective airflow. Electrolytes based on carbonate solvents are used to minimise solvent evaporation. [132]

### 7.2.11 Li-O<sub>2</sub> batteries with nanosize stabilized Li<sub>2</sub>xO<sub>2</sub>

The manipulation of composition, size and morphology of discharge products is an important strategy for improving cell performance. A large number of experimental studies focused on the selectivity of electrolytes and regulations such as the addition of redox mediators and soluble additives [5-8] There are few reports on the coordination of electrochemical and chemical reactions by the design of the cathode architecture. A high

load potential of Li<sub>2</sub>O<sub>2</sub> and active intermediates such as O<sub>2</sub><sup>-</sup> and LiO<sub>2</sub> can lead to a carbon or electrolyte substitution of irreversible carbonates. A major challenge is the development of a high-performance taxonomy to promote the formation of the discharge product, which can be disassembled with low charging potential. In nature, a large overpotential of the Li-O<sub>2</sub> battery is created by the chemical bonding of Li + with bivalent anions [16] Therefore, it is very important to suppress the Li<sub>2</sub>O<sub>2</sub> formation. Many experiments showed that Li<sub>2</sub> - xO<sub>2</sub> (0 < x < 1) products could form on the cathode surface. Previous studies indicated that LiO<sub>2</sub> is chemically unstable at room temperature [19] In contrast, Li<sub>2</sub> + + O<sub>2</sub> containing superoxide may be present in electrochemical environments. A fundamental principle of construction is the maintenance of a high electrical conductivity to reduce O<sub>2</sub> in O<sub>2</sub><sup>-</sup> while accelerating the cathode separation of LiO<sub>2</sub>. Semiconductor ZnO nanoparticles were introduced by atomic layer separation (ALD) to the surfaces of VACNTs. This design results in a bifunctional structure that suppresses dispersion reactions to lithium peroxide. The particle size of discharge products is about 5-6 nm. Meanwhile, the overpotential is reduced and the amount of carbonate species is suppressed. [133]

### 7.2.12 Nano-structured gas diffusion electrode – High power and stable cathode material

Renewable energy is considered an important source of energy for tomorrow, but its production is fluctuating. Batteries could serve as buffers to feed more renewable energy into the electricity grid. The current transport sector is heavily dependent on fossil fuel supply, which contributes significantly to environmental pollution and climate change. Electric cars appear as a realistic alternative for cars with combustion engines. The authors develop a three-dimensional nanoporous gas diffuser electrode (GDE) as a replacement for CE as an air cathode. It effectively improves battery capacity, performance and cycle life. The improvement mechanism is discussed using electrochemical and spectroscopic characteristics. The improvement mechanism is based on electrochemical and spectroscopic properties. [134]

### 7.2.13 CNTs-grafted cotton fabrics as binder-free, free-standing and cost-low materials

Carbon materials have been researched as cathodes for Li-O<sub>2</sub> batteries due to their low weight, low cost, high specific surface area and high electrical conductivity. Compared to commonly used unspooled carbon materials, biomass-conceived carbons show significant advantages in cathodic performance. Biomass carbons are increasingly used in energy storage. Cotton is selected as a Li-O<sub>2</sub> battery cathode with its biomass advantages and exceptional flexibility. Cotton is selected for its biomass advantage and flexibility to use it as a cathode. Cotton was used by a battery manufacturer in China as a battery battery battery. [135]

## 7.3 Conclusions

The fluorinated graphite hybrid air electrode shows the best electrochemical performance in the Li-O<sub>2</sub> battery. Compared to the battery that was assembled with the conventional KB-air electrodes, the battery that was assembled with this CF<sub>x</sub>/C-hybrid-air electricity showed a slightly lower performance loss due to KB-active carbon and PVDF-binding instability in the presence of Li<sub>2</sub>O<sub>2</sub> [4]. [123]

An amorphous low-oxygen TiO<sub>2</sub>-x thin layer on carbon nanotubes (CNTs) was synthesized by ALD and the prepared nanocomposite showed an increased electrochemical performance for lithium-air batteries. [124]

The weak oxygen adsorbability drives the solution growth model to form toroids, while the strong model drives the surface growth model. The authors can imagine that the surface technical cathode catalyst strategy offers many new opportunities for practical applications of Li-O<sub>2</sub> batteries and potentially other metal air batteries. [125]

CoFe<sub>2</sub>O<sub>4</sub> @ CC has a high specific capacity, a low overpotential and a high cycle performance in LOBs. The first full discharge specific capacity is 7259 mA h / g at 170 mA / g. The cycle life is over 100 cycles at the upper limit of 500 mA. [126]

For the first time, EIS and ECM results of a Li-O<sub>2</sub> cell are presented, which uses a binding-free co-Mn composite catalyst cathode. The EIS results are consistent with the results of a cell's discharge capacity, which results in increased polarization due to cycles, and the built-in equivalent circuit precisely model the same behavior. [127]

The discharge profiles of Li-Air batteries were successfully modelled and simulated with the COMSOL Multiphysics software package. Mass transport was simulated on the basis of the Nearest Planck equations. Electrode reactions were controlled by concentration-dependent butler-volmer kinetics with electrodeposition. The prediction for the optimized cell geometry suggests that a 30-60  $\mu\text{m}$  thick film, depending on the power demand of an application, could show optimum performance both in terms of specific capacity and surface capacity. This also indicates that the ratio and shape of the cathode components significantly influence battery performance. The introduction of hollow spaces into the cathode is beneficial for a relatively thick electrode. A maximum specific capacity of 1148 mAh g<sup>-1</sup> is expected if the volume ratio Carbon: Electrolyte: Void 4: 2. Geometric modifications could be considered as further experimental guidelines. [128]

Conventional oxygen cathodes with porous carbon and liquid electrolyte are first gelled with rationally constructed, highly elastic networked polymer and then split into granules. The columns between the gel granules facilitate oxygen diffusion in the inner part of the cathode enormously. [129]

A freestanding 3D-CNP, protected by highly stable and conductive  $\text{In}_2\text{O}_3$  layers, is successfully produced as a stable air cathode for Li-O<sub>2</sub> batteries.  $\text{Li}_2\text{CO}_3$  suppresses parasitic by-products such as  $\text{Li}_2\text{CO}_3$ , which occur at the boundaries between carbon and  $\text{Li}_2\text{O}_2$ . [130]

The influence of the cathode process on the performance of Li-Air batteries has been investigated in this work. A better performance could be achieved if larger carbon particles of 70  $\mu\text{m}$  are used than those of 40  $\mu\text{m}$  due to the reduced reunification of carbon particles. An intermediate pressure process could improve the performance of the electrode prepared by the coating method by creating a sufficient path for the oxygen diffusion. [131]

[132]

The nano-size nucleation at the interfaces is stabilized by the nano-size effect, which is related to ZnO's semiconductor behaviour. Compared to the impeccable VACNTs, the relevant electrochemical performance improves in terms of load overpotential and cycle life. [133]

The improvement mechanism of the GDE was proposed on the basis of loading/discharge curves, electrochemical and spectroscopic evidence. The superior nanostructure from GDE to CE played a key role by promoting the formation of a more effective three-phase region that functioned as a networked micronetwork with electrolyte-filled pore. [134]

KOH-activated and CNT-produced cotton cathodes showed good cyclic performance for over 250 cycles. The cathode showed the maximum discharge capacity of 22.4 mAh cm<sup>-2</sup> at 0.15 mA cm<sup>2</sup>. Based on this modified cotton is a promising cathode material for Li-O<sub>2</sub> batteries. [135]



# Chapter 8

## Li-O<sub>2</sub> Anode Materials

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### 8.1 Introduction

Li-Metal is used as an anode for Li-O<sub>2</sub> batteries due to its high specific capacity and its low negative electrochemical potential. However, Li-Metal has a low coulombic efficiency and a limited service life, which hampers its practical use. With sufficient oxygen, the growth of Li-Dendrites was suppressed by the formation of flexible and mechanically strong solid electrolyte-interphase layers. [136]

A new protected anode for lithium-air batteries has been developed from lithium foil and lithium-aluminium-germanium phosphoric glass (LAGP) with an improved specific conductivity of over 3.1 to 10<sup>-4</sup> S cm<sup>-1</sup> at 80 °C. Avoiding anode or electrolyte build-up provided stability of battery characteristics over 10 cycles. [137]

Li-air batteries with high solubility of discharge products have a higher potential to reach their slightly lower theoretical limits in practical devices. They are composed by sandwiching LAGP membranes between Li-Anode chamber and Cathodic solutions. If the two electron reduction mechanisms prevail, overpotentials below 0.2 V for currents up to 0.07 mA cm<sup>-2</sup> will be achieved, resulting in an energy efficiency of over 98%. [138]

### 8.2 Literature Reviews

#### 8.2.1 Li-O<sub>2</sub> battery anode with ultra-stable and enhanced reversibility

Li-O<sub>2</sub> batteries have been extensively investigated over the past ten years due to their ultra-high theoretical specific energy of 3500 Wh kg<sup>-1</sup>. This advantage is derived from the use of a Li-Metal-Anode, which has a higher specific capacity of 3860 mAh g<sup>-1</sup> and the lowest potential of - 3.04 V compared to conventional hydrogen electrodes [5-9]. Li-Anodes exhibit a low reversibility during the cycle, thus hampering their practical application. To stabilise the Li-Metalanode various strategies have been developed. One of these trials is the provision of host materials such as Si, Al and Carbon to form a Li-Metal Alloy-Anode [14-16] By avoiding the Li-Metal plating/Stripping process, the growth of Li-Dendrites is inhibited [17]. However, the use of Li-Leg-Alodes leads to the loss of both the output voltage and the capacity of whole cells. The modification of electrolytes is an effective approach to improving the reversibility of Li-metal anodes. In Li-O<sub>2</sub> batteries,

electrolytes based on DMSO and TEGDME are most commonly used due to their unstable chemical properties after contact with Li-metal [19,26,27] Electrolytes are added in this context, such as inorganic Li-salts and metal ions. Due to the rapid reaction between the additive and Li-metal, dense SEI layers form. Unfortunately, these additives suffer from rapid consumption during the cycle along with possible parasitic reactions on the cathode side. In order to improve the diffusion of O<sub>2</sub>, a porous anode electrode was used. The O<sub>2</sub> used in the Li coating / stripping process can be continuously refilled from the outside. In the ether-based electrolytes, the coulombic efficiency of a li-metal anode was significantly improved. [136]

### 8.2.2 Protected anodes for lithium-air batteries

Efficient energy storage is very much needed for various applications such as consumer electronics and pure electric vehicles. Lithium-air batteries are the most prominent solution due to their high specific energy and enormous capacity and exceed lithium-ion batteries by a magnitude. In this sense, lithium-air battery technology is the most powerful solution. Lithium-air batteries with lithium-conducting polymer electrolytes were reported by Abraham and Jiang in 1996. These prototype cells showed an idle voltage of about 3 V and an oxygen electrode capacity of 1600 mAh g<sup>-1</sup>. A catalyst additive to carbon cathode material makes the cell much more efficient and reversible. The highly reactive lithium must somehow be isolated from water vapour and oxygen that penetrates the anodising part of the cell from the surrounding atmosphere. We propose a new protected lithium anode based on a glass ceramic Nasicon electrolyte and a lithium foil for rechargeable lithium-air batteries. [137]

### 8.2.3 High efficiency aqueous and hybrid lithium-air batteries enabled by Li<sub>1.5</sub>Al<sub>0.5</sub>Ge<sub>1.5</sub>(PO<sub>4</sub>)<sub>3</sub>

Rechargeable Li-Air Batteries (LABs) are promising alternatives with a high energy density for Li-Ion batteries to meet the growing global energy demand. In aqueous and hybrid LABs, the discharge products in the Katholyt are highly soluble, improving cycle efficiency, performance and volumetric energy density. Protected anode systems with fast Li<sup>+</sup>-ion-conducting LAGP ceramics are examined in rechargeable aqueous and hybrid Li-air batteries, which are operated under open-air conditions at room temperature. According to our knowledge, there are no reports of the charging performance of Li-Air cells. [138]

## 8.3 Conclusions

Li polysulfide in Li-S batteries, which is usually considered a bad product for Li-Anode, can also protect Li-Metal. The O<sub>2</sub> contained in Li-O<sub>2</sub> batteries can also be used to improve the reversibility and cycle stability of the Li-Metal Anode. In the first cycle, O<sub>2</sub> can preferably react with Li-Metal to form a SEI layer consisting mainly of Li<sub>2</sub>O, Li<sub>2</sub>O<sub>2</sub> and LiOH. [136]

The Lithium-Aluminium-Germanium-Phosphorus-Glassceramics (LAGP) could play an important role in the construction of lithium-Air Batteries. It allows to prevent anode or electrolyte loss and increase the stability of the battery for at least 10 cycles. [137]

Hybrid Li-Air cells were expected for more than 90 hours with a polarization between charging and discharge of only  $\leq 0.1$  V for the first 50 hours at a current density of 0.03 mA cm<sup>-2</sup>. Performance increases are expected by improving the design of the cell and using thinner membranes. [138]

# Chapter 9

## Li-O<sub>2</sub> Electrolytes

### Contents

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### 9.1 Introduction

The discharge power of a lithium-air battery with this compound electrolyte membrane in the ambient atmosphere shows a higher capacity of 2800 mAh g<sup>-1</sup>. The cell with pure ionic liquid as electrolyte delivers a much lower discharge capacity of 1500 mAh G<sup>-1</sup>. [139]

The Li-Air cell has a discharge capacity of 221 mAh g<sup>-1</sup> at a current density of 0.5 mA cm<sup>-2</sup> with a good cycle life. The solid electrolyte separates the aprotic electrolyte from the aqueous catholy and provides ways for lithium-ion transport. [140]

New ionic liquid polymer electrolytes based on polymer poly (Vinylidene fluoride co-hexafluoropropylene) (PVdF-HFP), lithium bis (Tri-Fluoromethanesulfonyl) imid (LiTFSI) have been synthesized and applied to quasi-resistant Li-Air batteries. Electrochemical properties of the polymer electrolyte under the installation of EMITFSI improved the electrochemical stability window (4.9 V) with higher ionic conductivity ( $\leq 4.30 \times 10^{-3}$  S cm<sup>-1</sup>). [141]

A lithium-air fuel cell is proposed with a newly designed cell structure for improved stability. The cell consists of two subunits: an energy conversion unit that uses a cation exchange membrane, and a reaction product recycling unit that LiOH collects / removes, thus protecting the LiSICON plate from corrosion under highly alkaline conditions. [142]

A two-dimensional physical model that uses the deformed mesh method to track the electrolyte level in a Li-Air Button Cell Battery is presented and used to investigate the effects of the waste electrolyte level during the cell discharge. The electrolyte loss is caused by the decrease in the volume of the solid phases and the evaporation of the electrolyte solvent. [143]

The authors performed DFT calculations to investigate the role of the solvent of the non-hydraulic electrolytes for the oxygen reduction reaction (ORR) in Li-Air Batteries. Due to the IR analysis, the LiCF<sub>3</sub>SO<sub>3</sub> / DMSO electrolyte was considered the most favourable for ORR kinetics. The authors calculated the thermodynamic properties of ORR reactions occurring during the formation of superoxidants (O<sub>2</sub><sup>-</sup>) ions and the only discharge products lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) and lithium oxide (Li<sub>2</sub>O). [144]

The cell consists of a lithium-metal anode, a buffer layer of 4 M lithium-bis-imide (fluorosulfonyl) -imide in ethylene glycol-dimethylether and an activated MnO<sub>2</sub> air electrode. As a separating agent between lithium

anode and aqueous electrolyte, a bonded water-intransparent LANTP film with a small amount of epoxide resin was used. The conductivity and 3-point bending strength of the film was  $9.1 \times 10^{-4} \text{ S cm}^{-1}$  at  $25^\circ \text{ C}$  and 100 MPa. [145]

Watery Li-Air Batteries have attracted much attention due to their high theoretical energy capacities, but although they are still in the beginnings of research, the reported energy capacities are far from what was theoretically predicted. The addition of  $\text{LiClO}_4$  in the aqueous electrolytes slightly reduced the discharge voltage to 3.3 V, but drastically reduced the internal resistance of the battery to  $35.4 \text{ cm}^{-2}$ . [146]

N-Methyl-2-pyrrolidone (NMP) is a solvent for the non-hydrogen electrolyte of Li-Air Batteries. Oxygen reduction reactions (ORRs) and oxygen oxidation reactions (OER) are investigated on Au and glassy carbon electrodes (GC) in NMP-based electrodes. Raman and X-ray photoemission spectra are used to detect the species during the cell cycles on the electrode surface. [147]

The operating voltage of the lithium-air fuel cell decreases linearly with increasing current density, mainly due to the ohms limitation. Concentrations in the range of 0.5 to 1.0 m are considered as suitable parameters for the aqueous  $\text{LiOH}$ -electrolytes. [148]

Li-Metal can be reduced by factors such as irregular Li strips, Li-Dendrite growth and the growth of a solid electrolyte intermediate phase (SEI). The operation of the Li-Luft battery in the ambient air remains a challenge due to the possible occurrence of parasitic reactions to Li-Metal with moisture and other impurities diffused from the outside air. In this work, a protected Li-Electrode (PLE) consisting of Li-Metal, which is coated with a two-layer lithium phosphoroxynitride (LIPON) / aluminium-substituted lithium lanthanantanoate (A-LLTO)-Festrestrolyte. [149]

Electrolytes with polymer additives are considered as promising electrolyte systems with many advantages over non-hydraulic liquid electrolytes. The improvement of electrochemical properties was attributed to the positive effect of polymer additives on the inner resistance of the cells. A molar of the EMITFSI-LiTFSI-electrolyte showed a low and stable electrode resistance of  $47.4 \cdot \text{cm}^{-2}$  and a specific capacity of  $2.5 \text{ mAh g}^{-1}$  after 10 cycles. [150]

An ether-based electrolyte with TEGDME /  $\text{LiPF}_6$  has been optimised, with low viscosity and high ionic conductivity. TEGdME has been added to polymeric additives such as PETO and PVDF to promote the resolution of lithium peroxide excretions that formed during the discharge process and to protect the anode. [151]

Li-O<sub>2</sub> battery electrodes based on amorphous carbon materials have been analyzed by ex-situ Fourier Transformation Infrared Spectroscopy (FTIR) for products formed on the electrode-electrolyte border surface during the electrochemical cycle against metallic lithium. This analysis shows that FTIR spectroscopy offers several valuable capabilities. It identifies lithium oxygen species and lithium carbonate as the most important species that can be observed on cyclic electrodes. [152]

## 9.2 Literature Reviews

### 9.2.1 New composite polymer electrolyte for lithium air batteries

Lithium-Air Batteries (oxygen batteries) as a novel battery system have a huge theoretical specific energy of  $11,140 \text{ Wh kg}^{-1}$  without O<sub>2</sub>. Lithium-oxygen-anhydrous batteries, of which Jiang and Abraham first reported, had an operating voltage of 2.4 V and a specific energy density of 250-350  $\text{Wh kg}^{-1}$  [1] Using cobalt-phthalocyanin as a catalyst, an adequate Colombian efficiency was achieved during the cycle. Hydrophobic ionic liquids were first described by Kuboki et al. due to their hydrophobic and negligible vapour pressure as a promising candidate for waterproof electrolytes for lithium-air batteries [10]. The cobalt phthalocyanine oxygen catalyst cell showed a huge discharge capacity of  $5360 \text{ mAh g}^{-1}$  carbon at a discharge current density of  $0.01 \text{ mA cm}^{-2}$ . [139]

### 9.2.2 Li-air rechargeable battery with phosphate buffer catholyte

Li-Air batteries offer the highest theoretical energy density of all known batteries and compete with gasoline (13,000 Wh/kg) due to the high capacity of the electrodes and the high operating voltage of the Li-O<sub>2</sub> pair. Metal air batteries have the potential to provide solutions for these applications. Aprotic lithium oxygen cells are operated in pure oxygen or a mixture of dry oxygen and nitrogen. The humidity in the environment can degrade the non-hydrous electrolyte and the lithium-metal anode. Visco et al. [8] suggested the use of water-resistant solid NASICON electricity ( $\text{Li}_1 + x + y\text{Al}_x\text{Ti}_2 - x\text{Si}_y\text{P}_3 - y\text{O}_{12}$  or LTAP) for the protection of lithium metals. This idea was applied to many dual-electrolyte lithium cells, including Li-Luft cells [9-11] Phosphoric acid is a strong acid and could attack the LTAP membrane if used exclusively. However, a phosphate buffer solution consisting of a mixture of 0.1 M phosphoric acid and 1 M  $\text{LiH}_2\text{PO}_4$  with a net pH of 3.14 at room temperature can avoid corrosion. [140]

### 9.2.3 Liquid polymer electrolyte for quasi-solid state lithium air batteries

The theoretical specific energy is 3505 W h kg<sup>-1</sup> and is therefore about eight times higher than in lithium-ion batteries. It is suitable for the battery requirements of electric vehicles. However, the authors are still far from the practical application of Li-Air Technology in addition to laboratory studies. Conventional liquid electrolytes are not suitable for LABs due to inadequacies such as slight discharge, inflammability and corrosion of lithium metal. Gelpolymer electrolyte consists of polymers (such as poly (ethylene oxide) (PEO), poly (vinyl alcohol) (PVA) poly (methyl methacrylate) (PMMA), PVdF-HFP, etc.) is the polymer of choice for Bellcore's plastic Li-ion batteries. EMITFSI is not volatile, non-flammable, high thermal stability, large electrochemical windows and high ionic conductivity. It is hydrophobic, chemically stable in a damp atmosphere, so it can prevent the evaporation of electrolyte and the corrosion of anodes (even providing stable lithium deposition/-solution). In this study, the authors synthesized the ionic liquid polymer electrolyte (the ILP-based electrolyte) by adding PVdF-HFP / LiTFSI EMITFSI (specific volume ratio) and assembling the quasi-solid LABs. The electrochemical properties were investigated using raster electron microscopy (REM), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry. [141]

### 9.2.4 Li-air fuel cell with recycle aqueous electrolyte

Global warming and depletion of fossil fuels accelerate research efforts to search for alternative energy sources. Clean electrochemical energy generation is considered to be a sustainable and environmentally friendly system. The lithium-ion battery with the highest energy density among the available rechargeable batteries already dominates the market for portable consumer electronics. However, even this energy density cannot satisfy the industrial needs such as energy sources for the transport and residential sectors. The Li-Air battery with the LiSICON plate in the hybrid electrolyte still suffers from the following intrinsic disadvantages: i) Dendrite growth of lithium during the charging process leads to a reaction with the plate. ii) The additional water for the LiOH solution limits the energy density of the LiOH. ii: The additional solution of LiOH limits the amount of LiOH solution, and i: The LISICON plate is unstable in the highly alkaline aqueous solution. The practical application of the system depends on the solution of these three problems. [142]

### 9.2.5 Electrolyte level change in lithium air battery

A number of continuous-scale models have been developed to investigate the detailed charging and transport operations within a Li-air battery. Li-Air batteries (Li-Air) are considered promising candidates for the next generation of secondary-power supplies for portable devices and electric vehicles. During discharge, the metallic lithium of the anode is converted into lithium ions. In the micropores of the cathode, oxygen reduction reaction (ORR) occurs, which consumes lithium ions and electrons. For each mol lithium consumed, 0.5 mol  $\text{Li}_2\text{O}_2$  is produced. This means a reduction in the volume of the solid phase by 23.6% for each unit of

lithium anode consumed during discharge. This free space must be replaced by the liquid electrolyte, thereby reducing the electrolyte level. The Li-Luft-Knopf cell is usually located on a fixed surface with breathing holes exposed to an air chamber. In order to compensate for the change in volume, a spring is placed under the Anode current collector in the cell, which ensures close contact between anode, separator, cathode and current collectors. This effect is mentioned by Yuan et al. [13] as an unresolved problem. In most experimental studies in non-fluid Li-air batteries, volatile solvents such as 1,2-dimethoxyethane (DME) and acetonitrile (ACN) have been used to achieve high oxygen solubility and diffusibility. Evaporative solvent escapes the battery from the atmosphere and is lost in ambient air. Lithium-air batteries normally interact with their environment by consuming or releasing oxygen during the discharge and charging cycle. The calculation range of most existing Li-air battery models is usually bound to the interface between cathode and ambient air. The diffusion of oxygen from the environment into the cell and the diffusion of solvents into the environment were not taken into account in earlier studies. The Arbitrary Lagrangean-Eulerian (ALE) method is used to describe the deformed area of calculation and to track the moving electrolyte level. The air chamber that the cell supplies oxygen is included in the calculation area. The simulation results, both with or without consideration of these effects, are compared and discussed. [143]

### 9.2.6 Oxygen reduction reaction (ORR) kinetics through different solvents

Scientists have developed renewable energy resources alternately with conventional sources to solve the main problem of increased energy demand due to population growth and the environmental problem of global warming. Alternative energy sources are photovoltaics, batteries, fuel cells and fuel cells, electrochemical cells, capacitors, hydropower, wind power, geothermal etc. Li-Air batteries use the oxygen in the air as a positive electrode with a high energy density about ten times as strong as Li-Ion batteries. However, from the practical implementation of Li-Air batteries, the inventor is still far away. Li-Air batteries use oxygen in the air as a positive electrode. Oxygen cells have many problems such as poor cycle life, high charge and discharge overpotentials, low power density and secondary reactions with N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O during ambient air operation. Main factors are the electrode passivity due to irreversible product deposits, a high overpotential for their decomposition and oxidative instability of the electrolyte. A variety of electrolytes have been experimentally tested on Li-Air batteries, including organic carbonates, esters, nitrile, amide and dimethyl sulfoxide (DMSO)-based electrolytes. Organic carbonates have been discarded due to their rapid decomposition during discharge. The ORR-kinetics in non-aqueous electrolytes in Li-Air batteries strongly depend on the composition of the electrolyte solvent. The solution structure hypothesis of the interaction of Li<sup>+</sup> with O<sub>2</sub> is widely used to investigate the effects of solvents, ions and neutral additives. The solution (small amount of water) plays a key role in the cyclicity and capacity. However, a complete understanding of the reaction mechanism of cell discharge and rechargeability is still lacking. In this work, the authors performed DFT calculations for the first time to investigate the role of the solvent of non-aqueous electrolytes with stable salt LiCF<sub>3</sub>SO<sub>3</sub> [31] with respect to ORR kinetics in Li-Air Batteries. The authors analyzed the structural, vibrational and thermodynamic properties of electrolytes both in the gas and in the solution phase (water). [144]

### 9.2.7 Aqueous lithium-air batteries with a lithium-ion conducting solid electrolyte

The range of electric vehicles with conventional lithium-ion batteries is too low compared to those of an internal combustion engine. In this decade numerous types of highly developed batteries, such as water-free lithium-air [2,3] and lithium-sulphur batteries, have been proposed and fully investigated. Also serious problems such as the decomposition of the non-aqueous electrolyte by oxygen-reduction product, the oxidation of carbon electrode during the charging process and the blocking of H<sub>2</sub>O and CO<sub>2</sub> in the air still need to be solved. The key material for aqueous lithium-air cells is the water-stable lithium-ion conductive solid electrolyte. In this study, the authors investigated the cell performance with a NASICON-type lithium-ion

conductive electrolyte film of  $\text{Li}_1 + x + y\text{Al}_x (\text{Ti}, \text{Ge})_{2-x}\text{Si}_y\text{P}_3 - y\text{O}_{12}$  (LANTP) using a tape casting process. [145]

### 9.2.8 Effects of aqueous electrolytes on the voltage behaviors

Li-ion batteries are limited by the use of Li-intermittent calculation electrodes such as  $\text{Li}_x\text{C}_6$  and  $\text{Li}_1 - x\text{CoO}_2$  [1]. With air ( $\text{O}_2$ ) as a positive electrode and Li-metal as a negative electrode, a Li-Air battery has been developed with a specific energy density of between 5789 and 11248 Wh - 1. Li /  $\text{O}_2$  in non-hydraulic electrolytes [2] Li /  $\text{O}_2$  is a key component of the electrolytes of a liquid form of liquid electrolytes. Li /  $\text{OP}_2$  is used to identify molecules that occur in a form of water that does not have a liquid form. Seawater (pH 8.2:  $4\text{Li} + \text{O}_2 + 2\text{H}_2\text{O} = 4\text{LiOHE} = 3.79 \text{ V}$ ) Seawater is found in seawater waters all over the world. Seawater is a mixture of water and water with a temperature of 8.5 degrees Celsius. In 1996, the first non-aqueous Li-Air-Electrolyt battery was presented with a Li-organic Liquid-Electrolyt-Air-Electrode-Structure, which achieved in the air and in pure oxygen-atmosphere energy capacities of 1600 mAh g<sup>-1</sup>. Characteristic for these energy capacities was the weight of the carbon catalyst, since a decrease in the discharge voltage was often caused by the carbon electrode that could be suffocated by  $\text{Li}_2\text{O}_2$ . Non-fluid electrolytes allow humidity to penetrate the Li-Metalanode and decontaminated the Li-Metal. The  $\text{Li}_2\text{O}_2$  and  $\text{LiO}_2$  discharge products are insoluble in the non-cracking liquid electrolyte, and thus the product particles gradually clog the porous air electrodes, which ultimately leads to poor cycle life. The theoretical specific energy density of LiOH batteries in aqueous solutions is about 5789 Wh kg<sup>-1</sup> in relation to the weight of the battery. LiOH's solubility in water is also a limitation for LiOH to achieve high capacity [18] Compared to a non-water battery, better voltage efficiency and a longer life span should be possible. Recently, watery Li-air batteries were reported using a solid LiGC-electrolytes. Wang et al. [19] also proposed a new Li-Air fuel cell, which uses metallic copper as a catalyst for the electrochemical reduction of  $\text{O}_2$ . The LiGC electrolyte is the only ceramic fast electrolyte currently commercially available for use in aqueous Li-Air batteries. While there are worldwide efforts to develop Li-Ion leading ceramics that are stable in strong laurel or acid solutions, an alternative approach is to optimize the electrolyte and reduce its high pH value. weak alkaline aqueous solutions ( $\leq 0.05 \text{ M}$ ) were first used as electrolytes for a Li-Air battery of the following structure. Platinum was selected in this study as an electric catalyst for the air electrode because Pt is considered as a benchmark active and stable catalyst for the oxygen reduction reaction via a direct 4-electron pathway [21]. [146]

### 9.2.9 N-methyl-2-pyrrolidone as a solvent

Li-air batteries based on aqueous electrolytes could be the basic configuration for the future propulsion system of hybrid electric vehicles and electric vehicles [1-3]. Before this promising technology becomes reality, however, many scientific and technical challenges need to be met. Organic carbonate solvents are commonly used electrolytes in Li-ion batteries. During the discharge process, the products on the cathode were not  $\text{Li}_2\text{O}_2$  in organic carbonate electrolytes, but various alkyl carbonates.  $\text{CO}_2$  is the predominant oxidation product, which has been proven by in-situ differential electrochemical mass spectrometry (DEMS). The superoxide anion radical ( $\text{O}_2^-$ ) is a radical. It is the first radical found in the universe. In the past it has been found that there is a radical. The radicals are known as  $\text{O}_2^-$ , the second radical in the most extreme form of the world. The nucleophile attack of  $\text{O}_2^-$  ( $\text{O}_2^-$ ) as the primary intermediate in aprotic media during the oxygen reduction process is probably the reason for the decomposition of carbonate solvents. Bryantsev et al. showed that the nucleophile attack of  $\text{O}_2^-$ . Many other electrolytes have been studied for lithium-air batteries, especially electrolytes based on ether. McCloskey et al. reported that  $\text{Li}_2\text{O}_2$  was the main discharge product in dimethoxyethane (DME)-based electrolyte. Furthermore, the authors observed that aether molecules were unstable for the species of  $\text{CO}_2$  reduction. The increased stability of this solvent compared to the oxygen reduction type was attributed to the functional group of the ether. In addition to organic solvents, electrolytes based on ionic liquids were also investigated for lithium-air batteries. Kuboki et al. investigated the perfor-

mance of Li-O<sub>2</sub> batteries using an ionic liquid as electrolyte in the environment. In this article, the authors first identified the various oxygen reduction reactions (ORRs) and oxygen oxidation reactions (OERs) to gold (Au) and glassy carbon electrodes (GCs) in NMP-based electrolytes. The authors then examined the composition of the deposits that form during the cycles on the surface of the air electrode. [147]

### 9.2.10 Alkalinity and temperature on the performance of lithium-air fuel cell with hybrid electrolyte

Metal-air batteries use inexhaustible oxygen in the air as reagent instead of transporting the necessary chemicals within the battery. Metallic lithium is the most negative metal and has at the same time an ultra-high capacity of 3860 mAh g<sup>-1</sup>. In 1996 the first lithium-air battery with organic electrolyte was introduced, which aroused great interest due to its superior energy density. A hybrid electrolyte combines air cathode in aqueous electrolyte and metallic lithium anode in organic electrolyte with a water-stable lithium-super-ion lead glass plate (LISICON). This lithium-air fuel cell can deliver a high theoretical energy density of 5698 Wh kg<sup>-1</sup>. At the same time, Li<sup>+</sup>, the oxidation product of lithium metal in organic electrolyte, diffuses over the LISICON plate and forms LiOH. OH concentration can directly affect the energy and performance of the lithium-air fuel cell through the following three aspects: (i) the thermodynamic potential of oxygen reduction; (ii) the catalytic activity of the air catalyst electrode; (iii) the conductivity of the solution. On the other hand, the ambient temperature also has a significant influence on the cell system. [148]

### 9.2.11 Lithium degradation in lithium-air batteries

Li-Air batteries meet the requirements of key markets such as portable electronic devices, intelligent grids and electric vehicles. Due to their very high specific capacity (3862 mA h g<sup>-1</sup>) and its low electrochemical potential (3.04 V vs. SHE) Li-Air batteries is known as the ideal anode material that can be extracted from the environment without further delay. Li-metal comes into contact with a polar aprotic electrolyte, it reacts quickly with the electrolyte and forms a passive solid electrolyte interphase (SEI) layer on the surface of the Li due to the highly reactive nature of the Li-metal. The created SEI layer is useful to mitigate the corrosion of the metal. However, the uneven chemical composition of the layer can cause an uneven distribution of electricity on the electrode surface, which is responsible for the growth of Li-dendrites and the final electrical short circuit. To date, considerable efforts have been made to address the problems inherent in the Li-Metal anode by modifying the liquid electrolyte or using a solid electrolyte. Nevertheless, such methods can trigger the formation of a brittle SEI layer. It is not easy to prevent Li-Metal from reacting with harmful species such as H<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub> that can diffuse all from the outer atmosphere. Lithium-Lanthan titaniumate (LLTO) is considered one of the fastest Li-Ions leading solid electrolytes. LLTO ceramics were developed into an A-LLTO ceramic whose total conductivity was increased by up to  $3.17 \times 10^{-4}$  S<sup>-1</sup>. In this study, the authors investigated the degradation of a protected Li-Electrode (PLE) in the presence of two-layer solid electrolyte LiPON/A-LLTO in a Li-Air cell, which is operated in pure O<sub>2</sub>-Gas or ambient air. In this study, the entire process of initiating and growing Li-Dendrites is presented in detail with an optical microscope. [149]

### 9.2.12 Stability effect of polymer-based additives on EMITFSI-LiTF

The theoretical energy density for the cell response of the Li-Air Battery is 11,000 Wh kg<sup>-1</sup> and is thus 5- to 10-fold higher than in Li-Ion batteries. However, the practical application of the technology in the development is faced with many challenges. Generally, lithium-Air Batteries are believed to be the best alternative. The role of the electrolyte is of great importance in the lithium-air battery systems. Due to its superior properties there is an increasing interest in ionic liquids, especially in Li-air systems. Ionic liquids are defined as melted salts at room temperature, which have many incomparable properties besides other basic electrolyte properties such as their stability. The main problem of the Li-Luft cell is the decomposition of the electrolytes. The inability of frequently used electrolytes based on carbonates in Li-Luft cells has been investigated by several

research groups. Thermal stability, ionic conductivity and the resistance of electrolytes are still the biggest challenges. EMITFSI was proposed by Kuboki et al. as a desired electrolyte component with low viscosity and thermal properties. The effects of polymer additives on EMITFSI-LiTFSI-electrolytes have been studied on the performance of lithium-air batteries. Only a small amount of 0.1% by weight. PVDF and PEO-addition have significantly increased the cyclicity of EMIT FSI-LATK-electrolytes. [150]

### 9.2.13 High stable Li-air battery cells by using PEO and PVDF additives

The latest developments in battery technology are based on the need for high energy-density batteries for automotive applications. The reversible Li-Air Battery has the potential to revolutionise energy storage for hybrid and electric vehicles. The theoretical specific energy density corresponds to that of gasoline [1]. Aprotic electrolyte-li-air batteries have attracted great attention due to their very high theoretical specific energy. The removal of all important components of the O<sub>2</sub> electrode during the cycle has affected the efforts to develop this technology for practical purposes. The development of a stable electrolyte for rechargeable aprotic Li-O<sub>2</sub> cells is considered one of the greatest challenges. The development of non-hydraulic Li-Air or Li-O<sub>2</sub> batteries presents a number of challenges, such as the selection of an efficient and stable electrolyte, the reduction of charging voltage hysteresis, the design of catalysts and substrates to achieve high capacity and stability. There is more recent experimental and theoretical evidence that the organic carbonates used in Li-ion batteries are usually not stable against oxygen-reduction reactions during discharge. Li<sub>2</sub>CO<sub>3</sub> is not electrochemically reversible in an aprotic Li-air battery system, which limits its rechargeability, cycle life and stability in lithium-air batteries (22.12). Ionian liquids at room temperature (RTILs), which are mostly used in lithium-ion batteries, have also been proposed as suitable electrolyte for Li-O<sub>2</sub> cells. RTILs exert a beneficial effect on the kinetics at the cathode of a Li-Air cell. Ether and Glyme are considered as good candidates as solvents for the non-watery battery, as they can have relatively low vapour pressure. TEGDME's ether-based solvent (or tetraglyme) attracted the attention of the Li-O<sub>2</sub> battery. Polymer additives aimed at investigating the performance of lithium-air batteries. The authors examine the effects of electrolyte composition on the capacity and cyclical capacity of polymer-enhanced electrolytes on TEGdME/LiPF<sub>6</sub> basis. [151]

### 9.2.14 Electrode-electrolyte interface characterization of carbon electrodes

The progress in today's portable consumer electronics, electrical tools and electric vehicles will depend largely on the fast availability of rechargeable batteries. In this respect, a detailed understanding of the chemical reactions to the respective electrode-electrolyte boundaries is essential to rationalise the limitations and capabilities of both established and emerging battery technologies. Fourier-transformation-infrared spectroscopy is one of the most valuable instruments for investigating such interface reactions. This is particularly true for Li-O<sub>2</sub> battery technology, in which by definition solid, dissolved and volatile species are involved in battery chemistry. During discharge, lithium ions that are dissolved from a solid lithium electrode, with volatile/dissolved molecular oxygen, react to an appropriate electronic conductive, solid matrix material. Positive Li-O<sub>2</sub> battery electrodes at different charging conditions as well as mixtures of known carbon and lithium salts have been examined using ex-situ-FTIR spectroscopy with diffuser reflection. The results are discussed in the light of the analytical concentration requirements that must be met to provide useful information on battery chemistry. [152]

## 9.3 Conclusions

The innovative hydrophobic LiTFSI PMMITFSIFSIL silica-PVdF-HFP polymer compound electrolyte was synthesized and used in lithium-air batteries. The ion conductivity of the composite electrode was  $1.83 \times 10^{-3}$  S cm<sup>-1</sup>. The compact structure and the stable interface resistance favour a long life when the cell is tested in the ambient atmosphere. [139]

The cell has a high discharge capacity of 221 mAh g<sup>-1</sup> and an energy density of 770 Wh kg<sup>-1</sup> for H<sub>3</sub>PO<sub>4</sub>. The phosphate buffer solution proves to be promising Cathodic for this kind of novel dual-electrolyte Li-air batteries. [140]

In this work the authors have shown the production of the novel flexible polymer electrolytes under different EMITFSI integrations and put together the quasi-solid electrolytes. The authors have shown that the ILP3-based electrolyte has good compatibility with Li-Anode and Air-Cathode, which dramatically improves the first full discharge capacity. The novel polymer electrolyte with the installation of EMITFSI ion liquid (especially with 60% addition) has excellent electrochemical performance. The ILP-based electrolyte is still in the pre-stage, the Li<sup>+</sup> transport number and the cyclic stability need to be improved in the follow-up work. [141]

A newly designed Li-Air fuel cell integrates an energy conversion unit and a product recycling unit. This construction leads to continuous reduction of inexhaustible oxygen from the air and improves the stability of the LISICON plate. Meanwhile, the new structure can also realize product recovery and has the potential to deliver high energy. [142]

To track the electrolyte level during discharge, a physical model of a 2-D lithium-air coin is developed, which calculates the deformation of the network as well as the position of the electrolyte surface and its speed. The diffusion of the solvent vapour in the cell GDL and in the air chamber is also considered. The electrolyte surface velocity caused by the evaporation of solvents is highest at the beginning of discharge. The surface speed imposed by the solid volume gradually decreases due to increased Li<sub>2</sub>O<sub>2</sub> deposition and reduced porosity. It then decreases to zero when the air chamber is saturated with solvent vapour. A Li-Air Battery Model would predict a higher cathode-specific discharge capacity by including the effect of a waste of the electrolyte level. In the cases examined in this article, the increase for a cell using DMF-based electrolyte may be up to 22.5% and for 14.9% using TEGDME. The proposed model describes a different Li<sub>2</sub>O<sub>2</sub> distribution profile than in previous studies. If the electrolyte level decreases during discharge, the position of the largest Li<sub>2</sub>O<sub>2</sub> separation gradually moves with the surface of the cathode. The final distribution of the Li<sub>2</sub>O<sub>2</sub> volume share shows a peak value in the centre of the cathode. The air chamber has a significant influence on the discharge capacity of cells that use electrolytes on a DMF basis. The discharge capacity increased by 72% when the radius of the chamber was increased from 5 cm to 15 cm. At the end of the discharge, 33.8% of the cathode volume is exposed in the air instead of being immersed in electrolytes. [143]

The calculation of the functional density theory (DFT) was performed to investigate the role of the solvent in terms of the oxygen reduction reaction (ORR) in Li-Air Batteries. DMSO is the most stable solvent compared to other solvents DME and MeCN. The infrared spectroscopic (IR) data confirmed the formation of Li<sub>2</sub>O<sub>2</sub> and Li<sub>2</sub>O on the micro-electrode surface, assuming that the electrolyte LiCF<sub>3</sub>SO<sub>3</sub> / DMSO is the most favourable for ORR kinetics. [144]

Aqueous lithium-air battery with the high-lithium ion-conducting solid electrolyte Li<sub>1.3</sub>Al<sub>0.5</sub>Nb<sub>0.3</sub>(PO<sub>4</sub>) and an activated MnO<sub>2</sub> air electrode was successfully unloaded and charged under open atmosphere at room temperature. A high air electrode capacity of 1750 mAh g<sup>-1</sup> was observed at 0.32 mA cm<sup>-2</sup> and 25 °C. [145]

The Li-Air battery showed discharge and charge voltages of 3.53 V and 4.19 V at 0.05 mA cm<sup>-2</sup> respectively. It was found that the discharge voltage increased at lower concentrations of LiOH in the aqueous electrolyte due to higher oxygen solubility at lower alkaline concentrations. Experiments show that the modification of the aqueous electrolyte could be the cause of the high voltage efficiency of the Li-air battery. This approach could be useful for the pH control of the electrolyte. However, the various chemicals in the electrolytes need further research. [146]

The basic electrochemical reaction is a one-electron transfer process that generates O<sub>2</sub><sup>-</sup> / O<sub>2</sub>. Although the presence of Li-Salts strongly affects the behavior of ORRs and OER, the reaction of the reaction process that O<sub>2</sub><sup>-</sup> / O<sub>2</sub> produces is. Au atoms would catalyse the oxidation of Li<sub>2</sub>O<sub>2</sub>, whereby no passivity of the gold electrode surface can be detected by multiple cycles. Other chemical reactions, such as nucleophilic reactions between O<sub>2</sub><sup>-</sup> and O<sub>2</sub> pairs, remain. The increased chemical stability of NMP compared to oxygen reduction species

results in good performance of NMP-based cells. In addition, it is very important for further use of NMP-based electrolytes in rechargeable Li-air batteries with high cyclic performance to prevent the decomposition of NMP on the surface of porous air electrodes. [147]

The operating voltage of the lithium-air fuel cell decreases linearly with increasing current density, mainly due to the ohms limitation. The electric drive and internal resistance of the cell decreases with increasing LiOH concentration in aqueous electrolytes. As regards efficiency, increasing the LiOH concentration over 0.5 m is not effective for increased performance. [148]

LiPON / A-LLTO two-layer solid electrolyte with adequate ion conductivity as protection for a metallic Li-electrode. The Li-Luft cell, which uses the protected Li-electrode (PLE) with the solid electrolyte, showed improved cyclability both in operation with pure oxygen and in the standard atmosphere. [149]

Non-fluid rechargeable Li-Air cells with 1 M EMITFSI-LiTFSI, EMITFSI, 1 M. EMITFSI and 1 M. EMITESI-LiTFSI-0.1 % PVDF and. EMITS-PEO electrolytes were assembled and electrochemical tests were conducted. The presence of polymeric additives in the electrolyte not only ensured good safety, but also showed better compatibility with active and air-side electrodes. [150]

New electrolyte compositions have been prepared for Li-O<sub>2</sub> cells with graphene / 30 % w/w  $\alpha$ -MnO<sub>2</sub> air breathing cathode and Li-Metal anode. Electrochemical tests have shown that TEGDME-LiPF<sub>6</sub>-Electrolyt has low discharge capacity and low cycle life. [151]

Lithium oxygen species and lithium carbonate are the most important species that can be observed by ex-situ-FTIR spectroscopy in amorphous carbon-based Li-O<sub>2</sub> cell positive electrodes after discharge. The strong infrared absorption of carbon-containing materials has a major influence on the detectability of important intermediate and product types on the electrode-electrolyt borderline. [152]



## **Part IV**

# **Reference**



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