Two-dimensional layered cobalt sulfide derived from metal organic framework (MOF) as anode for lithium-ion batteries

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**TWO-DIMENSIONAL LAYERED COBALT SULFIDE
DERIVED FROM METAL ORGANIC FRAMEWORK (MOF)
AS ANODE FOR LITHIUM-ION BATTERIES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2020

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2020

Statement of Originality

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Abstract

Lithium-ion batteries (LIBs) as clean electrochemical energy devices have gained much attention because conventional fossil fuels and renewable energies are having limitations. LIBs can be applied in areas such as energy storage power stations, electronic vehicles, and portable electronic devices (smartphones, laptops, etc.). However, current LIBs in the market could not meet the ever-growing demand due to the capacity of the commercial graphite anode material has already reached its theoretical limits (372 mAh g^{-1}). Thus, developing alternative anode materials with a higher specific capacity, longer cycle life, better cycling stability, and more outstanding rate capability holds great promise. Nowadays, transition metal sulfides have attracted great interests as LIBs anode materials, due to their higher specific capacity ($500\text{-}900 \text{ mAh g}^{-1}$), moderate rate capability and cycling stability. Among these, cobalt sulfides (CoS) have advantages including relatively high theoretical capacity (589 mAh g^{-1}), abundant resources, and low cost.

However, CoS as anode materials also face challenges including low electronic conductivity, capacity attenuation due to large volume expansion during cycling. The motivation of this research is to improve CoS's capacity fading issue by reducing the large volume expansion during cycling, as well as to increase their electric conductivity.

In this research, two-dimensional layered cobalt sulfides (CoS) were prepared using a facile two-step in-situ formation method: Synthesizing cobalt metal-organic framework (Co-MOF) as precursor first, followed by sulfidation/carbonization at high temperatures. This novel MOF-converted CoS could fulfill nano-sizing and composition with carbon in one shot. Four calcination temperatures were investigated, samples synthesized at 700°C appear to have the best cycling stability and rate capability. The discharge capacity of the 2nd cycle is 828.1 mAh g^{-1} , while capacity still has a 50.9% retention rate after 100 cycles under the current density of 100 mA g^{-1} , which is 421.5 mAh g^{-1} . The reversible capacities of samples sulfurized at 700°C are 700.45, 586.45, 455.60, 364.20, and 273.29 mAh g^{-1} at current densities of 100, 200, 500, 1000, 2000 mA g^{-1} , respectively. When reverting back to 100 mA g^{-1} , the capacity of CoS increased back to $618.68 \text{ mAh g}^{-1}$,

implying good reversibility. During the second cycle of the galvanostatic charge-discharge cycling test, the coulombic efficiency is as high as 93.6%. The discharge capacity is higher than the theoretical capacity of graphite (372 mAh g^{-1}), indicating that samples in this research are a promising candidate for the anode of LIBs.

Compared with bulk materials, nano-structures are more stable upon reactions, resulting in smaller volume change. Moreover, the nano-sizing structure provides a high surface to volume ratio and more active sites for Li^+ storage, leading to the capacity increase. The short Li^+ diffusion path across nano-particles allows easy ion diffusion that enhances the power density and high electron transfer rate. With the incorporation of carbon, a carbon layer is wrapped around CoS nano-particles. Not only could this carbon layer provide mechanical support to prevent large volume expansion, but also it increases the electric conductivity of the anode materials, resulting in a better electrochemical performance of LIBs.

Lay Summary

Conventional energy resources have many limitations. Fossil fuels can cause environmental pollutions. Greenhouse gases are released by combustion of coal, petroleum and natural gas, thus leading to global warming problems. Conventional energy is also facing crisis, because fossile fuels are finite resources and are in danger of being depleted upon world's increasing energy demand. People are thinking of using renewable resources as a replacement. Solar energy, wind energy, geothermal energy and hydropower energy can cause much less pollution. However, they highly depend on natural conditions like climate change or geographic locations.

Lithium-ion batteries (LIBs) can fill in the gap as energy storage devices. They have advantages like high safety performance, long life, wide operating temperature range and environmental friendly. LIBs can be used in many areas, such as energy storage powerstation, electric vehicles and portable electronic devices (power banks, laptops, smart phones etc.). However, LIBs also have limitations, graphite as the conventional anode material is not sufficient to meet the high energy demand in modern life. Thus, there is a need to select or design anode materials with longer life, which can better fulfill the energy demand and are free from safety concerns. Transition metal sulfides are one of those alternative anode materials, among which, CoS has abundant resources, low cost and can better fulfill the energy demand compared with graphite. However, CoS also have disadvantages such as low electronic conductivity and large volume expansion, resulting in shorter usage life.

In order to reduce the large volume change of CoS as anode material and increase electric conductivity, two strategies were used: Nano-sizing, and composition with carbon. By synthesizing a metal-organic framework template, followed by sulfurization at high temperature. The products can achieve nano-sizing and composition with carbon in one shot. The in-situ two-step method is very convenient and easy to apply when synthesizing CoS anode materials which preserve the structure of the template. The sulfurization temperatures were being investigated to achieve an optimized one.

In conclusion, two-dimensional layered cobalt sulfide derived from metal organic template was successfully synthesized, and exhibits high potential to be the anode material candidate for LIBs. By using the two-step in situ synthesis method, the volume change of CoS is reduced, the conductivity is increased, and the overall electrochemical performance is increased. Among different sulfurization temperatures investigated, 700°C appears to be the optimized choice.

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Abbreviations

ATR	Attenuated Total Reflectance
BEI	Backscatter Electron Images
BET	Brunauer-Emmett-Teller
Co	Cobalt
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
EDX	Energy-dispersive X-ray spectroscopy
FIB	Focus ion Beam
FTIR	Fourier Transform Infrared Spectroscopy
FESEM	Field-emission Scanning Electron Microscopy
FETEM	Field-emission Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
LIBs	Lithium ion Batteries
MOF	Metal-organic framework
S	Sulfur
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

Fossil fuels as conventional energy resources, such as coal, petroleum and natural gas, would produce greenhouse gas while burning, resulting in severe global warming problems. Renewable resources like solar energy, wind, geothermal energy and hydropower can cause much less pollution and offer sustainable energy. However, those resources highly depend on natural conditions. Thus, concerning both the energy demand and ecological issues, lithium ion batteries (LIBs), as clean electrochemical devices, are needed in everyday life. Applications of LIBs are portable electronic devices (e.g., smart phones and laptops), hybrid electric vehicles and electricity storage units[1]. Nevertheless, the current LIBs still could not satisfy the requirements of growing mass markets of portable power supplies and electric vehicles. Graphite carbon (372 mA h g^{-1}) as the conventional anode material has almost reached the theoretical limit. Thus, developing electrode materials that possess higher specific capacity, longer cycle life, stabler cycling condition and more outstanding rate capability is the focus of nowadays LIBs researches[2].

1.1 Background

Among state-of-art anode materials for LIBs, transition metal sulfides (M_xS_y , $M=Co, Zn, Ni, Mo, Fe$, etc) have become prominent candidates due to their relatively higher specific capacity ($500-900 \text{ mAh g}^{-1}$) and better electronic conductivity compared to their counterpart metal oxides. Metal sulfides are widely used in areas like energy storage and catalysis. They follow the mechanism of the reversible conversion reaction[3].

However, the metal sulfides anode materials still face capacity fading issue, and conductivity is low during cycling, which is due to the pulverization caused by large volume expansion during lithium insertion and extraction. Moreover, polysulfide Li_2S_x ($2 < x < 8$) intermediates produced during lithiation could dissolve into the organic electrolyte, resulting in capacity attenuation [4]. Among the metal sulfides, cobalt sulfides ($Co_{1-x}S$) have attracted many interests because of their relatively high theoretical capacity (e.g., CoS : 590 mAh g^{-1}), abundance and moderate cost. Nevertheless, $Co_{1-x}S$ is affected by the same problems as other metal sulfides, such as collapse of structures and fading of electrical conductivity during discharging and charging process. Thus, applications of cobalt sulfides are limited in real world [5].

This research would like to base on current cobalt sulfides anode materials, combined with metal organic framework, also by optimizing the sulfurization temperature, to reduce the limitation mentioned above, so that to come up with a more promising candidate for LIBs anode applications.

Metal organic frameworks (MOFs) are porous materials which formed by self-assembly of transition metal ions and organic ligands [6]. Due to the merits like unique and tunable configurations, uniform pore sizes and distributions, and large surface area [7], MOFs have extensive applications in fields like catalysis, gas storage, adsorption and separation, chemical sensors and drug delivery. Through heat treatment, MOFs could be made into

hybrid materials like metal sulfides with carbon, metal oxides with carbon, metal phosphides with carbon, which make them promising templates and precursors to synthesize the transition metal compounds used in anodes in LIBs. The in-situ produced carbon during annealing process could restrict the excessive growth of metal sulfides/oxides/phosphides. Meanwhile, carbon encapsulated on the particle could enhance the electrical conductivity and mechanical stability. In addition, 2D MOFs nowadays are very popular because of the higher aspect ratio, larger surface areas and active sites that are more accessible on the surfaces. These advantages make 2D MOFs suitable to be applied in areas like gas separation and energy storage [8].

1.2 Hypothesis/Problem Statement

This thesis tests the hypothesis that when transition metal sulfides (taking Cobalt Sulfides as an example) are combined with MOF (Metal-Organic Framework), the new synthesized product would have higher capacity, better cycling stability and rate capability, compared with normal transition metal sulfides as LIBs. Moreover, the thesis validates the sulfurization temperature plays a critical role and will affect electrochemical properties of the anode materials.

To address the above mentioned limitations of conventional cobalt sulfides (or transition metal sulfides in general), one effective way is to design a novel porous nanostructure. Previous works have shown that the small particle sizes and high porosity level can provide extra volume to reduce the mechanical strain and alleviate the pulverization during the insertion/extraction of lithium ions [9]. The cycling stability and rate capability are improved because the diffusion path of lithium ions is shortened arising from nanoscale size compared to the bulk size, and the voids make lithium ions easily accessible. The second effective way is to blend the metal sulfides with conductive carbonaceous support, such as carbon nanotubes, porous carbon and graphene. The electrical conductivity is enhanced and the volume change could be accommodated by the carbonaceous matrix. Moreover, the matrix structure helps trap the polysulfide

intermediates, hindering polysulfides dissolving in organic electrolyte. The irreversible capacity decay is thus mitigated and leads to a prolonged cycling life.

1.3 Objectives and Scope

The present research is concerned with the synthesis and characterization of cobalt sulfides on metal organic framework template to enhance their performance to provide deeper understanding for applications as LIBs' anode material.

The objective/scope of the project are:

- To learn the background and mechanisms of lithium ion batteries and the electrode materials.
- To synthesize two-dimensional layered cobalt sulfides (Co_{1-x}S) derived from cobalt metal organic frameworks (MOFs) at various sulfurization temperatures.
- To characterize as-prepared samples by XRD, FESEM, TEM, BET, and investigate their electrochemical performance.
- To identify the best calcination temperature of Co_{1-x}S and discuss the mechanisms behind.

The more detailed explanation of scope of work includes synthesizing the two-dimensional (2D) layered cobalt metal organic framework materials using simple one-step method, followed by synthesizing the two-dimensional (2D) layered cobalt sulfides (Co_{1-x}S) nanocomposites using Co-MOFs as the precursor at various sulfurization temperatures (500 °C, 600 °C, 700 °C and 800 °C, respectively). The literature review was focused on the mechanisms of LIBs, conventional materials for electrodes, the applications of MOFs material in energy storage and the previous researches done on the transition metal sulfides, especially cobalt sulfides using as anode materials of lithium ion batteries. Next, the crystal structures and phase purity were determined by X-ray diffraction (XRD, Bruker D8, with Cu $K\alpha$ radiation). The morphologies and microstructures were examined by the field-emission scanning electron microscope (FESEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL JEM-

2100F). Then, the pore size and the surface area of the nanocomposites were measured by Brunauer-Emmett-Teller (BET, ASAP Tri-Star II 3020, analysis adsorptive: N₂). Finally yet importantly, electrochemical measurements were mainly carried out on Neware battery testing system (Neware, BTS-5V 10mA, China) and electrochemical workstation (Autolab, PGSTAT302N). The characterization results were further discussed in results and discussion section. The work of the next step were proposed in future work part.

1.4 Dissertation Overview

The thesis addresses the two-dimensional layered cobalt sulfide derived from metal organic framework (MOF) could be a potential candidate as anode material of LIBs. Furthermore, the optimized sulfurization temperature was investigated to achieve the best electrochemical performance.

Chapter 1 describes the background and rationale for the research. The hypothesis, objectives and scope were provided.

Chapter 2 reviews the literature concerning transition metal sulfides, especially CoS as anode materials for LIBs. The existing synthesis methods and the current electrochemical performance of CoS as anode have been identified. Based on the lesson learnt, nano-sizing and composition with carbon could be the two strategies to improve capacity fading issue, and thus provide direction to develop novel CoS anode material.

Chapter 3 discusses the principles underlying the experimental methodology, including synthesis approach, material characterization techniques and electrochemical tests employed. The rationale for selection of particular technique and the methods of data analysis are also included.

Chapter 4 elaborates the phase, morphology, porosity information of the synthesized two-dimensional layered cobalt sulfide. The electrochemical performance such as V-profile, CV curve, cycling stability, rate capability and EIS have been discussed. The optimized

sulfurization temperature was thus revealed.

Chapter 5 draws together the threads of the thesis. The hypothesis was proven and elaborated. The opportunities for future work are presented.

1.5 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Successfully synthesizing a two-dimensional layered cobalt sulfide derived from metal organic framework (MOF), which exhibits high potential to be the anode material candidate for LIBs.
2. Using the two-step in situ synthesis method, the products achieved preserve the structure of the 2D Co-MOF template, which contains nano-sized CoS particles with carbon layer wrapped around.
3. Achieving an overall better electrochemical performance of LIBs by reducing the volume expansion and increasing the electric conductivity of CoS as anode material.
4. Optimizing the sulfurization temperature to be 700°C, the CoS products synthesized at 700°C have the highest discharge capacity, best cycling stability and best rate capability.

References

- [1] Rui, X., Tan, H. & Yan, Q. Nanostructured metal sulfides for energy storage. *Nanoscale* **6**, 9889-9924 (2014).
- [2] Wang, Q. *et al.* Facile Synthesis of Ultrasmall CoS₂ Nanoparticles within Thin N-Doped Porous Carbon Shell for High Performance Lithium-Ion Batteries. *Small* **11**, 2511-2517 (2015).

- [3] Wu, R. *et al.* In-Situ Formation of Hollow Hybrids Composed of Cobalt Sulfides Embedded within Porous Carbon Polyhedra/Carbon Nanotubes for High-Performance Lithium-Ion Batteries. *Advanced Materials* **27**, 3038-3044 (2015).
- [4] Yin, D. *et al.* Coated/Sandwiched rGO/CoS_x Composites Derived from Metal-Organic Frameworks/GO as Advanced Anode Materials for Lithium-Ion Batteries. *Chemistry-A European Journal* **22**, 1467-1474 (2016).
- [5] Cao, F. *et al.* Synthesis of two-dimensional CoS_{1.097}/nitrogen-doped carbon nanocomposites using metal-organic framework nanosheets as precursors for supercapacitor application. *Journal of the American Chemical Society* **138**, 6924-6927 (2016).
- [6] T. Chen et al., “Recent progress on metal-organic framework-derived materials for sodium-ion battery anodes,” *Inorg Chem Front*, vol. 7, no. 3, pp. 567–582, 2020, doi: 10.1039/C9QI01268K.
- [7] Armand, M. & Tarascon, J. Issues and challenges facing rechargeable batteries. *Nature* **414**, 359-367 (2001).
- [8] Z. Wu et al., “Highly Conductive Two-Dimensional (2D) Metal-Organic Framework (MOFs) for Resilient Lithium Storage with Superb Rate Capability,” *ACS Nano*, 2020, doi: 10.1021/acsnano.0c05200.
- [9] Thackeray, M. M., Wolverton, C. & Isaacs, E. D. Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries. *Energy & Environmental Science* **5**, 7854-7863 (2012).

Chapter 2

Literature Review

In this chapter, definition of primary, secondary battery was introduced. Lithium-ion battery (LIB) as one of the most advanced secondary batteries, has advantages like high working voltage, long cycle life, high charging and discharging efficiency, high energy density, no memory effect and good design flexibility. The mechanism and composition of LIBs is being illustrated. Electrodes, especially anode materials are critical in determining LIB's electrochemical properties. Three types of anode materials are being summarized, including intercalation, alloying, conversion type. Among which, this review paid more attention on the transition metal sulfides, especially cobalt sulfides as anode materials, for it is more relevant to this project. The preparation methods, advantages, breakthroughs and gaps of cobalt sulfides as anode materials are shown below.

2.1 Batteries

2.1.1 Definition

Batteries are electrochemical cells that can convert stored chemical energy into electrical energy through electrochemical oxidation-reduction reactions. They are composed of cathode, anode and electrolyte. Batteries can be classified into two main categories: primary and secondary batteries.

2.1.2 Primary batteries

Primary batteries need to be disposed after single use, because its transformation from chemical to electrical power is irreversible. The advantage of primary batteries is having low self-discharge rate, thus having high energy density and long shelf life. Examples are alkaline batteries, zinc carbon batteries, silver-oxide batteries and mercury batteries [1].

2.1.3 Secondary batteries

The secondary batteries can be restored with a reverse current, because the electrochemical reaction is reversible. The electrode materials can be restored both chemically and structurally, and the secondary batteries have the ability to charge and discharge repeatedly, so they are also called rechargeable batteries. For instance, nickel-cadmium battery, lead acid battery, lithium-based battery and nickel metal hydride battery are all belong to secondary batteries.

Figure 2.1: Comparison of batteries in energy density [2].

Among secondary batteries, LIBs have many advantages, like large energy density (Fig. 2.1), little self-discharge, and no memory effect. It also offers good flexibility of sizes and shapes [3].

2.2 Lithium Ion Batteries

As modern society is having a fast pace development, the overuse of conventional fossil fuels is increasingly threatening the environment and human health. These pollution problems already drew great attention around the globe and to be resolved urgently [4][5][6]. Renewable energy like solar, wind, tidal energy has been recognized to be abundant and environmental-friendly. However, the new energy is highly affected by seasonal or geometric conditions. The energy density is low, not sustainable or controllable. Moreover, new energy is also not suitable to apply to the power grid in large scale or use on energy equipment with high power. Therefore, developing energy storage equipments with high efficiency is necessary for the above mentioned renewable energy to be stored, converted and utilized.

In the field of new energy, lithium-ion batteries, fuel cells, super capacitors and solar cells have been recognized as efficient and environmentally friendly energy storage devices. To a certain extent, they meet people's daily energy need. Among which, LIBs, as one of the most advanced secondary batteries, have attracted wide attention around the globe. The advantages include high working voltage, long cycle life, high charging and discharging efficiency, no memory effect, good design flexibility and high energy density.

Recent years, electric vehicles and power grid energy storage have developed rapidly. Portable electronic products are becoming smaller, lighter and updated. The market demands and sales volume of lithium-ion batteries are likewise increasing year by year. As shown in figure 2.2, with the continuous development of small mobile devices like handphones, laptops and digital cameras, higher requirements have been put forward for LIBs' energy density and cyclic stability [7].

Figure 2.2: The demand of LIBs in recent 20 years[8].

In energy storage device industry, lithium ion batteries have great significance in national economy, defense and security. The main factor to determine its lithium storage performance is the electrode materials. Current commercial graphite has theoretical capacity of 372mAh g^{-1} , which limits the LIBs' further development [8]. Applying LIBs in hybrid electric vehicles needs much more energy density, current stage can provide

150 Wh/kg [9][10][11]. Therefore, the next step is to design and synthesize new electrodes materials which own high theoretical capacity, low price, as well as high safety.

2.2.1 Mechanism of Lithium Ion Batteries

LIBs are also being named as “rock chair batteries” because their energy convention are originated from Li-ions shuttling in between electrodes [13]. The reaction mechanism for LIBs is represented by figure 2.3:

Figure 2.3: Operation mechanism of a LIB [14].

If LiCoO_2 is cathode, anode material is graphite, when charging, an outer voltage needs to be applied onto system, Li-ions will be extracted from LiCoO_2 (cathode), migrate through electrolyte, cross the separator, and insert into the layered structures of anode (graphite), electrons move via external circuit. The direction starts from cathode to anode. After charging is done, graphite is rich in lithium-ion while LiCoO_2 is lack of lithium-ion. Electrical energy has been converted to chemical energy [15].

When discharging, the whole process is reversed. Li-ions are extracted from graphite (anode), migrated in electrolyte and intercalated into the layered structures of LiCoO_2 (cathode). Meanwhile, electrons travel from the anode to cathode externally, anode is

oxidized and cathode is reduced. After discharging is done, both cathode and anode recover to the original state before charging, LiCoO_2 is rich in lithium-ion while graphite is lack of lithium-ion. Chemical energy has been converted to electrical energy. LIBs are batteries of Li-ion concentration difference [5][8].

The electrochemical equations are shown as below ($n=6$, $x \approx 0.6$) [14]. Forward direction is for charging, the revert direction is for discharging:

Repeated lithiation usually only change atomic layer spacing of the electrodes, without damaging their crystal structure. This electrode reaction is quite ideal and reversible, which helps in longer cycle life. This is one of the reasons why LIBs are widely used.

Lithium ion battery has the following main characteristics [13][16]:

- Long cycle life: the charge and discharge cycles can be up to 2000 cycles, much higher than other batteries.
- No memory effect: the LIB could be discharged and charged at any time, no need to finish discharging then to be recharged.
- High specific energy: good for building smaller sized devices.
- High operating voltage: a LIB is up to 3.7V-3.8V.
- Low self-discharge: the self-discharge rate is about 3%-9%, far lower than that of nickel-cadmium battery.

With above advantages, lithium ion battery has brought convenience and speed in all aspects of human life.

However, lithium-ion batteries still have some drawbacks:

- Capacity attenuation: as the number of uses is increasing, the capacity of LIBs will gradually decline, which is more likely to occur in electronic products with high working current.
- Not safe when overcharging and overdischarging: a protective circuit is needed.
- High battery cost.

Above are the issues to be solved in development of LIBs.

2.2.2 The Structure and composition of LIBs

LIBs include four parts: cathode, anode, separator, electrolyte. In conventional LIBs, metal oxide (e.g., LiCoO_2) is used as cathode and graphite is used as anode. A separator is the porous membrane in electrolyte (e.g., LiPF_6), which enables lithium ion transmission and prevent electrodes from immediate touch [17].

1) Electrolyte

The electrolyte could be in liquid, gelled and dry formats. At present, liquid electrolyte of an organic system is widely used in LIB, which is mainly made of conductive Li salt and organic solvent like cyclic carbonate with high dielectric constant.

The commonly used electrolyte is LiPF_6 , which is generally dissolved in a certain proportion of diethyl carbonate (DMC), methyl ethyl carbonate (EMC), dimethyle carbonate (DEC), other mixed solvents as well [12][18]. It serves as a catalyst to promote ions to migrate between electrodes while charging and discharging.

Electrolyte has characterization such as high chemical stability, wide range of working voltage, high ionic conductivity and good thermal stability.

With Li-ion, the electrolyte is not stable as it should be. A solid electrolyte interface (SEI) which is a passivation film form on the anode, this layer separates the electrodes but allows the ions to pass through, just like a separator. The SEI film must be formed to enable the battery work. It stabilizes the system and ensures lithium-ions a long life. However, forming SEI film results in a reduced capacity. In the mean time, electrolyte oxidation happens on cathode which also permanently reducing the capacity.

2) Separator

The permeable membrane between cathode and anode is a kind of micro-porous film with certain porosity and is electron-insulated. The main function of a separator is to prevent cathode and anode to contact. Connection of cathode and anode would cause short circuit. Li-ions can penetrate through the membrane. The separator has characterization like high chemical stability, 40%-50% porosity rate and thin enough. Commonly used separators are polyethylene (PE) and polypropylene (PP) [19][20]. The physical properties of some commercialized separators are indicated below in table 2.1.

Table 2.1: Properties of commercial polyolefin membranes as the separators for LIBs [22].

Characteristics	Commercially available separator membranes				
	Celgard 2730	Celgard 2400	Celgard 2325	Asahi Hipore	Tonen Setela
Structure	single layer	single layer	trilayer	single layer	single layer
Material	PE	PP	PP-PE-PP	PE	PE
Thickness (μm)	20	25	20	25	25
Ionic resistivity (Ω/cm)	2.23	2.55	1.85	2.66	2.56
Porosity (%)	~43	~40	~42	~40	~41
Melting temperature ($^{\circ}\text{C}$)	~135	~165	135/165	~138	~137

3) Cathode

In LIBs, the materials for cathode and anode are mainly determine the battery performance. In current commercial LIB, the cathode materials is the Li-ion source. The common choices are transition metal oxides and phosphates, includes LiCoO_2 [23][23], LiMn_2O_4 [25][26], LiFePO_4 [27][28], and $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ ternary compound [29][30]. The structures of three typical cathode materials are introduced in fig. 2.4.

Figure 2.4: Crystal patterns and the insertion modes of lithium ions in three types of cathodes [29].

Among all, lithium transition metal oxides are known as the most successful ones [31]. They are generally divided into LiMO_2 and LiM_2O_4 . M represents a transition metal and its combinations or substitutions. LiMO_2 sometimes owns a layered structure while LiM_2O_4 usually has a spinel structure [32]. For instance, LiCoO_2 is the best-commercialized composite because it has low self-release, large voltage, high volumetric capability and great cycling stability. However, LiCoO_2 has the disadvantages such as toxicity, high cost, limited cobalt resource, low thermal stability in the charged state and high irreversibility level when voltage is larger than 4.2V. Thus, further investigations for alternative cathode materials are required [33].

In general, cathode materials need to have high oxidation-reduction (redox) potential, stable structure which allows many Li-ions to be reversibly intercalated, high electron conductivity, high ion dispersion rate, good thermal stability, low price, easy for preparation and environmental friendliness.

4) Anode

Anode is significant in LIBs. When charging and discharging, Li-ions are intercalated into and separated from anode layered materials, which is crucial in overall performance, cost and safety of LIBs.

Anode materials are required to have good stability, high coulomb efficiency, high reversible discharge specific capacity, long cycle life, good electronic conductivity, large ionic diffusion rate, low cost, environmental-friendly, and have promising prospects for applications and commercialization.

Some general properties need to be considered in order to compare different electrodes. For example, specific capacity, cycle life, energy density, and rate capability.

The energy density (Wh/L), specific energy (Wh/kg) are both describing the energy storage ability.

Rate capability of LIBs is reflected by specific power (W/kg), as well as power density (W/L). Power density is energy density divided by the battery discharging time. It is associated to the lithium ions diffusion rate and electron transfer between electrodes. The faster the transmission of electrons and Li-ions, the higher the charge and discharge rate, thus greater the rate capability.

The specific capacity (mAh/g) and cell potential (V) are related to the chemistry of the electrode, the more energy stored in a certain volume or mass, the higher the specific capacity.

The specific capacity can be calculated from the below expression for an electrode:

$$\text{Specific Capacity} = \frac{\Delta x \cdot F}{M} \times \frac{1000}{3600} \quad [\text{mAh/g}] \quad (2-4)$$

F is the Faraday constant.

Δx represents how many moles of lithium are participating in an electrochemical reaction. Δx also indicates the number of Li-ions that could be reserved in the cathode or anode. This factor is dependent on electrode materials' crystal structure and lithium-ion insertion site numbers.

M is electrode materials' molar mass.

The cycle life is how many charging and discharging cycles already performed when the specific capacity of cathode or anode declined to a specific limit. If the electrodes are stable in contact with electrolyte, and they are stable during lithiation, the cycle life is tend to be longer.

2.3 Anode Materials for LIBs

With above properties being considered, various materials were investigated to be applied as anode. At present, one of the most commonly used anode materials is graphite.

Graphite materials are commercialized and widely utilized anode due to its low working potential platform, high coulomb efficiency, low cost, good cycle stability and long cycle time [34]. Li-ions could reversibly insert into or de-intercalate from its lattice. When Li-ions insert into graphite, the space of interlayers among graphite cells increases about 10.3%. Up to 1 Li atom per 6 carbon atom could be inserted into the layered structure, which gives the material a nominal composition of LiC_6 . The graphite's theoretical specific capacity is 372mAh/g, but practical specific capacity is only 330mAh/g, low specific capacity indicates a low energy density, which is not enough to fulfil increasingly energy demands for modern electronic gadgets.

Besides that, graphite also have other disadvantages: low power density, because the diffusion rate of Li-ions into graphite is slow ($10^{-9} \sim 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) [35], serious safety issues because graphite has a lower potential Vs. Li, lithium deposition may cover the anode during fast charging, degrade the electrochemical performance of LIBs and cause thermal runaway [36]. In addition, graphite has a small Li embedding potential ($\sim 0.1\text{V}$

Vs. Li/Li+) during charging/discharging, which makes part of the electrolyte to decompose and generate a SEI membrane on cathode or anode. Both the first cycle of SEI formation and the subsequent regeneration of SEI film consume lithium ions, which reduce the first cycle of charge and discharge efficiency and cycle stability [37][38]. Alternative anode materials need to be developed with high power density and specific capacity [39].

Large amount of researches have been conducted on carbon and non-carbon materials to enable anode in LIBs a higher performance, including carbon nanotubes, nanofibers, graphene, porous carbon, SiO, silicon, germanium, tin, transition metal oxides/phosphides/sulfides, Li-alloys, polymers, and others.

The theoretical energy density E_d of current LIB system could be achieved by below formula:

$$E_d = (m_+ * C_+ * E_f) / (m_+ + m_-) \quad (2-5)$$

m_+ and m_- are respectively the mass of active substance of cathode and anode.

C_+ and C_- are respectively the theoretical specific capacity of cathode/anode materials.

E_f is voltage difference between electrodes.

Suppose that inside a whole battery system, the cathode and the anode material have the same capacity, like shown in equation (2-6), then (2-5) and (2-6) combined together can be converted to equation (2-7).

$$m_+ * C_+ = m_- * C_- \quad (2-6)$$

$$E_d = E_f / [(C_+ + C_-) / (C_+ * C_-)] \quad (2-7)$$

According to the specific capacity of current commercial cathode and anode material, if C_+ and C_- are 150 and 372 mAh g⁻¹ respectively, then the specific capacity density E_d calculated to be 385 Wh kg⁻¹. Since in the actual calculation of specific energy also need to count in the mass of the entire electrodes, including the mass of current collector,

conductive agent, and binder, thus the actual specific energy density is half the theoretical value. If the purpose is increasing energy density, one way is to reduce the additives' mass for electrodes. The other way is improving the theoretical specific capacity of the electrodes.

At present, the theoretical capacity of cathode materials is hard to be increased. If the theoretical capacity of anode could be improved, and the mass of additives for electrodes can be reduced, then the purpose to increase energy density could be realized. Therefore, development of anode materials is critical in improving the energy density of LIBs.

Studies have found that many kinds of materials are capable of reversibly embedding and extracting Li-ions, thus have the potential to be anode for LIBs. According to charging/discharging mechanism, they can be mainly classified into three kinds: intercalation/alloying/conversion materials [40]. The schematic diagram of their reaction mechanism with lithium ion is indicated in fig. 2.5.

Figure 2.5: Diagrams of 3 reaction mechanisms for anode materials, the black, yellow and blue circles represent vacancy, lithium ion and metal in a crystal structure respectively [40].

2.3.1 Insertion/Intercalation Reaction and Materials

The insertion reaction requires materials with layered structure, one common example would be conventional graphite. The insertion reaction mechanism can be shown in figure below:

Figure 2.6: Diagrams of Li-ion intercalation/de-intercalation mechanism for anode materials.

In a typical insertion reaction, Li-ions are disembedded from cathode materials, followed by intercalating into the layered structures of the anode materials during charging. The electrons will transfer from cathode to anode through an outer circuit simultaneously. When discharging, Li-ions transfer out from the interior of layered anode materials, and again inserted into the cathode materials, this process is known as deintercalation or deinsertion. The electrons thus move back from anode to cathode through the external circuit.

The theoretical capacity of the anode depends on how many of lithium ions that can intercalate or deintercalate through electrode layers. The more the lithium ions can be inserted, the higher the theoretical capacity. However, maximum achievable capacity for insertion type of electrode is low, for the amount of lithium ions that could be embedded into electrode layers has a limit.

Furthermore, insertion is mainly suitable for electrode materials with layered structures which has sufficient space between the layers. So that the lithium ions could be

intercalate and de-intercalate out of the structure without undergoing significant volume and structure changes [41].

Typical intercalation materials include carbon-based type or titanium based type like TiO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, etc. Li-ions could be reversibly intercalated into such materials with little changes in structure and volume, this process also is known as a “topological reaction”. This kind of material has excellent structural and cyclic stability, and it provides a fast lithium migration rate. However, only one electron per mole of mass can be stored into this kind of material. As a result, such materials are usually limited because of its low specific capacity by mass in practical applications.

1) Graphite

Carbon based materials are considered as LIBs' appropriate choice due to less cost, availability, electrochemical stability in environment and good reversibility [12]. They can be categorized into graphitic carbon (crystallites have ordered orientation, like graphite) and non-graphitic carbon (crystallites are stacking in different directions, like graphene). Non-graphitic carbon can be further classified into soft or hard carbon (upon annealing), high or low specific charge carbon (according to the capacity of reversible lithium storage) [42].

Graphite is a kind of crystalline-state carbon material. The degree of graphitization will affect the conductivity, structure and thermodynamic stability of the carbon material. Graphite has high conductivity, high voltage platform and low cost, thus being widely used commercially. It is orderly stacked by hexatomic ring carbon network structure which is composed of sp^2 hybridized carbon atoms, and its layer spacing $d(002)$ is 0.336 nm. The graphite phase crystal structure is mainly thermodynamic stable 2H (ABAB) phase [38]. Therefore, the volume expansion rate of graphite caused by the lithium embedding process is relatively moderate, only 10.3%, indicating that graphite has excellent structural stability in the charging and discharging process [33][43].

Lithium ions' storage capacity and de-lithiation potential are determined by microstructure, degree of crystallization and macro-morphology of graphite. During charging and discharging at atmospheric pressure, for every six C atoms, one Li-ion could be embedded into anode. The reversible conversion between C and Li_xC_n can realize the mutual conversion of electrical energy and chemical energy. The process of graphite deintercalating lithium ions can be written as equation (2-8) [44].

Graphite material also has many disadvantages. Its theoretical capacity is much lower than silicon, tin, etc. Graphite has low lithium intercalation potential, easy to form lithium dendrites in charging and discharging process, which can cause safety issue. Moreover, the diffusion rate of Li-ions is 10^{-9} - $10^{-7} \text{ cm}^2 \text{ s}^{-1}$, the low diffusion rate leads to the low energy density [37][38], which restricts the application of battery.

Presently, methods to improve graphite materials' specific capacity mainly include the preparation of special structures [45] and heteroatomic doping [46]. For example, Jintao Huang et al. [46] melted polystyrene and mixed it with azodicarbonamide. After pre-carbonization, it was mixed with urea with different contents and under further heat treatment to obtain nitrogen doped porous carbon (NPC). NPC was used as anode material. How morphology and structure would influence electrochemical performance was analyzed.

As shown in figure 2.7, the authors believe that although the amount of nitrogen doping is small, it can promote the formation of disordered carbon and defective structure. The porous structure can increase the specific surface area, which is helpful to provide many diffusion channels of Li-ions, increase the conductivity and thus improve rate capability and the specific capacity of electrode materials.

Figure 2.7: Nitrogen-doped porous carbon materials: (a) Diagram for sample preparation; (b)XRD figure; (c-i)Morphology and element plane distribution; (j-k) Rate capability and cyclic performance; (l) impedance spectrum (EIS) [46].

Graphene has theoretical capacity of 764 mAh g^{-1} , twice of the traditional graphite electrode. Due to its high long-range ordered π -conjugated structure, graphene exhibits high ion migration rate and ballistic electron transmission rate. However, there are some defects on the graphene surface. So when anode of LIB is pure graphene, at the 1st cycle, more SEI film will be formed, which will consume many Li-ions, resulting in low

coulomb efficiency, rapid capacity attenuation and poor cycle stability in the subsequent cycling process [47].

At present, methods of improving cycling performance and specific capacity of graphene include compositing with other carbon-based materials [48], inducing defect formation [49], heteroatomic doping [50], etc. Huan Liu et al. [51] prepared a nitrogen and chlorine double-doped graphene using carbon tetrachloride and pyrrole as raw material through solvothermal synthesis method. Then its lithium ion storage performance (figure 2.8) was studied. Results show that the P-type chlorine dopants can enhance carrier mobility and graphene conductivity, nitrogen doping can increase the number of active sites and electron migration rate. Benefit from the abundance of defects and the increased layer spacing, nitrogen and chlorine double-doped graphene exhibits high discharge specific capacity, better retention rate for capacity, good rate capability, and overall electrochemical performance is improved.

Figure 2.8: Nitrogen, chlorine double-doped graphene: (a) Diagram for sample preparation; (b-f) Morphology vs. element plane distribution; (g) Rate capability; (h-i) Cycling performance diagram [51].

2) Titanium oxide

Titanium-based materials mainly refer to titanium dioxide (TiO_2) and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$). Their theoretical specific capacities are 330 mAh g^{-1} , 175 mAh g^{-1} as anode materials. They have advantages include small volume expansion (less than 3%), cheap and easy to obtain, good safety, etc. [52][53]. TiO_2 is promising as anode material due to

its high electrochemical activity, strong oxidation capacity, abundant reserves and diverse structures and morphology. The reaction equation (2-9) of TiO_2 is as below [54]:

In theory, 1 mol of lithium ions can be embedded into per mole of TiO_2 , forming LiTiO_2 . However, the reality is that only 0.5mol of lithium ions can be embedded per mole of TiO_2 . The amount of lithium ions could be inserted mainly depends on the crystalline forms, particle size, crystallinity and specific surface area of TiO_2 [55]. Thus, how to utilize the full capacity of TiO_2 is still a big challenge.

Currently the commonly used method is to make TiO_2 particles nano-sized to improve their specific surface area. So that the volume expansion can be minimized, capacity is higher while cycling is more stable [56]. It can also be compounded with carbon material to improve its conductivity, so as to improve its rate capability [57]. In order to improve its reversible specific capacity, TiO_2 can be compounded with a substance of high specific capacity [58].

Yitao Liu et al. [59] reported a method that two dimensional $\text{TiO}_2/\text{MXene}$ nanocomposite with heterostructure was formed through electrostatic self-assembly(as shown in figure 2.9), and studied its lithium ion storage performance. The nanocomposites was formed by two dimensional titanium carbide (Ti_3C_2) MXene nanosheet and TiO_2 nano-rod. The Mxene phase, as a potential base matrix, not only can help the positive and negative charge to transport at interface, but also can inhibit the agglomeration of TiO_2 in the cycling process. TiO_2 can be used as an interval to prevent the recombination of Mxene, thus preventing the loss of the active area. Together, they can make the transmission path of Li-ions shorter, add active sites, and increase rate capability and reversible specific capacity of TiO_2 composites.

Figure 2.9: TiO₂/MXene composites [59]: (a) Diagram of sample preparation; (b-d) Morphology; (e-f) Cycling diagram vs. Rate capability diagram.

Li₄Ti₅O₁₂ is a spinel structure, which can rapidly and stably intercalate/de-intercalate lithium ions. Each molecular formula can have three lithium ions completely de-intercalate, and the corresponding voltage platform is relatively high, which is 1.5V vs Li/Li⁺. There is almost no side reaction with the electrolyte under this voltage platform [60]. However, irreversible reactions will occur between Li₄Ti₅O₁₂ and common pollutants in the electrolyte, such as water, HF and PF₅, resulting in loss of active lithium ions [61], and capacity attenuation. Therefore, its low conductivity [62], low specific capacity and energy density limit the commercial application of Li₄Ti₅O₁₂ in power batteries. At present, methods to increase conductivity and specific capacity of Li₄Ti₅O₁₂ are mainly focused on the composites with carbon-based materials [63] and composites with high specific capacity materials.

2.3.2 Alloying Reaction and Materials

The process of alloying reaction involves metallic or semi-metallic elements that are reactive with lithium. The general equation for a typical alloying reaction (2-10) is shown below:

Where M can be an element or compound, Li ions react with lithium active elements to form Li_bM_a phase [64].

The advantage of alloy-type electrodes is that they have higher volumetric and gravimetric theoretical capacities compared to intercalation-type electrodes, for each mole of lithium-active element can alloy with one or more moles of lithium.

However, the alloying-type of electrodes also has disadvantages. The main problem is the pulverization and fracture of the active materials caused by volumetric expansion during lithiation process within the dense alloy particles [65]. Thus, the capacity will decrease within a few cycles, for the cracked active particles may discontact from current collector [66].

Reports showed that the structural stability remains a huge issue for lithium-alloying anodes. Moreover, lithium dendrites might form during the cycling process if the potential is close to lithium metal, which may lead to safety issues [67].

Among all alloying materials, the group IV A elements are researched the most, including silicon (Si), germanium (Ge), tin (Sn) and their compounds like silicon dioxide (SiO₂), silicon monoxide (SiO), etc. Lithium ions can have alloying reaction with these materials when Li-ions are embedding to form alloy. Above materials' energy density, specific capacity are high, they also have good safety as anode materials [12]. Thus, they provide the possibility for application of high energy/power consumption equipment, like pure electric vehicle as well as hybrid electric vehicle.

The theoretical capacity of alloy anode materials increases from 783 mAh g⁻¹ of SnO₂ to 4200 mAh g⁻¹ of Si, much higher than commercial graphite anode materials [68][69]. Although these materials have a high specific capacity, they also have obvious defects. Because of the great volume expansion in the initial cycle, alloying materials have capacity attenuation, low rate capability and cyclic stability. In order to address above problems, researchers have tried to adopt different methods to improve the original alloy materials. Effective methods include reducing the structure size [70], controlling the morphology [71] and preparing alloy composites [72][73] to alleviate its volume expansion.

Silicon (Si) and its derivatives are promising candidates as anode for LIBs for three reasons. First, silicon's gravimetric capacity (4200mAh g⁻¹, Li₂₂Si₅) is high, volumetric capacity (9786 mAh cm⁻³) is as well high [74][75]. Second, discharge potential of silicon is 0.4 V vs. Li/Li⁺, similar as graphite (~0.1V vs. Li/Li⁺). Third, on earth, silicon is the 2nd most abundant element, so it's cost is relatively low [76][77]. Under atmospheric pressure, one Si atom could have 4.4 Li atoms embedded in. The process of lithium ions extraction can be written as equation (2-11) below [78]:

The alloying reaction of Li and Si is generally carried out step by step, and Li₁₂Si₇, Li₇Si₃, Li₁₃Si₄, Li₁₅Si₄ and Li₂₂Si₅ alloys are formed at different stages [79]. Silicon amorphization happens in the meantime of the alloying process. The high specific

capacity of Si is caused by the formation of $\text{Li}_{22}\text{Si}_5$ crystal type (theoretical specific capacity 4200 mAh g^{-1}), but in this process, Si volume expansion will reach 400% [80][81]. The volume expansion might be due to large atomic radius difference between Si ($1.46 \text{ \AA}$) and Li ($2.05 \text{ \AA}$), leading to cracking of the electrode [67]. Repeated volume expansion and contraction during lithiation will lead to silicon particles crushing, thus causing them to be detached from current collector [82][83]. At the same time, SEI membrane generated around the silicon particles will be broken and regenerated many times, thus continuously consuming the electrolyte, affecting the transmission of lithium ions, resulting in the battery's internal resistance increasing and rapid capacity attenuation [70]. In addition, the electron conductivity of Si at room temperature (10^{-5} - $10^{-3} \text{ S cm}^{-1}$) and the diffusion rate of Li-ions ($10^{-13} \text{ cm}^2 \text{ s}^{-1}$) are relatively low [78], which would also affect the cycling of Si at high rate. Due to the serious defects mentioned above, practical application of Si was hindered. At present, to address the issue of low cyclic stability caused by large volume expansion of Si during cycling, the main solutions are to make Si particles nano-sized, and to compound them with other highly conductive phases or lithium inert materials.

Nano-sizing the Si particles an effective way to reduce volume change. It can bring large specific surface area, which can not only reduce transmission distance between electrons and Li-ions, thus accelerating electrochemical reaction, but also can relieve the mechanical stress inside the particle and keep the particle structure intact. The researchers used a variety of methods to prepare nano-Si materials with different morphology and structures, which showed good cyclic stability when used as lithium ion batteries.

To prepare Si matrix composites is to combine Si with other second phase materials such as highly conductive phase materials or lithium inert materials. The second phase material is used as a conductive material or a structural buffer to hinder the volume expansion and improve cycling stability. Many researchers have compounded Si with highly conductive materials like carbon-based material, Cu and Ge [84], with TiO_2 and metal oxides which has good cyclic stability [85], and also have compounded Si with polypyrrole, polyaniline or other organic polymers which have high conductivity and

mechanical strength [86]. Above methods have the perspectives of improving the conductivity of Si, alleviating the volume expansion, and forming a stable SEI film. The structural stability and cyclic stability of Si is improved, so as the overall electrochemical performance.

2.3.3 Conversion Reaction and Materials

In conversion reaction, Li ions can react reversibly with a number of binary compounds, M-X: M is a kind of transition metal, X is a type of anion. The conversion process is shown in fig.2.10 below:

Figure 2.10: Diagram illustration of conversion reaction [87].

From figure 2.10, binary compounds like M_aX_b react with lithium ions to form metallic M and Li_nX after the first lithiation, which is known as the forward reaction. In delithiation process, the compounds are formed back into the initial state, which is known as the reverse reaction.

This can be described in equation (2-12) below:

where X is an anion, n is the X's formal oxidation state, M is a transition metal.

In lithiation process, the metallic M is reduced to neutral state metal nanoparticles [88]. They homogeneously distributed in an amorphous Li_nX matrix. The homogeneous distribution structure can help prevent the metal nanoparticles from agglomeration. When a reverse voltage is applied, the Li_nX matrix will break down and form back to the M_aX_b binary compound. Previous reports had shown that the number of reduction-oxidation cycles would not affect the sizes of the metal particles for conversion-type anodes. Thus, the cycling stability of conversion reaction anodes is good [89].

The anode materials adopting conversion reaction mechanisms have higher energy density and higher specific capacity compared to intercalation-type materials. This is because more than one electrons are transferred per transition metal ion in conversion reaction. Namely, the oxidation state is often fully utilized so that more than one electrons are participated [90]. Furthermore, the actual potential of conversion reaction can be greatly affected by both the anionic element and the transition metal in the binary compound. Thus, by finely matching the types of transition metal and anion, the conversion reaction potential can be flexibly adjusted. However, the large volumetric expansion remains as the main issue for conversion reaction.

Conversion type of materials include transition metal oxides/ sulphides/ phosphides/ nitrides (M_xX_y ; here X= S, P, N). Their specific capacity is generally larger than 500 mAh g^{-1} [12]. Figure below shows the potential vs. the capacity density of the next generation materials for anode.

Figure 2.11: Choices of anodes for LIBs [12].

As shown in figure 2.11, transition metal compounds like MO_x , MS_x , MP_x and transition metal nitride (MN_x) can all be as anode materials of LIB to conduct reactions with Li^- ions and achieve purpose of lithium storage.

Common transition metal oxides are ferric oxide (Fe_2O_3) [91] and ferroferric oxide (Fe_3O_4) [92], cobalt oxide (CoO) [93], the cobalt oxide (Co_3O_4) [94], nickel oxide (NiO) [95], manganese oxide (MnO), manganese sesquioxide (Mn_2O_3) [96], four oxidation three manganese (Mn_3O_4) [97], ceria (CeO_2) [98], which own high reversible capacity ($500\text{--}1200 \text{ mAh g}^{-1}$) [99]. Among them, cobalt oxide base and manganese oxide base anode materials are studied the most. They have better structural stability, cost is low and environmental friendliness. However, they also have drawbacks as anode materials. For instance, the volume expansion is large during cycling. SEI film is unstable, thus cycle stability is poor. The electron and ion conductivity are low [100], leading to poor coulomb efficiency and low rate capability in the first cycle. Those issues need to be solved before the materials being put into use practically. At present, methods used include synthesizing nano-sized materials, preparation of special morphologies and composite them with conductive materials. Above three methods are often combined to improve electronic conductivity, ion conductivity and activity of metal oxides.

Using Cu_2O as the template, Liu Jun et al. [101] prepared a $\text{Fe}_3\text{O}_4@\text{ppy}$ nanocage material with multi-layer structure by combining interface reaction and polymerization (see figure 1-10 (a-c)). The electrochemical properties of $\text{Fe}_3\text{O}_4@\text{ppy}$ were significantly enhanced by the synergistic effect of multi-layer hollow structures and nanocomposites. Hao Wenjun et al. [102] prepared three different morphology of Co_3O_4 (Fig. 1-10 (d-f)) nanoparticle, nanowire and three-dimensional fluff sphere-like porous structure through controlling the hydrothermal reaction process (Fig. 2.12 (d-f)).

Figure 2.12: (a) Diagram of sample preparation of the multi-layer Fe₃O₄@ppy nanocage [101]; (b) Morphology; (c) Cycle performance diagram; (d) Morphology of Co₃O₄ with three different morphologies: nanoparticles, nanowires and three-dimensional fluff sphere-like porous ball [102]; (e) Rate capability diagram; (f) Cycle performance diagram; (g) Schematic diagram of 3D multi-

layer sea urchin shaped $\text{Mn}_3\text{O}_4/\text{C}$ micron ball [103] preparation process; (h) Diagram of lithium ion insertion mechanism; (i-j) Morphology; (k) Multiplier performance diagram.

Among them, Co_3O_4 with three-dimensional fluff sphere-like porous structure showed better performance, because the unique multi-layer structure provides many active sites. The increased contact area between electrode/electrolyte shortens transmission path of Li-ions. Huang Shaozhuan et al. [103] prepared a three-dimensional multi-layered sea urchin-like $\text{Mn}_3\text{O}_4 / \text{C}$ micron ball (Fig. 2.12 (g-k)) through liquid phase reaction and subsequent carbonization process. Three-dimensional multi-layer nanostructure can offer many electrochemical active sites, reduce Li-ion's transmission path, inhibit the volume expansion, and thus improve the comprehensive electrochemical performance of Mn_3O_4 .

Metal phosphide (such as cobalt phosphate (CoP) [104], copper phosphide (Cu_3P) [105], nickel phosphide (Ni_5P_4) [106], etc., can also be used as anodes. Metal phosphide (A_xP_y) and Li, often are under the dual control of the conversion reaction mechanism and insertion/extraction reaction mechanism. However, it is more greatly affected by the properties of transition metal itself and whether the phosphorus bond in the electrochemical environment is stable [107]. In the electrochemical reaction, A-P bond (A is metal, P is phosphorous) is broken to generate nano metal particles and LiP_x . The reaction equation (2-13) is as follows:

Metal phosphide as anode material has a relatively strong lithium storage ability. Its capacity is usually between 500-1800 mAh g^{-1} . Moreover, compared with transition metal oxide, metal phosphide has a lower charge and discharge platform and smaller polarization. However, its volume change is bigger in the process of circulation, leading to a poor stability [108]. Metal phosphide also has higher toxicity, which is another drawback for their practical application.

Transition metal nitride is a kind of conversion anode material which has been studied in recent years. Compared with transition metal oxides, transition metal nitrides have many advantages, such as high conductivity, strong lithium ion transport capacity, large electrochemical activity, small volume change of charge and discharge, good cyclic stability, etc. [109]. It has great application prospect in the LIB field of high power/energy density.

Transition metal nitrides which being researched the most are antimony nitride (Sb_3N) [110], tin nitride (SnN_x) [111], vanadium nitride (VN) [112], iron nitride (Fe_2N) [113], iron nitride (Fe_3N) [114], etc. Among these nitrides, the iron nitride-based anode material has a high conductivity. Iron in nature is rich in lithium storage and low in price, so it has attracted more attention [115]. The theoretical lithium storage capacity of Fe_2N and Fe_3N is $\sim 900 \text{ mAh g}^{-1}$, and the lithiation products are both Fe and Li_3N . They have superior capacity density, energy density and have great potential for application. However, the volume change of Fe_2N and Fe_3N anode materials during cycling is relatively large, which will lead to poor cyclic performance [116]. Moreover, the preparation method of nitride anode material is more complicated. The cost is higher, thus it is difficult to scale up the production.

For a long time, transition metal sulfides (MSs, $\text{M} = \text{Co}, \text{Fe}, \text{Cu}, \text{Mn}, \text{Ni}$ and so on) had been recognized as a high potential candidate for LIBs. Their electrical conductivity is higher than respective metal oxides, moreover, mechanical and thermal stability is also better. MSs also have specific capacities which are much higher than carbon-based anodes. The physical and chemical properties of MSs is unique [117].

However, transition metal sulfides also have disadvantages. They have low power density, due to lithium ions diffused in MSs can limit the lithiaion rate. The lithiation process generates intermediate products which is polysulfide Li_2S_x ($2 < x < 8$). It could dissolve into and react with organic electrolyte, causing capacity attenuation [80][81]. The polysulfides layer which is insulated can be deposited on the electrode surface. This can reduce its conductivity and hinder further electrochemical reactions.

Many transition metal sulfides have been researched. Overall speaking, their capacity are relatively higher than graphite but have capacity decay issue after numbers of cyclings. MnS with sub micro-cystals which is rock salt type has the first cycle discharge capacity of 900-1300 mAh g⁻¹, but 20 cycles later, capacity decay to 400-600 mAh g⁻¹ [118]. FeS [119] can achieve higher than 500 mAh g⁻¹ in terms of capacity, FeS₂ [120] can have capacity up to 600 mAh g⁻¹ for, but both of their reversibility are poor. As for NiS₂ [121], NiS [122], and Ni₃S₂ [123], their cyclic performance are not satisfying as well. CoS₂ [124] has a relatively high theoretical value, which is 870 mAh g⁻¹. However capacity drop below 400 mAh g⁻¹ a few tens of cycles later. Co₉S₈ [125] faces the same capacity decay issue.

Before they can be used as effective anodes, limitations like large volume change, low electronic conductivity, small coulombic efficiency and decay of capacity have to be overcome. Diverse methods are investigated to solve above issues. For instance, transition metal sulfides with nanostructures [126], transition metal sulfides hybridized with conductive matrices like composites integrated graphene and nickel foam [127]. Nanostructure is good to reduce the volume change during cycling. Composite with carbon-based material like graphene is beneficial to increase the electronic conductivity.

Table 2.2 summarized the nanostructure metal sulfides for LIBs, including their preparation methods and electrochemical performances.

Table 2.2: Nanostructured metal sulfides for lithium ion batteries [128].

Nanostructured metal sulfides	Preparation method	Electrochemical performance
FeS ₂ nanocrystals	Hydrothermal	885 mA h g ⁻¹ (1st) and 408 mA h g ⁻¹ (40th) at 89 mA g ⁻¹
FeS ₂ nanowires	Sulfidation	668 mA h g ⁻¹ (1st) and 350 mA h g ⁻¹ (50th) at 89 mA g ⁻¹
C@FeS nanosheets	Solution-based method	1022 mA h g ⁻¹ (1st) and 615 mA h g ⁻¹ (100th) at 0.1 A g ⁻¹ 349 mA h g ⁻¹ (9th) at 3 A g ⁻¹
PAN-FeS ₂	Planetary ball mill	470 mA h g ⁻¹ after 50 cycles at 89 mA g ⁻¹
Hexagonal CuS nanosheets	Soft colloidal template	640 mA h g ⁻¹ after 360 cycles at 2 A g ⁻¹
Oriented CuS nanoflakes	Electrodeposition	545 mA h g ⁻¹ in the first cycle under 28 mA g ⁻¹
Cu ₂ S nanowire arrays	Solution-based method	470 mA h g ⁻¹ (1st) and 230 mA h g ⁻¹ (100th) at 560 mA g ⁻¹
Cu ₂ S nanotubes	Solvothermal and sulfidation	779 mA h g ⁻¹ (1st) and 526 mA h g ⁻¹ (50th) at 200 mA g ⁻¹
Co ₉ S ₈ yolk-shell spheres	Spray pyrolysis and sulfidation	1008 mA h g ⁻¹ in the first discharge at 1 A g ⁻¹ with 82% capacity retention after 100 cycles
Flower-like CoS	Solvothermal	890 mA h g ⁻¹ in the initial discharge at 50 mA g ⁻¹
CoS ₂ hollow structures	Solvothermal	1210 mA h g ⁻¹ in the initial discharge at 100 mA g ⁻¹
C@Co ₉ S ₈ dandelions	Solution-based method	848 mA h g ⁻¹ (1st) and 520 mA h g ⁻¹ (50th) at 1 A g ⁻¹ 373 mA h g ⁻¹ (10th) at 6 A g ⁻¹
Urchin-like NiS	Solvothermal	567 mA h g ⁻¹ in the initial discharge at 10 mA g ⁻¹
Hierarchical NiS microspheres	Hydrothermal	588 mA h g ⁻¹ in the initial discharge at 50 mA g ⁻¹
Porous NiS ₂	Spark-plasma-sintering	820 mA h g ⁻¹ in the initial discharge at 175 mA g ⁻¹
Ni ₃ S ₂ nanowire arrays	Precipitation and sulfidation	480 mA h g ⁻¹ (1st) at 45 mA g ⁻¹ with 80% retention (100th)
NiS nanosheets/graphene	Hydrothermal	481 mA h g ⁻¹ after 100 cycles at 50 mA g ⁻¹
Ni ₃ S ₂ nanoparticles/	Thermal pyrolysis	809 mA h g ⁻¹ after 150 cycles at 50 mA g ⁻¹
N-doped graphene		
MnS hollow boxes	Sulfidation	1117 mA h g ⁻¹ (1st) and 495 mA h g ⁻¹ (100th) at 200 mA g ⁻¹
MnS/C nanowires	CVD	1036 mA h g ⁻¹ (1st) and 503 mA h g ⁻¹ (25th) at 1 A g ⁻¹
MnS-C hollow spheres	Spray pyrolysis	1445 mA h g ⁻¹ (1st) and 967 mA h g ⁻¹ (200th) at 100 mA g ⁻¹
MnS hollow spheres/rGO	Hydrothermal	1240 mA h g ⁻¹ (1st) and 500 mA h g ⁻¹ (50th) at 50 mA g ⁻¹
MoS ₂ nanoplates	Solvothermal	700 mA h g ⁻¹ after 20 cycles at 53.1 A g ⁻¹
Hierarchical MoS ₂ spheres	Hydrothermal	676 mA h g ⁻¹ after 50 cycles at 1 A g ⁻¹
Graphene/MoS ₂	CVD	1000 mA h g ⁻¹ after 50 cycles at 1 A g ⁻¹
SnS nanoflowers	Solution-based method	580 mA h g ⁻¹ after 30 cycles at 50 mA g ⁻¹
yolk-shell SnS	Spray pyrolysis	672 mA h g ⁻¹ after 150 cycles at 1 A g ⁻¹
Hexagonal SnS ₂ nanoplates	Thermal decomposition	583 mA h g ⁻¹ after 30 cycles at 323 mA g ⁻¹
SnS ₂ nanoplates/graphene	Solution approach and CVD	480 mA h g ⁻¹ (1.6 A g ⁻¹) and 230 mA h g ⁻¹ (6.4 A g ⁻¹)
3D spherical SnS ₂ /graphene	Hydrothermal	920 mA h g ⁻¹ after 50 cycles at 100 mA g ⁻¹
WS ₂ /N-doped graphene	Hydrothermal	900 mA h g ⁻¹ (100 mA g ⁻¹) and 700 mA h g ⁻¹ (5 A g ⁻¹)
In ₂ S ₃ nanosheets	Solution-based method	800 mA h g ⁻¹ (1st) and 450 mA h g ⁻¹ (40th) at 700 mA g ⁻¹
RGO-In ₂ S ₃	One-step mild method	1072 mA h g ⁻¹ (1st) and 1015 mA h g ⁻¹ (100th) at 0.1 A g ⁻¹
Sb ₂ S ₃ nanocrystals/rGO	Sulfidation	720 mA h g ⁻¹ after 50 cycles at 250 mA g ⁻¹
Sb ₂ S ₃ /C nanorods	Solvothermal	960 mA h g ⁻¹ after 30 cycles at 100 mA g ⁻¹
Bi ₂ S ₃ /C nanocomposite	High-energy milling	490 mA h g ⁻¹ after 100 cycles at 100 mA g ⁻¹
TiS ₂ -MWCNT	Physical grinding	360 mA h g ⁻¹ after 50 cycles at 100 mA g ⁻¹

In summary, the current commercial lithium ion battery anode materials like graphite have low capacity, which cannot meet the energy density requirements of high capacity lithium ion battery. Si, SiO₂ and other alloying materials have high capacity. However, their conductivity is low and volume expansion during cycling is large, resulting in rapid capacity attenuation, which limits their practical application. Transition metal oxides, sulfides and phosphates have low conductivity and capacity decay. Thus, developing new anode materials is significant.

As shown in table 2.3, the current LIBs anode materials of three classifications are summarised below:

Table 2.3: Common used LIBs Anode Materials [128].

Active anode material	Theoretical capacity (mAh g ⁻¹) [Reference]	Advantages	Common issues
Insertion/de-insertion materials			
A. Carbonaceous	200-600 [83–85]	➤ Good working potential	❖ Low coulombic efficiency
a. Hard carbons	1116 [91–94]	➤ Low cost	❖ High voltage hysteresis
b. CNTS	780/1116 [45]	➤ Good safety	❖ High irreversible capacity
c. Graphene			
B. Titanium oxides	175 [121]	➤ Extreme safety	❖ Very low capacity
a. LiTi ₄ O ₅	330 [121]	➤ Good cycle life	❖ Low energy density
b. TiO ₂		➤ Low cost	
		➤ High power capability	
Alloy/de-alloy materials			
a. Silicon	4212 [156]	➤ Higher specific capacities	❖ Large irreversible capacity
b. Germanium	1624 [191,192]	➤ High energy density	❖ Huge capacity fading
c. Tin	993 [61]	➤ Good safety	❖ Poor cycling
d. Antimony	660 [150]		
e. Tin oxide	790 [52]		
f. SiO	1600 [47]		
Conversion materials			
a. Metal oxides(Fe ₂ O ₃ , Fe ₃ O ₄ , CoO, Co ₃ O ₄ , Mn _x O _y , Cu ₂ O/CuO, NiO, Cr ₂ O ₃ , RuO ₂ , MoO ₂ /MoO ₃ etc.)	500–1200 [51–53, 56]	➤ High capacity	❖ Low coulombic efficiency
		➤ High energy	❖ Unstable SEI formation
		➤ Low cost	❖ Large potential hysteresis
		➤ Environmentally compatibility	❖ Poor cycle life
		➤ High specific capacity	❖ Poor capacity retention
b. Metal phosphides/sulfides/nitrides (MX _y ; M = Fe, Mn, Ni, Cu, Co etc. and X = P, S, N)	500–1800 [54–56]	➤ Low operation potential and Low polarization than counter oxides	❖ Short cycle life
			❖ High cost of production

2.4 The research of Cobalt Sulfides (Co_xS)

2.4.1 The introduction of Cobalt Sulfides

The cobalt sulfides include Co₉S₈, CoS, CoS₂, Co₃S₄, Co₄S₃, and Co₂S₃. Their distinguishable crystal structures and properties can suit different applications [129].

Co₉S₈, CoS, and CoS₂ have been studied the most among all kinds of cobalt sulfides, as anodes for LIBs. CoS in nature has a hexagonal crystal structure [130]. It has a space group of P6₃/mmc (a = b = 3.37 Å and c = 5.14 Å). The theoretical capacity of CoS is 590 mA h g⁻¹, higher than commercialized graphite. The conversion equation (2-14) [131] for CoS is shown below:

Pyrite CoS_2 with a space group of $\text{Pa}\bar{3}$ ($a = b = c = 5.53 \text{ \AA}$), has a cubic crystal structure (Fig. 10a) [132]. The theoretical capacity of CoS_2 is 870 mA h g^{-1} , higher than CoS , but capacity tends drop to 400 mAh g^{-1} tens of cycles later [133, p.]. The conversion equation [134] (2-15) for CoS_2 is expressed below:

C_9S_8 crystal is cubic structure with the $\text{Fm}\bar{3}\text{m}$ space group ($a = b = c = 9.927 \text{ \AA}$) [135], shown in (Fig. 10b) [136]. The theoretical capacity of C_9S_8 is 539 mAh g^{-1} [137], slightly lower that of CoS . The conversion equation [134] (2-16) at $\sim 1.0 \text{ V}$ (vs. Li/Li^+) for C_9S_8 is indicated below:

Figure 2.13: Structures (crystal) of a) Pyrite CoS_2 and b) Co_9S_8 (T: tetrahedral, O: octahedral)

The summary of the important properties of cobalt sulfides in different stoichiometric compositions are summarized below:

Table 2.4: Properties of cobalt sulfides in different stoichiometric compositions [129].

Compound	Investigation	Results	Remarks
Co_3S_2	Magnetic properties	Ferrimagnetic below 325°C, $T_N = 325^\circ\text{C}$	$g = 1.9 \pm 15\%$ in ferrimagnetic resonance. Mössbauer spectra do not clearly indicate presence of Fe^{+3}
	Electrical properties	Synthetic, semiconductor. Natural, metallic, p -type above 165 K, n -type below 165 K, p -type along c -axis	Holes seem to be the majority carriers
Co_3S_4	Preparation and properties	Reaction of the elements and quenching from 1100°C Metallic, paramagnetic	This is a high-temperature phase with a homogeneity range between 29.2 and 30.6%S. Structural data not available Detailed investigation of properties not reported
	Preparation and crystal structure	Direct reaction of the elements and annealing at 600°C. Cubic, $Fm\bar{3}m$, $a = 9.928 \text{ \AA}$, $Z = 4$	—
CoS	Properties	Susceptibility = $1 \times 10^{-6} \text{ emu/g}$ at 300 K and $4 \times 10^{-6} \text{ emu/g}$ at 1106 K, metallic	Antiferromagnetism reported earlier with $\theta = -50 \text{ K}$ may be due to other phases
	Preparation and crystal structure	Reaction of the elements and annealing at 800 K. NiAs type, $a = 3.367 \text{ \AA}$, $c = 5.177 \text{ \AA}$ Metallic, constant paramagnetism	At higher temperature Co_{1-x}S with variable composition is formed Magnetic susceptibility depends upon the sulfur content
Co_3S_4	Preparation and structure	Reaction of the elements in vacuum and annealing at 700°C. Spinel, $Fd\bar{3}m$, $a = 9.405 \text{ \AA}$	—
	Properties	Metallic, weakly paramagnetic $\alpha = +4.8 \mu\text{V/deg}$	Co in octahedral and tetrahedral holes
Co_2S_3	Preparation and crystal structure	$\text{CoCO}_3 + \text{K}_2\text{SO}_4 + \text{S}$ at 900°C Cubic, $a = 9.44 \text{ \AA}$, $F41/d32/m$ (spinel type); hexagonal, $a = 6.68 \text{ \AA}$, $c = 16.36 \text{ \AA}$	Graphite like shining crystals density = 4.85 g cm^{-3} . Properties not reported
CoS_2	Preparation and crystal structure	Direct reaction of the elements at high temperature. Cubic (pyrite), $a = 5.521 \text{ \AA}$	—
	Electrical and magnetic properties	Metallic, $\rho = 2 \times 10^{-4} \text{ ohm-cm}$ at 300 K, $\mu_{\text{eff}} = 1.85 \mu\text{B}$, $\mu_{\text{int}} = 0.84 \mu\text{B}$, $T_c = 120 \text{ K}$ (ferromagnetic), $\alpha = -28 \mu\text{V/deg}$, $R_H = -1.1 \times 10^{-3} \text{ cm}^3/\text{C}$	Narrow band ferromagnetism; resistivity shows change in slope at T_c . $g = 2.06$ ($T > T_c$); below T_c ferromagnetic resonance
	Optical properties	Absorption edge below 1 eV. Several peaks above 1 eV due to $\sigma \rightarrow e_g$ transition	—

2.4.2 The preparation and properties of cobalt sulfides

Currently, cobalt sulfides are synthesized in many ways. In summary, the methods can be classified into hydrothermal/solvent thermal method, high temperature solid phase, precipitation, spray pyrolysis and microwave synthesis, thermal decomposition and sulfidation method, etc. A relatively new way to prepare cobalt sulfides is using carbonaceous support and metal organic framework as template, which also will be introduced in this chapter.

1) Hydrothermal/solvothermal method

Using water or organic solvent as the reaction medium, reaction materials are placed in a reaction kettle, then being heated in the oven. An environment of high temperature and high pressure is formed, and those insoluble materials can also be dissolved, so that they can participate in chemical reactions and generate products. Generally, products prepared by hydrothermal method do not need to be calcinated at a high temperature because it can directly obtain crystallized materials. Moreover, the temperature of hydrothermal reaction is not very high, which can save energy. Thus, it is a relatively environmentally friendly and valuable method.

Taking one-step solvothermal method as an example, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was used as the cobalt source, elemental sulfur as the sulfur source, and ethanol as the reaction medium. The CoS_2 hollow spheres with uniform morphology were synthesized. The particle size is 2-3 μm and the thickness of the shell is about 300nm.

3D-flower-like CoS [138] and CoS_2 hollow structures [132] can be synthesized by solvothermal method as well. The first cycle's discharge capacity of CoS is 890 mAh g^{-1} at 50 mA g^{-1} . The discharge capacity at the 1st cycle of CoS_2 is 1210 mAh g^{-1} when current density is 100 mA g^{-1} .

Co_9S_8 nanotubes can be prepared in two steps by hydrothermal means. Hydrothermal reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ vs. $\text{CO}(\text{NH}_2)_2$ was used to synthesize the nano-rod precursor

$\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.20}(\text{OH})_{1.10}$. Co_9S_8 nanotubes were then obtained by hydrothermal reaction of the precursor with Na_2S solvent. The diameter of the synthesized Co_9S_8 nanotube is about 150-300nm and the length of the nanotube ranges from a few microns to more than ten microns.

2) High temperature solid phase method

This method has become a common chemical synthesis way in industry due to its simple operation and synthesis steps. Taking elemental Co and elemental S as reaction items, potassium halide (KCl, KBr, KI) as reaction medium/flux, CoS_2 material with polyhedron structure was synthesized by this method. However, the solid phase reaction temperature is high, and the product size is relatively large.

A ball mill is usually needed to refine the products. In the meantime, various impurities are easily introduced. The powder particle size is hard to be controlled, morphology as well, which may affect the battery performance.

3) Precipitation method

In the field of liquid phase preparation, precipitation is the most commonly used method to synthesize nanoparticles with high purity. When some precipitators (such as OH^- , Cl^- , SO_4^{2-} , CO_3^{2-} , S^{2-} , etc. or the compound that produces these ions in reaction) are added, under certain temperature, the solution is hydrolyzed or directly precipitated to form insoluble products. The required nanoparticles are obtained directly or by post-processing such as decomposition.

Precipitation methods are mainly divided into five categories: co-precipitation method, uniform precipitation method, direct precipitation method, compound precipitation method and hydrolytic precipitation. Different precipitation methods tend to generate products with various morphologies and different range of particle sizes. So we can choose the most suitable precipitation method according to the different requirements of the products. Liu huakun et al. successfully synthesized CoS nanoparticles by direct

precipitation. CoS nanoparticles were synthesized by slowly dropping cobalt sulfate and sodium sulfide into ethylenediaminetetraacetic acid (EDTA) solution.

4) Spray pyrolysis

Each metal salt is prepared into precursor solution according to the stoichiometric ratio required by the synthetic product, followed by being atomized through the atomizer. Then the atomized precursor solution is introduced into the high-temperature reactor through gas. Evaporation of solvent and precipitation of solute happens in the reactor in a very short time. After a series of physical and chemical changes such as solid particle formation, particle drying, particle thermal decomposition and sintering forming, the powder with minimal particle size is finally formed. Spray pyrolysis has advantages of both gas phase method and liquid phase method. For example, the chemical composition is uniform, the preparation process is simple, the yield is high, the product is spherical and not agglomerated, the particle size is relatively uniform, the purity of the product is high and so on. The mixed solution of $\text{Co}(\text{NO}_3)_2$ and thiuron was placed in a spray pyrolyzer. Mixed gas with 10% H_2/Ar was introduced in and heated to 900°C . Finally, spherical Co_9S_8 material was obtained.

Accessible surface area plays an important role, which draws attention on synthesizing different nanomorphologies of cobalt sulfides.

Ko et al. [139] used a two-step method, which is spray pyrolysis followed by sulfidation, to synthesize $\sim 700\text{nm}$ diameter Co_9S_8 yolk-shell spheres as anode. At a constant current density of 1A g^{-1} , its discharge capacity is 1008 mA h g^{-1} , while the charge capacity is 767 mA h g^{-1} . Moreover, 82% of its original capacity is reserved after 100th cycle. Compared study was done on the filled Co_9S_8 microspheres. At the same constant current density of 1A g^{-1} , its discharge capacity is 838 mA h g^{-1} , while the charge capacity is 638 mA h g^{-1} . The filled Co_9S_8 microspheres would experience capacity decay and can only maintain 66% of the first cycle capacity. Similarly, Wang et al. [140] discovered that the Co_9S_8 nanotubes have better electrochemical performance than the Co_9S_8 nanoparticles, which proves that larger accessible surface area can lead to higher capacity

and better capacity retaining. Hollow structure is more beneficial than its solid counterpart.

5) Microwave synthesis

Microwave synthesis refers that polar molecules in matters interact with microwave electromagnetic fields. Under an external alternating electromagnetic field, the polar molecules in the material become polarized and change their orientation with the polarity change of the applied alternating electromagnetic field. Due to the frequent friction between a large number of polar molecules, energy loss is caused, which transforms electromagnetic energy into heat energy, so as to achieve the synthesis of materials.

As a new synthesis method, microwave synthesis has been widely used since its discovery. Microwave heating not only has the advantages of fast heating speed, small heat loss, simple operation, uniform heating, easy to control, sensitive reaction, environmental-friendly, but also can heat materials selectively.

In a certain range of microwaves, the ability of various substances to absorb microwaves are different. Generally speaking, substances with large dielectric constants are easy to be heated with microwaves. In contrast, materials which has too small dielectric constant are difficult to microwave. Porous CoS_2 nm sheets were prepared by placing the mixed $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and thiourea solution in a microwave oven and heat treatment for 20mins at a power of 700W.

6) Thermal decomposition and sulfidation

Yin et al. [141] assembled colloidal Co_9S_8 and Co_3S_4 hollow structures through thermal decomposition of $\text{Co}_2(\text{CO})_8$ to form Co nanocrystals, before sulfidation process.

7) Carbonaceous support

To improve electrochemical properties of LIBs, one way is to apply nanosizing effects. Other than that, carbonaceous support can increase the conductivity, hinder electro-active material agglomeration, and provide a rigid mechanical structure. Examples are CNT and

rGO [142]. In addition, carbon base can buffer the volume change, prevent pulverization and capacity decay during charging and discharging process. Gu et al. [142] reported that CoS/graphene has better electrochemical performance than its original counterpart CoS. Xie et al. [133] found that CoS₂/graphene has improvements in rate capability and cycling performance than pristine CoS₂. Summary for some cobalt sulfides with carbonaceous support and their performances is shown in the table 2.5 below:

Table 2.5: Summary for cobalt sulfides nanocomposites with carbonaceous support [143].

Samples	Current density/ mA g^{-1}	Discharge capacity/ mAh g^{-1}
CoS@PCP/CNTs	200	1400 (50th cycle)
CoS-graphene composites	58.9	1000 (50th cycle)
Flower-like CoS	50	300 (25th cycle)
Graphene-wrapped CoS	62.5	864 (40th cycle)
Hierarchical Co _{1-x} S	100	320 (50th cycle)
NC/CoS ₂	100	560 (50th cycle)
RG0/Co ₉ S ₈	545	850 (50th cycle)
CoS/CNTs	100	780 (50th cycle)

8) Template assisted method using metal organic framework (MOF)

Template assisted method is used to achieve well defined nanostructures of cobalt sulfides. Research have shown that CoS polyhedral nanocage can be synthesized from mesoporous MOF structure.

Zou ruqiang et al. skillfully synthesized a cobalt sulfide composite (CoS₂) anode material by using nano metal organic skeleton material as the precursor system They firstly heated the nano metal organic framework material (ZIF-67) in a protective gas. This is to carbonize the organic ligands in ZIF-67 and generate nitrogen-doped porous carbon material. In carbonization, Co-ions in raw material were reduced to metal cobalt nanoparticles.

Cobalt sulfide nanoparticle composite coated with nitrogen-doped porous carbon was obtained by further vulcanization treatment. In the composite structure, the carbon structure covered at the outer layer could increase conductivity of the material and prevent volume change, fragmentation and agglomeration of cobalt sulfide particles.

Nitrogen-doped porous carbon not only can provide the necessary transport path for the electrolyte, but also can effectively adsorb the polysulfide which are the intermediates generated during cycling to alleviate its dissolution problem. Meanwhile, internal nano-scale cobalt sulfide particles could reduce Li-ions' diffusion path.

Electrochemical properties of cobalt sulfide as anode material can be significantly improved by the synergistic effect of the above factors. Battery test results show that: under the current density of 100 mA g^{-1} , 50 cycles of charge/discharge later, its mass specific capacity is still maintained to 560 mAh g^{-1} . Increasing the current density to 2500 mA g^{-1} , 50 cycles later, its mass specific capacity is still up to 410 mAh g^{-1} .

In this work, a new method for synthesizing porous carbon coated nano-sulfide particle composites based metal organic framework (MOF) is proposed. This will provide reference to improve similar electrodes' battery performance.

Metal organic frameworks (MOF-s) are synthesized by joining organic and inorganic groups with covalent bonds. Interactions like hydrogen bonding, van der Waals forces can be involved in MOF formation as well. Metal organic frameworks can be employed for drug delivery [144], optoelectronics [145], proton conduction [146], gas storage and separation [147] and catalysis. Some applications in electrochemical industry are like supercapacitors [148], batteries [149] and fuel cells [150]. Other than using MOF materials along, they can be used as template for active nanomaterials in energy storage or energy conversion reactions [151]. MOFs can also act as sacrificial templates to build different ordered nano-structures with high surface area under various treatments. Because they have special topology and compositions (fig. 2.14) [152].

Figure 2.14: Diagram of MOF-based nanostructures [153].

Materials derived from metal organic frameworks (MOFs) have many advantages. First, they are convenient to be synthesized. Second, the porosity can be controlled. Third, the functional surface area is larger due to the structure is more porous. The initial MOF precursor is significant in defining the surface area and pore size of final products [154]. Utilizing a porous MOF precursor would result in higher surface area products. On the contrary, non-porous MOF tends to derive products with lesser surface area [155].

2.4.3 The advantages and disadvantages of Cobalt Sulfides

Cobalt sulfides has advantages like high specific capacity, abundant resources and low cost. They also have disadvantages like low electronic conductivity, large volume expansion, thus capacity attenuation after several cycles. To solve above issues, one method is to synthesize nano-sized materials, so that the volume change would be lowered. The second way is to enlarge accessible surface area, modify morphology to be more porous, research showed that porous morphology materials have better capacity

retention than their solid counterpart. The third way is to composite with high conductivity materials like graphite, graphene, etc., then composite products tend to have a higher capacity and electronic conductivity. In this research, CoS was prepared using one-step in-situ formation method, which utilized metal organic framework (MOF) as precursor and template, followed by sulfidation, which is a very convenient method. The stoichiometric ratio and cobalt sulfide properties can be tuned by different calcination temperatures.

Metal organic framework (MOF) converted cobalt sulfides have many advantages. First, materials are nano-sized, the volume change is relatively smaller, structure is more stable and not easy to collapse compared with bulk materials during cycling. Stable structural support is one of the keys to prevent capacity decay. Moreover, nano-particles could reduce Li-ions' diffusion path, which increases the lithium ion transmission rate. Second, after calcination, a thin layer of carbon would form and uniformly cover the nano-particle of cobalt sulfides. One of the function of this layer of carbon is to significantly improve material's conductivity. The other function is to provide a film of mechanical support, so that huge volume change is not easy to happen during cycling. Last but not least, carbon film can provide excess number of active sites, so that both conversion and intercalation reaction can occur during the lithiation process, which would increase the overall capacity of the materials.

References

- [1] K. Tamura, T. Kahara, T. Horiba, N. Ebato, and O. Asai, *Primary battery*. Google Patents, 1981.
- [2] J. M. Tarascon and M. Armand, “Issues and challenges facing rechargeable lithium batteries,” *Nature*, vol. 414, no. 6861, pp. 359–67, 2001.
- [3] R. Marom, S. F. Amalraj, N. Leifer, D. Jacob, and D. Aurbach, “A review of advanced and practical lithium battery materials,” *J. Mater. Chem.*, vol. 21, no. 27, p. 9938, 2011, doi: 10.1039/c0jm04225k.
- [4] J. R. Dahn, T. Zheng, Y. Liu, and J. S. Xue, “Mechanisms for Lithium Insertion in Carbonaceous Materials,” *Science*, vol. 270, no. 5236, p. 590, 1995, doi: 10.1126/science.270.5236.590.
- [5] B. Dunn, H. Kamath, and J.-M. Tarascon, “Electrical Energy Storage for the Grid: A Battery of Choices,” vol. 334, no. 6058, pp. 928–935.
- [6] X. Chen, S. Shen, L. Guo, and S. S. Mao, “Semiconductor-based Photocatalytic Hydrogen Generation,” *Chem. Rev.*, vol. 110, no. 11, pp. 6503–6570.
- [7] A. Yoshino, “The Birth of the Lithium-Ion Battery,” *Angew. Chem. Int. Ed.*, vol. 51, no. 24, pp. 0–0.
- [8] D. Larcher and J.-M. Tarascon, “Towards greener and more sustainable batteries for electrical energy storage,” *Nat. Chem.*, vol. 7, no. 1, pp. 19–29.
- [9] M. Winter and R. J. Brodd, “What Are Batteries, Fuel Cells, and Supercapacitors?,” *Chem. Rev.*, vol. 104, no. 10, pp. 4245–4270, Oct. 2004, doi: 10.1021/cr020730k.
- [10] M. M. Thackeray, C. Wolverton, and E. D. Isaacs, “Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries,” *Energy Environ. Sci.*, vol. 5, no. 7, p. 7854, 2012, doi: 10.1039/c2ee21892e.
- [11] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. Proietti Zaccaria, and C. Capiglia, “Review on recent progress of nanostructured anode materials for Li-ion batteries,” *J. Power Sources*, vol. 257, pp. 421–443, Jul. 2014, doi: 10.1016/j.jpowsour.2013.11.103.
- [12] Abraham and M. K., “Prospects and Limits of Energy Storage in Batteries,” *J. Phys. Chem. Lett.*, vol. 6, no. 5, pp. 830–844.

- [13] J. Lee, A. Urban, X. Li, D. Su, G. Hautier, and G. Ceder, “Unlocking the Potential of Cation-Disordered Oxides for Rechargeable Lithium Batteries,” *Science*, vol. 343, no. 6170, pp. 519–522.
- [14] P. Voelker, “Trace Degradation Analysis of Lithium-Ion Battery Components,” p. 5.
- [15] M. K. Song, S. Park, F. M. Alamgir, J. Cho, and M. Liu, “Nanostructured electrodes for lithium-ion and lithium-air batteries: the latest developments, challenges, and perspectives,” *Mater. Sci. Eng. R*, vol. 72, no. 11, p. p.203-252.
- [16] “Structure design and mechanism analysis of silicon anode for lithium-ion batteries,” *Sci. China Mater.*, 2019.
- [17] C. Joseph, “Air breathing lithium power cells,” 2014.
- [18] J. B. Goodenough and K. S. Park, “The Li-Ion Rechargeable Battery: A Perspective,” *J. Am. Chem. Soc.*, vol. 135, no. 4, pp. 1167–1176.
- [19] “Polyethylene Oxide-Coated Electrospun Polyimide Fibrous Separator for High-Performance Lithium-Ion Battery,” *J. Mater. Sci. Technol.*, no. 3, pp. 200–206.
- [20] H. Ling, C. Lu, C. Ping, Q. Wen, and Y. Qi, “The Effect of in situ Generated Titanium Dioxide on the Mechanical and Electrochemical Properties of Electrospun Polyvinylidene Fluoride Separator for Lithium-ion Battery,” *Acta Polym. Sin.*, vol. 012, no. 11, pp. 1319–1325, 2012.
- [21] J. Y. Kim and D. Y. Lim, “Surface-Modified Membrane as A Separator for Lithium-Ion Polymer Battery,” *Energies*, vol. 3, no. 4, pp. 866–885, Apr. 2010, doi: 10.3390/en3040866.
- [22] S. Oh, J. K. Lee, D. Byun, W. I. Cho, and B. W. Cho, “Effect of Al_2O_3 coating on electrochemical performance of LiCoO_2 as cathode materials for secondary lithium batteries,” *J. Power Sources*, vol. 132, no. 1–2, pp. 249–255.
- [23] T. K. Fey, J.-G. Chen, and T. P. Kumar, “Enhanced cyclability of LiCoO_2 cathodes coated with alumina derived from carboxylate–alumoxanes,” *J. Appl. Electrochem.*, vol. 35, no. 2, pp. 177–184.
- [24] Y. Koyama, I. Tanaka, H. Adachi, Y. Uchimoto, and M. Wakihara, “First principles calculations of formation energies and electronic structures of defects in oxygen-deficient LiMn_2O_4 ,” *J. Electrochem. Soc.*, vol. 150, no. 1, pp. A63–A67, 2003.

- [25] H. W. Lee, P. Muralidharan, R. Ruffo, C. M. Mari, and D. K. Kim, "Ultrathin Spinel LiMn_2O_4 Nanowires as High Power Cathode Materials for Li-Ion Batteries," *Nano Lett.*, vol. 10, no. 10, pp. 3852–3856, 2010.
- [26] J. Wang and X. Sun, "Olivine LiFePO_4 : the remaining challenges for future energy storage," *Energy Environ. Sci.*, vol. 8, 2015.
- [27] M. S. Islam, D. J. Driscoll, C. A. J. Fisher, and P. R. Slater, "Atomic-Scale Investigation of Defects, Dopants, and Lithium Transport in the LiFePO_4 Olivine-Type Battery Material," *Chem. Mater.*, vol. 17, no. 20, pp. 5085–5092.
- [28] C. M. Julien, A. Mauger, K. Zaghib, and H. Groult, "Comparative Issues of Cathode Materials for Li-Ion Batteries," *Inorganics*, vol. 2, pp. 132–154.
- [29] H. Lu *et al.*, "High capacity $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$ synthesized by sol–gel and co-precipitation methods as cathode materials for lithium-ion batteries," *Solid State Ion.*, vol. 249–250, no. Complete, pp. 105–111.
- [30] B. J. Hwang, Y. W. Tsai, D. Carlier, and G. Ceder, "A Combined Computational/Experimental Study on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$," *Chem. Mater.*, vol. 15, no. 19, pp. 3676–3682, 2003, doi: 10.1021/cm030299v.
- [31] F. Cheng, J. Liang, Z. Tao, and J. Chen, "Functional Materials for Rechargeable Batteries," vol. 23, no. 15, pp. 1695–1715.
- [32] M. Winter, J. O. Besenhard, M. E. Spahr, and P. Novák, "Insertion Electrode Materials for Rechargeable Lithium Batteries," *Adv. Mater.*, vol. 10, no. 10, pp. 725–763, 1998.
- [33] B. Scrosati and J. Garche, "Lithium batteries: Status, prospects and future," *J. Power Sources*, vol. 195, no. 9, pp. 2419–2430.
- [34] K. Persson *et al.*, "Lithium Diffusion in Graphitic Carbon," *Physics*, vol. 1, no. 8, pp. 1176–1180.
- [35] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, and C. Chen, "Thermal runaway caused fire and explosion of lithium ion battery," *J. Power Sources*, vol. 208, pp. 210–224, 2012, doi: 10.1016/j.jpowsour.2012.02.038.
- [36] M. Gauthier *et al.*, "The Electrode-Electrolyte Interface in Li-ion Batteries: Current Understanding and New Insights," *J. Phys. Chem. Lett.*, p. acs.jpcclett.5b01727.

- [37] M. Nie, D. Chalasani, D. P. Abraham, Y. Chen, A. Bose, and B. L. Lucht, "Lithium Ion Battery Graphite Solid Electrolyte Interphase Revealed by Microscopy and Spectroscopy," *J. Phys. Chem. C*, vol. 117, no. 3, pp. 1257–1267, 2013, doi: 10.1021/jp3118055.
- [38] R. A. Huggins, "Alternative materials for negative electrodes in lithium systems," *Proc. Int. Conf. SOLID STATE Ion. Mater. Process. ENERGY Environ. CAIRNS Aust. 8-13 JULY 2001*, vol. 152–153, pp. 61–68, 2002, doi: 10.1016/S0167-2738(02)00337-5.
- [39] M. R. Palacín, "Recent advances in rechargeable battery materials: a chemist's perspective," *Chem. Soc. Rev.*, vol. 38, no. 9, p. 2565, 2009, doi: 10.1039/b820555h.
- [40] Z. Q. Jin, J. R. Zhang, S. L. Tang, and Y. W. Du, "Structure and magnetic properties of melt-spun PrFeMoN compounds," *J. Appl. Phys.*, vol. 87, no. 9, p. 5290.
- [41] F. Yao and C. S. Cojocaru, "Carbon-Based Nanomaterials as an Anode for Lithium Ion Battery," *Bibliogr. Réf*, 2013.
- [42] N. A. Kaskhedikar and J. Maier, "ChemInform Abstract: Lithium Storage in Carbon Nanostructures," *Cheminform*, vol. 40, no. 37, 2009.
- [43] Franklin and R. E, "Crystallite Growth in Graphitizing and Non-Graphitizing Carbons," *Proc. R. Soc. Math. Phys. Eng. Sci.*, vol. 209, no. 1097, pp. 196–218.
- [44] T. Lin *et al.*, "Nitrogen-doped mesoporous carbon of extraordinary capacitance for electrochemical energy storage," *Science*, vol. 350, no. 6267, pp. 1508–1513.
- [45] Jintao Huang, Yemao Lin, Muwei Ji, Guangtao Cong, Huichao Liu, Jiali Yu, Bo Yang, Cuihua Li, Caizhen Zhu*, and Jian Xu., "Nitrogen-doped porous carbon derived from foam polystyrene as an anode material for lithium-ion batteries.," *Appl. Surf. Sci.* 504 2020 144398.
- [46] Ming-Hua Jiang, D. Cai, and T. Ni, "Nitrogen-doped graphene sheets prepared from different graphene-based precursors as high capacity anode materials for lithium-ion batteries.," *Int. J. Electrochem. Sci.*, no. 2017, 12(8): 7154-7165., Aug. 2017, doi: 10.20964.
- [47] E. Yoo, J. Kim, E. Hosono, H. Zhou, T. Kudo, and I. Honma, "Large Reversible Li Storage of Graphene Nanosheet Families for Use in Rechargeable Lithium Ion Batteries," *Nano Lett.*, vol. 8, no. 8, pp. 2277–2282, 2008, doi: 10.1021/nl800957b.

- [48] D. Pan *et al.*, “Li Storage Properties of Disordered Graphene Nanosheets,” *Chem. Mater.*, vol. 21, no. 14, pp. 3136–3142.
- [49] Z. J. Jiang and Z. Jiang, “Fabrication of Nitrogen-Doped Holey Graphene Hollow Microspheres and Their Use as an Active Electrode Material for Lithium Ion Batteries,” *Acs Appl. Mater. Interfaces*, vol. 6, no. 21, pp. 19082–19091.
- [50] H. Liu, Y. Tang, Z. Wei, D. Wei, and F. Huang, “Facile Synthesis of Nitrogen and Halogen Dual-Doped Porous Graphene as an Advanced Performance Anode for Lithium-Ion Batteries,” *Adv. Mater. Interfaces*, vol. 5, no. 5, p. 1701261, 2018.
- [51] P. Kubiak *et al.*, “Electrochemical evaluation of rutile TiO₂ nanoparticles as negative electrode for Li-ion batteries,” *J. Power Sources*, vol. 194, no. 2, pp. 1099–1104.
- [52] Y. Liu and Y. Yefeng, “Recent Progress of TiO₂-Based Anodes for Li Ion Batteries,” *J. Nanomater.*, vol. 2016, pp. 1–15.
- [53] P. Bottke, Y. Ren, I. Hanzu, P. G. Bruce, and M. Wilkening, “Li ion Dynamics in TiO₂ Anode Materials with an Ordered Hierarchical Pore Structure—Insights from Ex Situ NMR,” *Phys. Chem. Chem. Phys. Pccp*, vol. 16, no. 5, 2013.
- [54] W. Li *et al.*, “General Strategy to Synthesize Uniform Mesoporous TiO₂/Graphene/Mesoporous TiO₂ Sandwich-Like Nanosheets for Highly Reversible Lithium Storage,” *Nano Lett.*, vol. 15, no. 3, pp. 2186–2193, 2015, doi: 10.1021/acs.nanolett.5b00291.
- [55] S. Ma, Q. Li, Z. Cai, Z. Ye, and Y. Zhou, “Facile fabrication of ZnO/N-doped helical carbon nanotubes composites with enhanced photocatalytic activity toward organic pollutant degradation,” *Appl. Organomet. Chem.*, p. e3966.
- [56] Y. Zhang *et al.*, “Preparation and lithium storage properties of C@TiO₂/3D carbon hollow sphere skeleton composites,” *J. Alloys Compd.*, vol. 815, p. 152511, 2020, doi: 10.1016/j.jallcom.2019.152511.
- [57] Q. Tian, Z. Zhang, L. Yang, and S. Hirano, “Encapsulation of SnO₂ nanoparticles into hollow TiO₂ nanowires as high performance anode materials for lithium ion batteries,” *J. Power Sources*, vol. 253, pp. 9–16.
- [58] Y. T. Liu *et al.*, “Self-Assembly of Transition Metal Oxide Nanostructures on MXene Nanosheets for Fast and Stable Lithium Storage,” *Adv. Mater.*, p. 1707334.

- [59] E. M. Erickson, C. Ghanty, and D. Aurbach, "New Horizons for Conventional Lithium Ion Battery Technology," *J. Phys. Chem. Lett.*, vol. 5, no. 19, pp. 3313–3324.
- [60] B. J. Landi, M. J. Ganter, C. D. Cress, R. A. Dileo, and R. P. Raffaele, "Carbon nanotubes for lithium ion batteries," *Energy Environ. Sci.*, vol. 2, no. 6, pp. 638–0.
- [61] Deng and Da, "Li-ion batteries: basics, progress, and challenges," *Energy Sci. Eng.*, vol. 3, no. 5, pp. 385–418.
- [62] C. Sun, S. Liu, X. Shi, C. Lai, J. Liang, and Y. Chen, "3D printing nanocomposite gel-based thick electrode enabling both high areal capacity and rate performance for lithium-ion battery," *Chem. Eng. J.*, vol. 381, p. 122641, 2020, doi: 10.1016/j.cej.2019.122641.
- [63] D. Cai and C. Wang, "Facile synthesis of N and S co-doped graphene sheets as anode materials for high-performance lithium-ion batteries," *J. Alloys Compd.*, vol. 731 (2018) 235–242.
- [64] L. Sun *et al.*, "In situ coating of graphene-like sheets on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles for lithium-ion batteries," *Electrochimica Acta*, vol. 230, pp. 508–513, 2017, doi: 10.1016/j.electacta.2016.11.165.
- [65] M. J. Lindsay, G. X. Wang, and H. K. Liu, "Al-based anode materials for Li-ion batteries," *J. Power Sources*, vol. 119/121, no. Jun, p. p.84-87.
- [66] J.-G. Zhang *et al.*, "Vapor-induced solid-liquid-solid process for silicon-based nanowire growth," *J. Power Sources*, vol. 195, no. 6, pp. 1691–1697.
- [67] C. M. Park, J. H. Kim, H. Kim, and H. J. Sohn, "Li-alloy based anode materials for Li secondary batteries," *Chem. Soc. Rev.*, vol. 39, no. 8, pp. 3115–3141, Jan. 2010.
- [68] A. L. M. Reddy, S. R. Gowda, M. M. Shaijumon, and P. M. Ajayan, "ChemInform Abstract: Hybrid Nanostructures for Energy Storage Applications," *Cheminform*, vol. 43, no. 46, p. no-no.
- [69] C. K. Chan *et al.*, "High-performance lithium battery anodes using silicon nanowires," *Nat. Nanotechnol.*, vol. 3, no. 1, p. 31, 2008.
- [70] M. H. Park *et al.*, "Silicon Nanotube Battery Anodes," *Nano Lett.*, vol. 9, no. 11, pp. 3844–3847.
- [71] "Superior Storage Performance of a $\text{Si@SiO}_2/\text{C}$ Nanocomposite as Anode Material for Lithium-Ion Batteries," *Angew. Chem.*, vol. 47, no. 9, pp. 1645–1649, 2008.

- [72] T. D. Hatchard, J. M. Topple, M. D. Fleischauer, and J. R. Dahn, "Electrochemical Performance of SiAlSn Films Prepared by Combinatorial Sputtering," *Electrochem. Solid State Lett.*, vol. 6, no. 7, p. A129.
- [73] J. Szczech and S. Jin, "Nanostructured silicon for high capacity lithium battery anodes," *Energy Environ. Sci.*, vol. 4, no. 1, pp. 56–72, Jan. 2011.
- [74] H. Wu and Y. Cui, "Designing nanostructured Si anodes for high energy lithium ion batteries," *Nano Today*, vol. 7, no. 5, pp. 414–429.
- [75] H. Kim, E. J. Lee, and Y. K. Sun, "Recent advances in the Si-based nanocomposite materials as high capacity anode materials for lithium ion batteries," *Mater. Today*, vol. 17, no. 6, pp. 285–297.
- [76] F. Du, K. X. Wang, and J. S. Chen, "Strategies succeed in improving the lithium-ion storage properties of silicon nanomaterials," *J. Mater. Chem. A*, vol. 4, no. 1, pp. 32–50, 2015.
- [77] L. Liu *et al.*, "Well-constructed silicon-based materials as high-performance lithium-ion battery anodes," vol. 8, no. 2, pp. 701–722, 2015.
- [78] U. Kasavajjula, C. Wang, and A. J. Appleby, "Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells," vol. 163, no. 2, pp. 1003–1039.
- [79] M. Ashuri, Q. He, and L. L. Shaw, "Silicon as a potential anode material for Li-ion batteries: where size, geometry and structure matter," *Nanoscale*, vol. 8, no. 1, pp. 74–103, 2016, doi: 10.1039/C5NR05116A.
- [80] F. Luo *et al.*, "Review—Nano-Silicon/Carbon Composite Anode Materials Towards Practical Application for Next Generation Li-Ion Batteries," *J. Electrochem. Soc.*, vol. 162, no. 14, pp. A2509–A2528.
- [81] L. Pan, H. Wang, D. Gao, S. Chen, L. Tan, and L. Li, "Facile synthesis of yolk-shell structured Si-C nanocomposites as anodes for lithium-ion batteries," *Chem. Commun.*, vol. 50, no. 44, pp. 5878–5880.
- [82] M. Holzapfel *et al.*, "Nano silicon for lithium-ion batteries," vol. 52, no. 3, pp. 973–978.
- [83] H. Song *et al.*, "Highly Connected Silicon-Copper Alloy Mixture Nanotubes as High-Rate and Durable Anode Materials for Lithium-Ion Batteries," *Adv. Funct. Mater.*, 2015.

- [84] S. Fang *et al.*, “Rational Design of Void-Involved Si@TiO₂ Nanospheres as High-Performance Anode Material for Lithium-Ion Batteries,” *Acs Appl. Mater. Interfaces*, vol. 6, no. 9, pp. 6497–6503.
- [85] H. Wu *et al.*, “Stable Li-ion battery anodes by in-situ polymerization of conducting hydrogel to conformally coat silicon nanoparticles,” *Nat. Commun.*, vol. 4.
- [86] M. Armand and J.-M. Tarascon, “Building better batteries,” *Nature*, vol. 451, no. 7179, pp. 652–657.
- [87] G. Parzych and D. Mikhailova, “Study of the Conversion Reaction Mechanism for Copper Borate as Electrode Material in Lithium-Ion Batteries,” *Electrochem. Soc.*, Jun. 2011.
- [88] S. Grugeon, S. Laruelle, L. Dupont, and J. M. Tarascon, “An update on the reactivity of nanoparticles Co-based compounds towards Li,” *Solid State Sci.*, vol. 5, no. 6, pp. 895–904, 2003.
- [89] “Conversion Reaction Mechanisms in Lithium Ion Batteries: Study of the Binary Metal Fluoride Electrodes,” *J. Am. Chem. Soc.*, vol. 133, no. 46, p. p.18828-18836.
- [90] L. Zhang, H. B. Wu, S. Madhavi, H. H. Hng, and X. W. (David) Lou, “Formation of Fe₂O₃ Microboxes with Hierarchical Shell Structures from Metal–Organic Frameworks and Their Lithium Storage Properties,” *J. Am. Chem. Soc.*, vol. 134, no. 42, pp. 17388–17391, 2012, doi: 10.1021/ja307475c.
- [91] F. X. Ma, H. Hu, H. B. Wu, C. Y. Xu, and X. W. D. Lou, “Formation of Uniform Fe₃O₄ Hollow Spheres Organized by Ultrathin Nanosheets and Their Excellent Lithium Storage Properties,” *Adv. Mater.*, vol. 27, no. 27, 2015.
- [92] “Homogeneous CoO on Graphene for Binder-Free and Ultralong-Life Lithium Ion Batteries,” *Adv. Funct. Mater.*, vol. 23, no. 35, pp. 4345–4353.
- [93] D. Cheng, Y. Yang, Y. Luo, C. Fang, and J. Xiong, “Growth of Ultrathin Mesoporous Ni-Mo Oxide Nanosheet Arrays on Ni Foam for High-performance Supercapacitor Electrodes,” *Electrochimica Acta*, vol. 176, no. Complete, p. S0013468615302164.
- [94] M. Chen, X. Xia, M. Qi, J. Yuan, J. Yin, and Q. Chen, “Controllable synthesis of hierarchical porous nickel oxide sheets arrays as anode for high-performance lithium ion batteries,” *Electrochimica Acta*, vol. 184, pp. 17–23.

- [95] Y. Wang, Y. Wang, D. Jia, Z. Peng, and G. Zheng, "All-Nanowire Based Li-Ion Full Cells using Homologous Mn_2O_3 and LiMn_2O_4 ," *Nano Lett.*, vol. 14, no. 2, p. 1080, 2014.
- [96] "Mn₃O₄ Nanocrystals: Facile Synthesis, Controlled Assembly, and Application," *Chem. Mater.*, vol. 22, no. 14, pp. 4232–4236.
- [97] Z. Bai *et al.*, "Facile synthesis of mesoporous Mn₃O₄ nanotubes and their excellent performance for lithium-ion batteries," *J. Mater. Chem.*, vol. 1, no. 36, pp. 10985–10990, Jan. 2013.
- [98] M. Ma, H. Wang, S. Liang, S. Guo, Y. Zhang, and X. Du, "Porous carbon-wrapped cerium oxide hollow spheres synthesized via microwave hydrothermal for long-cycle and high-rate lithium-ion batteries," *Electrochimica Acta*.
- [99] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, and J. M. Tarascon, "Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries," *Nature*, vol. 32, no. 3, p. no-no, 2010.
- [100] Cherian *et al.*, "Morphologically Robust NiFe₂O₄ Nanofibers as High Capacity Li-Ion;Battery Anode Material," vol. 5, no. 20, pp. 9957–9963, 2013.
- [101] J. Liu, X. Xu, R. Hu, L. Yang, and Z. Min, "Uniform Hierarchical Fe₃O₄@Polypyrrole Nanocages for Superior Lithium Ion Battery Anodes," *Adv. Energy Mater.*, vol. 6, no. 13, 2016.
- [102] "Three-dimensional hierarchical pompon-like Co₃O₄ porous spheres for high-performance lithium-ion batteries," *J. Mater. Chem. A*, vol. 2, 2014.
- [103] S. Z. Huang *et al.*, "Hierarchical mesoporous urchin-like Mn₃O₄/carbon microspheres with highly enhanced lithium battery performance by in-situ carbonization of new lamellar manganese alkoxide (Mn-DEG)," *Nano Energy*, vol. 12, pp. 833–844.
- [104] K. Wang, C. Wu, F. Wang, and G. Jiang, "MOF-Derived CoPx Nanoparticles Embedded in Nitrogen-Doped Porous Carbon Polyhedrons for Nanomolar Sensing of p-Nitrophenol," *ACS Appl. Nano Mater.*
- [105] C. Sun and A. Lin, "In Situ Conversion of Cu₃P Nanowires to Mixed Ion/Electron-Conducting Skeleton for Homogeneous Lithium Deposition," *Adv. Energy Mater.*, vol. Volume 10, no. Issue 3, Nov. 2019.

- [106] Jiang *et al.*, “One-pot synthesis of carbon-coated Ni_3P_4 nanoparticles and CoP nanorods for high-rate and high-stability lithium-ion batteries,” *J. Mater. Chem. Mater. Energy Sustain.*
- [107] L. Li, Y. Peng, and H. Yang, “Phase structure changes of MnP anode material during electrochemical lithiation and delithiation process,” *Electrochimica Acta*, vol. 95, pp. 230–236.
- [108] Z. Li *et al.*, “Core-shell structured CoP/FeP porous microcubes interconnected by reduced graphene oxide as high performance anodes for sodium ion batteries,” *Nano Energy*, vol. 32, no. Complete, pp. 494–502.
- [109] B. Das, M. V. Reddy, G. V. S. Rao, and B. V. R. Chowdari, “Synthesis of porous-CoN nanoparticles and their application as a high capacity anode for lithium-ion batteries,” *J. Mater. Chem.*, vol. 22, no. 34, p. 17505.
- [110] Q. Sun, W. J. Li, and Z. W. Fu, “A novel anode material of antimony nitride for rechargeable lithium batteries,” *Solid State Sci.*, vol. 12, no. 3, pp. 397–403.
- [111] M. Z. Ansari *et al.*, “Low-Temperature Atomic Layer Deposition of Highly Conformal Tin Nitride Thin Films for Energy Storage Devices,” *ACS Appl. Mater. Interfaces*, vol. 11, no. 46, pp. 43608–43621, 2019, doi: 10.1021/acsami.9b15790.
- [112] X. Peng *et al.*, “Lithiation Kinetics in High-Performance Porous Vanadium Nitride Nanosheet Anode,” *Electrochimica Acta*, vol. 214, pp. 201–207, 2016, doi: 10.1016/j.electacta.2016.08.023.
- [113] D. Liu and X. Xu, “Micrometer-sized porous $\text{Fe}_2\text{N}/\text{C}$ bulk for high-area-capacity and stable lithium storage,” *Small*, 2018, doi: 10.1002/smll.201803572.
- [114] Hao *et al.*, “ Fe_3N constrained inside C nanocages as an anode for Li-ion batteries through post-synthesis nitridation.”
- [115] “Binder-free Fe_2N nanoparticles on carbon textile with high power density as novel anode for high-performance flexible lithium ion batteries,” *Nano Energy*, vol. 11, pp. 348–355, 2015.
- [116] Q. Sun and Z. W. Fu, “CrFeN Ternary Transition-Metal Nitrides as Anode Materials for Lithium-Ion Batteries,” *Electrochem. Solid State Lett.*, vol. 11, no. 12, p. A233.

- [117] X. Dong *et al.*, “Synthesis of graphene–carbon nanotube hybrid foam and its use as a novel three-dimensional electrode for electrochemical sensing,” *J. Mater. Chem.*, vol. 22, no. 33, p. 17044.
- [118] Y. Liu *et al.*, “Coral-like α -MnS composites with N-doped carbon as anode materials for high-performance lithium-ion batteries,” *J. Mater. Chem.*, vol. 22, no. 45, p. 24026.
- [119] L. Fei *et al.*, “Reduced Graphene Oxide Wrapped FeS Nanocomposite for Lithium-Ion Battery Anode with Improved Performance,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 11, pp. 5330–5335, 2013, doi: 10.1021/am401239f.
- [120] Ling *et al.*, “A novel FeS₂/CNT micro-spherical cathode material with enhanced electrochemical characteristics for lithium-ion batteries.”
- [121] N. Mahmood, C. Zhang, and Y. Hou, “Nickel Sulfide/Nitrogen-Doped Graphene Composites: Phase-Controlled Synthesis and High Performance Anode Materials for Lithium Ion Batteries,” *Small*, vol. 9, no. 8, pp. 1321–1328.
- [122] N. H. Idris, M. M. Rahman, S. L. Chou, J. Z. Wang, D. Wexler, and H. K. Liu, “Rapid synthesis of binary α -NiS– β -NiS by microwave autoclave for rechargeable lithium batteries,” *Electrochimica Acta*, vol. 58, no. none, pp. 456–462.
- [123] N. Feng, D. Hu, P. Wang, X. Sun, X. Li, and D. He, “Growth of nanostructured nickel sulfide films on Ni foam as high-performance cathodes for lithium ion batteries,” *Phys. Chem. Chem. Phys.*, vol. 15, no. 24, pp. 9924–9930, 2013.
- [124] G. Huang, T. Chen, Z. Wang, K. Chang, and W. Chen, “Synthesis and electrochemical performances of cobalt sulfides/graphene nanocomposite as anode material of Li-ion battery,” *J. Power Sources*, vol. 235, pp. 122–128, Aug. 2013, doi: 10.1016/j.jpowsour.2013.01.093.
- [125] R. Jin, J. Liu, Y. Xu, G. Li, and G. Chen, “Solvothermal synthesis and excellent electrochemical performance of polycrystalline rose-like Co₉S₈ hierarchical architectures,” *J. Mater. Chem. A*, vol. 1, no. 27, pp. 7995–7999, 2013.
- [126] Y. Du *et al.*, “A general method for the large-scale synthesis of uniform ultrathin metal sulphide nanocrystals,” *Nat. Commun.*, vol. 3, p. 1177.

- [127] S. Ni, X. Yang, and T. Li, "Fabrication of a porous NiS/Ni nanostructured electrode via a dry thermal sulfuration method and its application in a lithium ion battery," *J. Mater. Chem.*, vol. 22, no. 6, p. 2395.
- [128] X. Rui, H. Tan, and Q. Yan, "Nanostructured metal sulfides for energy storage," *Nanoscale*, vol. 6, no. 17, p. 9889, Jun. 2014, doi: 10.1039/C4NR03057E.
- [129] C. N. R. Rao and K. P. R. Pisharody, "Transition metal sulfides," *Prog. Solid State Chem.*, vol. 10, pp. 207–270, Jan. 1976, doi: 10.1016/0079-6786(76)90009-1.
- [130] J. Ge and Y. Li, "Controllable CVD route to CoS and MnS single-crystal nanowires," *Chem Commun*, no. 19, pp. 2498–2499, 2003, doi: 10.1039/B307452H.
- [131] A. Débart, L. Dupont, R. Patrice, and J.-M. Tarascon, "Reactivity of transition metal (Co, Ni, Cu) sulphides versus lithium: The intriguing case of the copper sulphide," *Solid State Sci.*, vol. 8, no. 6, pp. 640–651.
- [132] Q. Wang *et al.*, "CoS₂ Hollow Spheres: Fabrication and Their Application in Lithium-Ion Batteries," *J. Phys. Chem. C*, vol. 115, no. 16, pp. 8300–8304.
- [133] J. Xie, S. Liu, G. Cao, T. Zhu, and X. Zhao, "Self-assembly of CoS₂/graphene nanoarchitecture by a facile one-pot route and its improved electrochemical Li-storage properties," *Nano Energy*, vol. 2, no. 1, pp. 49–56, Jan. 2013, doi: 10.1016/j.nanoen.2012.07.010.
- [134] J. M. Yan, H. Z. Huang, and J. Zhang, "A study of novel anode material CoS₂ for lithium ion battery," *J. Power Sources*, vol. 146, no. 1/2, p. p.264-269.
- [135] Y. Wang, H. Li, P. He, E. Hosono, and H. Zhou, "Nano active materials for lithium-ion batteries," *Nanoscale*, vol. 2, no. 8, p. 1294.
- [136] S and Geller, "Refinement of the crystal structure of Co₉S₈."
- [137] J. Wang, S. H. Ng, and G. X. Wang, "Synthesis and characterization of nanosize cobalt sulfide for rechargeable lithium batteries," *J. Power Sources*, vol. 159, no. 1, p. p.287-290.
- [138] Q. Wang *et al.*, "Novel flower-like CoS hierarchitectures: one-pot synthesis and electrochemical properties," *J Mater Chem*, vol. 21, no. 2, pp. 327–329, 2011, doi: 10.1039/C0JM03121F.

- [139] Y. N. Ko, S. H. Choi, S. B. Park, and Y. C. Kang, "Preparation of yolk-shell and filled Co₉S₈ microspheres and comparison of their electrochemical properties," *Chem Asian J*, vol. 8, pp. 572–576, 2013.
- [140] Z. Wang, L. Pan, H. Hu, and S. Zhao, "Co₉S₈ nanotubes synthesized on the basis of nanoscale Kirkendall effect and their magnetic and electrochemical properties," *Crytengcomm*, vol. 12, no. 6, p. 1899.
- [141] Y. Yin, C. K. Erdonmez, A. Cabot, S. Hughes, A. P. Alivisatos, "Colloidal Synthesis of Hollow Cobalt Sulfide Nanocrystals," *Adv. Funct. Mater.*, Jul. 2006, doi: 10.1002/adfm.200690040.
- [142] Y. Gu, Y. Xu, and Y. Wang, "Graphene-Wrapped CoS Nanoparticles for High-Capacity Lithium-Ion Storage," *ACS Appl. Mater. Interfaces*, vol. 5, no. 3, pp. 801–806, Feb. 2013, doi: 10.1021/am3023652.
- [143] H. Wang *et al.*, "CoS/CNTs hybrid structure for improved performance lithium ion battery," *J. Alloys Compd.*, vol. 676, pp. 551–556, Aug. 2016, doi: 10.1016/j.jallcom.2016.03.132.
- [144] P. Horcajada *et al.*, "Porous metal–organic-framework nanoscale carriers as a potential platform for drug delivery and imaging," *Nat. Mater.*, vol. 9, no. 2, pp. 172–178, Feb. 2010, doi: 10.1038/nmat2608.
- [145] M. E. Foster, J. D. Azoulay, B. M. Wong, and M. D. Allendorf, "Novel metal–organic framework linkers for light harvesting applications," *Chem. Sci.*, vol. 5, no. 5, p. 2081, 2014.
- [146] S. C. Sahoo, T. Kundu, and R. Banerjee, "Helical Water Chain Mediated Proton Conductivity in Homochiral Metal-Organic Frameworks with Unprecedented Zeolitic unh-Topology," *J. Am. Chem. Soc.*, vol. 133, no. 44, p. p.17950-17958.
- [147] R. Banerjee *et al.*, "High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO₂ Capture," *Science*, vol. 319, no. 5865, p. p.939-943.
- [148] R. Díaz, M. G. Orcajo, J. A. Botas, G. Calleja, and J. Palma, "Co₈-MOF-5 as electrode for supercapacitors," *Mater. Lett.*, vol. 68, no. none, pp. 126–128.
- [149] X. Wu, W. Deng, J. Qian, Y. Cao, X. Ai, and H. Yang, "Single-crystal FeFe(CN)₆ nanoparticles: a high capacity and high rate cathode for Na-ion batteries," *J. Mater. Chem. A*, vol. 1, no. 35, p. 10130.

- [150] Kein Bedarf an Edelmetallen, “A Metal–Organic Framework as an Electrocatalyst for Ethanol Oxidation,” *Angew. Chem. Int. Ed.*, vol. 49, no. 31, pp. 5348–5351.
- [151] C. Wang, Z. Xie, K. E. deKrafft, and W. Lin, “Doping Metal–Organic Frameworks for Water Oxidation, Carbon Dioxide Reduction, and Organic Photocatalysis,” *J. Am. Chem. Soc.*, vol. 133, no. 34, pp. 13445–13454.
- [152] J. K. Sun and Q. Xu, “Functional materials derived from open framework templates/precursors: synthesis and applications,” *Energy Environ. Sci.*, vol. 7, no. 7, p. 2071.
- [153] W. Xia, A. Mahmood, R. Zou, and Q. Xu, “Metal–organic frameworks and their derived nanostructures for electrochemical energy storage and conversion,” *Energy Environ. Sci.*, vol. 8, no. 7, pp. 1837–1866, 2015, doi: 10.1039/C5EE00762C.
- [154] P. Pachfule, B. P. Biswal, and R. Banerjee, “Control of Porosity by Using Isorecticular Zeolitic Imidazolate Frameworks (IRZIFs) as a Template for Porous Carbon Synthesis,” *Chem. Eur. J.*, vol. 18, no. 36, pp. 11399–11408.
- [155] H. B. Aiyappa, P. Pachfule, R. Banerjee, and S. Kurungot, “Porous Carbons from Nonporous MOFs: Influence of Ligand Characteristics on Intrinsic Properties of End Carbon,” *Cryst. Growth Des.*, vol. 13, no. 10, pp. 4195–4199.

Chapter 3

Experimental Methodology

This section introduces the synthesis method of Co-MOF precursor and MOF-derived cobalt sulfides as lithium-ion batteries' anode materials. Detailed preparation processes and essential equipment settings are described. Advanced materials characterisations and eletrochemical performance testing techniques are also elaborated.

3.1 Materials

Chemicals used no need further purification and were commercial: H₂NDC (2,6-Naphthalene dicarboxylic acid, Sigma-Aldrich), Co(acac)₂ (Sigma-Aldrich).

3.2 Preparation of the 2D layered Co-MOF

Experimentally, 300mg H₂NDC and 300mg Co(acac)₂ were added in 90 ml water, being mixed intensely at 25°C. Then, mixed product was put into the autoclave, which was kept at 70°C for 20hrs. After the solution was taken out of the autoclave, centrifugation was done to collect the solid product of the sample. The solid product was rinsed in DI water three times, followed by being dried at 80°C overnight [1].

3.3 Synthesis of Co_{1-x}S derived from 2D layered Co-MOF

In a typical procedure, 100mg Co-MOF and 100mg sulfur powder was mixed thoroughly. In a tube furnace, a combustion boat loaded with the mixture of two was heated up to 500 °C, 600 °C, 700 °C, 800 °C, respectively, at the rate of 2 °C min⁻¹. Respective temperature was held for 2 hrs under an argon gas flow. The gas flow rate is 60 ml min⁻¹. Sample color turned from light pink to black when furnace was completely cooled down [2].

3.4 Materials Characterization

1) X-ray diffraction (XRD)

To test sample's crystal structure and the phase purity, a Bruker D8 Focus power X-ray diffractometer was used. The Cu K α radiation was produced at 40kV and 30mA, with wavelength $\lambda \approx 0.154059$ nm. The samples were scanned with angle of $10^\circ \leq 2\theta \leq 160^\circ$. The scanning rate is 2° min⁻¹, while scanning step size is 0.02°.

The basic principle of XRD is illustrated in figure 3.1 below. The X-ray is shed onto the crystalline sample, where the regular array of atoms generates interference patterns as a

response. The constructive interference takes place when the diffraction angle θ satisfies the Bragg's Law:

$$n\lambda = 2d\sin\theta \quad (3-1)$$

where n denotes the integer number; λ is the wavelength of the X-ray beam (1.5418 Å for Cu radiation in this dissertation); d refers to the d-spacing of the crystal plane. The signal of the constructive interference X-rays is recorded and quantified. Scanning the sample within the angle range of 2θ produces all possible constructive interferences, and thus giving the diffraction peaks as a function of 2θ . Each sample has a unique set of XRD pattern, which is considered as the fingerprint for phase identification [3].

Figure 3.1: Schematic illustration of the interaction between X-ray and the crystal lattices.

The essential components of diffractometer shown in figure 3.2 include X-ray source, sample holder and a detector measuring the intensity of the diffracted beam. In the most common θ - 2θ scan, the angle between the sample surface and the incident X-ray is fixed at half the diffraction angle 2θ .

Figure 3.2: Essential component of typical diffractometer.

For crystalline samples, the XRD pattern would show peaks, and the smaller they crystal size, the broader the peaks; while for amorphous samples, no peaks can be observed, instead, a broad hump would appear at 2θ around 30° , shown in figure 3.3.

Figure 3.3: Typical XRD patterns of crystalline and amorphous structures[4].

2) Field-emission scanning electron microscopy (FESEM)

Surface morphologies and microstructures of the sample were characterized by FESEM, JEOL JSM-7800F microscope as shown in figure 3.4 at an acceleration voltage of 5kV [5].

Figure 3.4: The detailed structure of JEOL JSM-7600F FESEM.

The scanning electron microscope is a topographic technique and it produces images by acquiring signals generated from the interactions between the high-energy electron beam and specimen. When shining incident electron towards the sample surface, the energetic electrons are able to penetrate and produce a series of signals by interacting with the specimen atoms as shown in figure 3.5. The penetration depth and volume depend on the electron energy, incident angle and the elements atomic number/composition of the solid specimen.

Figure 3.5: a) Signals emitted from the sample-electron interaction. b) Mechanism of emission of secondary electron (SE), backscattered electron (BSE) and characteristic X-ray.

Specifically, the penetration depth and volume increase with increasing electron beam energy and drop with an increase of atomic number. Elements with a higher atomic number are more capable in consuming the energy of the electron beam and reduce the penetration. The beam energy can be adjusted by the accelerating voltage. A higher

accelerating voltage gives a deeper penetration depth, while as a consequence, some of the surface details might be lost [6].

3) Field-emission transmission electron microscopy (FETEM)

To know interfacial morphology of sample, HRTEM and TEM were performed on a JEOL JEM-2100F microscope with 200kV as shown in figure 3.6. In terms of elemental distribution, EDX spectroscope in JEM-2100F was used to do elemental mapping [7][8].

Figure 3.6: The detailed structure of JEOL JEM-2100F microscope (Blue marks the electron source part, yellow marks the illumination system and green marks the imaging system).

Transmission electron microscopy (TEM) is a very useful tool for obtaining the morphological, crystallographic and compositional information of nanomaterials, where electrons are emitted by the electron gun on the top, accelerated by an electric field, deflected by a column of magnetic lenses, and finally transmit through an ultrathin specimen to form an image. Then an imaging device magnifies and focuses the image [9].

TEM allows for various techniques to acquire different information of the specimen. In this report, the techniques used to analyze samples are imaging and SEAD.

Imaging

The primary function of TEM is to directly observe the morphology, structure, size and distribution of nanomaterials. In TEM images, sufficient contrast is needed to recognize a sample. There are different types of image contrast, including mass-thickness contrast, diffraction contrast, and Z-contrast.

In the area with higher mass or higher thickness, more electrons will be scattered at larger angles. After deflection by the objective lens, the electrons at larger angles are excluded by the objective aperture, and thus fewer electrons from the high mass area contribute to the imaging, forming a darker imaging on the image plane.

Diffraction contrast is induced by diffraction phenomena from crystalline samples. For example, the sample contains grains A and B, and we suppose that the incident electrons are either diffracted or transmitted (unscattered). Grain A is at the Bragg diffraction position, so some of the incident electrons are diffracted and the rest of electrons are transmitted (unscattered). Grain B is not at the Bragg diffraction position, so all the incident electrons are transmitted (unscattered), which contribute to the imaging. This means that, in grain B, more electrons contribute to the imaging as compared to grain A, therefore grain B appears brighter than grain A. In amorphous samples, since no diffraction happens over the sample, the image contrast comes only from mass-thickness contrast.

In Z-contrast, Z represents the atomic number. Z-contrast is mainly used for STEM imaging. In the dark-field imaging of STEM, the scattered electrons are detected and

used to form the images. For the element with higher atomic number, more electrons will be scattered, therefore it will appear brighter. Therefore, STEM imaging is also an important technique for composition analysis. In addition, for STEM, the thickness contrast has similar effect with the Z-contrast.

SAED

Electron diffraction is caused by the wave nature of the electrons. Since the wavelength of electrons is very short, which is comparable with crystal lattices, diffraction occurs when electrons pass through the sample. Electron diffraction gives information on the specimen structure, crystallinity and lattice parameters. In TEM, it is possible to select a small area for diffraction, so it is common to get a SAED pattern.

Similar to XRD, the formation of electron diffraction can be described by Bragg's law. As illustrated in figure, when the crystal is at the Bragg diffraction orientation, the geometry relationship follows the equation:

$$2\theta = r/L \quad (3-2)$$

Where L is the camera length. According to Bragg's law,

$$2\sin\theta = \lambda/d \quad (3-3)$$

Since θ is very small, θ approximately equals to $\sin\theta$, and thus,

$$\frac{r}{L} = \frac{\lambda}{d}, \quad rd = L\lambda \quad (3-4)$$

Here, the product $L\lambda$ is camera constant.

Figure 3.7 a) Schematics illustrating the Bragg diffraction in TEM. (b-d) Representative diffraction patterns of single crystalline b) Polycrystalline c) and amorphous d) samples.

From the electron diffraction patterns, the crystal structure and lattice parameter can be determined. For single crystalline structures, diffraction spots can be clearly observed figure 3.4b. By observing the pattern of the spots and the distance between the spots and the central beam, the crystal structure as well as the lattice parameters of the sample can be determined. For polycrystalline structures, since each crystallite is oriented in different direction and each crystallite will have a set of diffraction spots, the superposition of diffraction spots results in a set of concentric circles figure 3.4c. For amorphous samples, atoms are randomly arranged, so diffraction will not occur. As a result, no diffraction spots or concentric rings can be observed as figure 3.4d.

4) Energy-Dispersive X-Ray (EDX) Spectroscopy

EDX is an ideal technique to analyse elemental compositions and distributions. The EDX spectrometer is usually attached to SEM or TEM to provide in-situ analysis [10]. It works at higher voltage (20kV) to provide the beam electrons with enough energy to kick out the innermost shell electrons in the sample as shown in figure 3.8.

Figure 3.8 EDX working principle.

The kick out inner shell electrons are momentarily excited to a higher state but drop back into the original state with the emission of x-ray. Since each element has unique

electronic structure, the energy of the emitted x-ray will differ. Thus, this method is used as a fingerprint method to identify the elements. The intensity of the x-ray can be measured and is correlated to the number of interested elemental atoms. One limitation of this method is that if the elements have similar electronic structure, then it would be difficult to differentiate.

5) Brunauer-Emmett-Teller (BET)

Sample pore sizes and surface areas were measured by a porosimetry and accelerated surface area analyzer (Micromeritics Instrument Corp, ASAP Tristar II 3020, analysis adsorptive: N_2) at -196°C after pretreatment under vacuum at 100°C for overnight [11].

The Brunauer-Emmett-Teller (BET) method is one of the most common techniques to characterize porous materials allowing for the determination of the surface area, pore size distribution, and pore volume of samples. There are six types of adsorption isotherms. The BET method is only applicable to type II (non-porous powders) and type IV (mesoporous with pores in the range of 1.5-100 nm). The testing is conducted at a constant temperature, typically in N_2 , 77K, and an adsorption isotherm is plotted by measuring the amount of gas adsorbed over a wide range of pressure. Conversely, desorption isotherms are obtained by measuring the amount of gas as pressure is released [12]. The main steps of BET measurement process is shown in figure 3.9.

Figure 3.9 The BET measurement processes.

3.5 Coin-type cells assembling

CR2016 coin cells are the type of cells for electrochemical measurements. Anode was built through placing a slurry of active material (80%), poly(vinylidene fluoride) binder (PVDF Kynar) (10%) and Super-P carbon black (10%) in N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) onto a piece of copper foil. Then the anode was dried at 80°C for 12hrs in a vacuum oven.

A glove box containing argon gas (MBraun, Germany) was used to assemble coin cells. The moisture as well as oxygen concentration inside the glove box is < 1ppm. The mass loading range from 0.8 to 1mg cm⁻². In half-cell configuration, lithium metal was the counter electrode, separator was using Celgard 2400 membrane, electrolyte was made of LiPF₆ (1mol L⁻¹) dissolved in diethyl carbonate/ethyl carbonate (DEC:EC=1:1 by volume, Charslton Technologies Pte. Ltd.) [13].

3.6 Cyclic votammetry (CV) test

Cyclic voltammetry is one of the most important electrochemical analysis methods. It is widely used in the fields of electrochemistry, inorganic chemistry, organic chemistry and biochemistry, for it is efficient and simple to characterize a redox system. It is used to study the properties, mechanism and kinetic parameters of electrode reaction. Moreover, it can also be utilized to study the side chemical reactions in the process of electrode reaction, as well as SEI film formation.

In CV measurements, a voltage is added to battery system, respective current response is recorded. The current here is referring to faradaic current, which is due to the reduction-oxidation (redox) reaction. The current response is being collected over a potential window. A potential window refers to a range of potentials, starting from an initial value, then increasing/decreasing linearly to a pre-set limit voltage. This pre-set limit voltage is called switching potential. Upon reaching the switching potential, the scan would be reversed in terms of direction, and would sweep across the same potential window. This

is why the term is called cyclic. This indicating that the product generated by oxidation at forward scan can be reduced at reverse scan.

The triangular wave voltage is applied in the form of a fast linear scan. A triangle wave scan completes a cycle of reduction and oxidation processes, and then the analysis based on the $i-\phi$ (i : Current; ϕ : Electric potential) curve is called the cyclic voltammetry method. The triangular wave is shown in figure 5.1 below:

Figure 3.10: Triangular wave sweep voltage.

The CV test method involves potential sweeps, the linear scanning voltage is applied to the electrode. The sweep direction is inverted at a chosen potential. After the starting voltage U_i is scanned in a certain direction to the ending voltage U_s , it is then scanned in the opposite direction at the same speed. The pressurized line is formed into an isosceles triangle to complete a cycle. Depends on the actual situation, continuous cyclic scanning can be carried out. When the voltammetric wave shape is obtained, the slow and fast electrode reactions can then be analysed.

When the electric potential is scanned from positive to negative direction, the oxidation state active substance O in the solution will gain electrons on the electrode and undergo reduction reaction, resulting in reduction peak.

When scanned reversely, the reducing substance R generated on the electrode surface would undergo oxidation reaction, producing oxidation peak.

The voltammetric wave shape is shown in image below:

Figure 3.11: Typical voltammetric wave.

When the triangular wave potential sweeps from U_i to U_s , the oxidized state substance on electrode surface would undergo reduction reaction for anode material. The current peak is i_{pa} , the potential peak is ϕ_{pa} . The voltammetric wave is shown as the bottom half of figure 5.2. When the triangular wave potential sweeps from U_s to U_i , the reduced state substance on electrode surface would undergo oxidation reaction. The current peak is i_{pc} , the potential peak is ϕ_{pc} . The voltammetric wave is shown as the top half of figure 5.2.

CV test can be measured on Autolab, PGSTAT302N, which is an electrochemical workstation. The scanning rate is 0.1 mV s^{-1} . The potential sweep range of the coin-type cell is 0.01-3.0V vs. Li^+/Li . From cycling and rate results, samples which sulfurized at 700°C showed an advantage in capacity retention and cyclic stability.

The purpose of conducting the CV test as future work is to zoom in to the electrode reactions happening when the samples are generated from different sulfurization

temperatures. CV results can tell the electric potential of each redox reactions happened on electrodes and provide electron transfer rate. SEI film formation potential can also be revealed. Moreover, CV results can also tell informations like whether any side chemical reactions like electrolyte decomposition is ongoing. With above information, the comparisons can be done between each anode materials synthesized at different sulfurization temperatures. So that optimized sulfurization temperature could be identified and the respective operation mechanism could be explained in details.

3.7 Electrochemical impedance spectroscopy (EIS)

This is a non-destructive and effective testing method for parameter determination and batteries' dynamic behavior[14]. If a sine wave voltage signal with a small amplitude of frequency ω_1 is applied to the battery system, the system would generate a sine wave current response with frequency ω_2 . The ratio change of excitation voltage to response current is the impedance spectrum of the electrochemical system. This test method can be used from a very low scanning frequency (μHz) to a very high frequency (MHz), in order to study electrochemical interface reactions. Taking EIS results of CoS, CNTs, CoS-CNTs as an example, the Nyquist plots are shown below:

Figure 3.12: Nyquist plots for a) CNTs, b) CoS-CNTs, c) CoS [15].

As shown in figure 5.3, all three spectras of Nyquist plots are consist of two parts. One is the semi-circle at high to medium frequencies which is related to charge-transfer impedance (R_{ct}) and solid electrolyte interface (SEI). The other one is the slope at low

frequencies which is related to ion diffusion rate in electrodes. Upon getting the EIS results, equivalent circuit approach was used to achieve the fitting simulation circuit model, taking below model as an example:

Figure 3.13: An example of a fitting simulation circuit model for EIS.

R_{Ω} is the internal resistance, including the resistance of electrolyte solution, separator, and electrode materials. C_d is electrical double layer capacitance. R_{ct} is the charge transfer resistance, which is corresponded to the semi-circle in Nyquist plots. The value of R_{Ω} , C_d , R_{ct} can be calculated through the Nyquist plot or the circuit simulation software.

The purpose of conducting EIS test as future work was to get Nyquist plots and fitting simulation circuit model for synthesized anode materials at different sulfurization temperatures. Comparing R_{Ω} , C_d , R_{ct} values between samples can further explain the mechanism of the two-dimensional CoS derived from MOF prepared at 700°C, and the reason why it has the best cyclic stability and rate capability.

EIS measurements need to be carried out through Solartron SI 1260 Impedance/Gain Phase Analyzer at room temperature. The analyzer has a frequency range of 100kHz - 0.01Hz.

References

- [1] T. Huang, Y. Chen, and J.-M. Lee, “Two-Dimensional Cobalt/N-Doped Carbon Hybrid Structure Derived from Metal–Organic Frameworks as Efficient Electrocatalysts for Hydrogen Evolution,” *ACS Sustain. Chem. Eng.*, vol. 5, no. 7, pp. 5646–5650, Jul. 2017, doi: 10.1021/acssuschemeng.7b00598.
- [2] J. Liu et al., “MOF-Derived Hollow Co_9S_8 Nanoparticles Embedded in Graphitic Carbon Nanocages with Superior Li-Ion Storage,” *Small*, vol. 12, no. 17, pp. 2354–2364, May 2016, doi: 10.1002/smll.201503821.
- [3] Y. Waseda, E. Matsubara, and K. Shinoda, *X-ray diffraction crystallography: introduction, examples and solved problems*. Springer Science & Business Media, 2011.
- [4] B. D. Cullity and S. R. Stock, *Elements of X-ray diffraction*. Prentice Hall, 2001.
- [5] Cherian et al., “Morphologically Robust NiFe_2O_4 Nanofibers as High Capacity Li-Ion;Battery Anode Material,” vol. 5, no. 20, pp. 9957–9963, 2013.
- [6] S. H. Aharinejad and A. Lametschwandtner, *Microvascular Corrosion Casting in Scanning Electron Microscopy*. Springer-Verlag Wien, 1992.
- [7] S. Kong, Z. Jin, H. Liu, and Y. Wang, “Morphological Effect of Graphene Nanosheets on Ultrathin CoS Nanosheets and Their Applications for High-Performance Li-Ion Batteries and Photocatalysis,” *J. Phys. Chem. C*, vol. 118, no. 44, pp. 25355–25364, Nov. 2014, doi: 10.1021/jp508698q.
- [8] R. Wu et al., “In-Situ Formation of Hollow Hybrids Composed of Cobalt Sulfides Embedded within Porous Carbon Polyhedra/Carbon Nanotubes for High-Performance Lithium–Ion Batteries,” *Adv. Mater.*, vol. 27, no. 19, pp. 3038–3044, May 2015, doi: 10.1002/adma.201500783.
- [9] D. B. Williams and C. B. Carter, *Transmission Electron Microscopy: A Textbook for Materials Science*. Springer, 2nd Edition, 2009.
- [10] A. J. Dalfonso, B. Freitag, D. O. Klenov, and L. J. Allen, “Atomic-resolution chemical mapping using energy-dispersive x-ray spectroscopy,” *Phys. Rev. B*, vol. 81, no. 10, 2010, doi: 10.1103/physrevb.81.100101.

- [11] D. Yin et al., “Coated/Sandwiched rGO/CoS_x Composites Derived from Metal-Organic Frameworks/GO as Advanced Anode Materials for Lithium-Ion Batteries,” *Chem. - Eur. J.*, vol. 22, no. 4, pp. 1467–1474, Jan. 2016, doi: 10.1002/chem.201504399.
- [12] F. Ambroz, T. J. Macdonald, V. Martis, and I. P. Parkin, “Evaluation of the BET Theory for the Characterization of Meso and Microporous MOFs,” *Small Methods*, vol. 2, no. 11, 2018, doi: 1800173.
- [13] G. Yang et al., “Solvothermal synthesis of Li₃VO₄: Morphology control and electrochemical performance as anode for lithium-ion batteries,” *Int. J. Hydrog. Energy*, vol. 42, no. 34, pp. 22167–22174, Aug. 2017, doi: 10.1016/j.ijhydene.2017.02.186.
- [14] E. Samadani et al., “Empirical Modeling of Lithium-ion Batteries Based on Electrochemical Impedance Spectroscopy Tests,” *Electrochimica Acta*, vol. 160, pp. 169–177, 2015, doi: <https://doi.org/10.1016/j.electacta.2015.02.021>.
- [15] H. Wang et al., “CoS/CNTs hybrid structure for improved performance lithium ion battery,” *J. Alloys Compd.*, vol. 676, pp. 551–556, Aug. 2016, doi: 10.1016/j.jallcom.2016.03.132.

Chapter 4

Results and Discussion

This section summarises the data of experiments. Results are analyzed based on the material characterisations and testing. The reasons which contributing the results are also discussed.

4.1 X-ray diffraction (XRD)

Crystal framework of two-dimensional Co-MOF precursor is shown in figure 4.1. The framework has a shape of a thin layer.

XRD pattern of two-dimensional Co-MOF precursor is shown in Figure 4.2. The typical X-ray diffraction peaks of the product matched well with a known Co-MOF: $\text{Co}(\text{C}_{12}\text{H}_6\text{O}_4)(\text{H}_2\text{O})_4$, indicating the composition of the prepared Co-MOF [1].

Figure 4.1 (Left): Crystal information framework of two-dimensional Co-MOF.

Figure 4.2 (Right): XRD patterns of the as synthesized two-dimensional Co-MOF.

Mixing the synthesized Co-MOF and sulfur at a 1:1 weight ratio, sulfurized at different temperatures, the XRD patterns of synthesized product are introduced below:

Figure 4.3: XRD patterns of the Co_{1-x}S particles formed at sulfurization temperature of 500, 600, 700, 800°C, respectively.

Five diffraction peaks were presented at $2\theta = 31.8^\circ$, 38.6° , 47.6° , 50.6° and 55.4° in curve 500°C. The five peaks are corresponded with the lattice plane (311), (400), (422), (511), (440) of the cubic phase $\text{Co}_{2.67}\text{S}_4$ (JCPDS no. 74-6715) with a space group of $\text{Fd}\bar{3}\text{m}$. In the same time, peaks shown at $2\theta = 31.0^\circ$, 35.6° and 47.2° were related to CoS's (JCPDS no. 65-3418) lattice plane (101), (100), (102) of which has the hexagonal phase. The space group is $\text{P63}/\text{mmc}$ [2].

When sulfurized at 600°C, 700°C, 800°C, respectively, Co_{1-x}S particles have a pattern which matched well with CoS (JCPDS card no. 65-3418). No additional peaks observed, showing the product has less impurities. This is because that 600°C, 700°C, 800°C are much higher than the boiling point of sulfur, which is 444.6 °C. The excessive sulfur is evaporated, generating stable CoS [3].

Five diffraction peaks appeared at $2\theta = 31.0^\circ$, 35.6° , 47.2° , 54.7° and 74.9° in curve 600, 700 and 800°C. These five peaks are linked to the lattice plane (100), (101), (102), (110), (202) of CoS (JCPDS no. 65-3418) which has the hexagonal phase. The space group is $\text{P63}/\text{mmc}$.

The diffraction peaks become more intense (increasing peak length) and sharper (decreasing peak width) when sulfurization temperature is increasing. This trend indicates that the higher the sulfurization temperature, the larger the crystallites can grow. Thus, the crystallinity is improved at higher calcination temperatures.

4.2 Field-emission scanning electron microscopy (SEM)

The FESEM images at lower and higher magnifications of the 2D Co-MOF precursor, the Co_{1-x}S sulfurized at 500, 600, 700, 800°C, are presented in figure 4.4.

The bowknot-like precursor is composed of layered rectangular shaped pieces, with thicknesses of 10-20nm. The rectangular pieces have a smooth surface and clear edges [4].

At 500°C, the two-dimensional Co-MOF precursor is able to react with sulfur powder and the obtained product. The dimensions and the structure of the templates are retained.

When sulfurization temperature was at 600, 700 and 800°C, the product (CoS) still retained the template dimensions, indicating a good structural stability. However, in terms of morphology, the higher the temperature, the rougher the surface. This is because of the growth of particle sizes. Moreover, the edges of the rectangular pieces became less clear because of the sintering effect.

Figure 4.4: FESEM images of a) two dimensional layered Co-MOF precursor; b-e) Co_{1-x}S synthesized at sulfurization temperature of 500, 600, 700, 800°C. FESEM images at a higher magnification of f) two dimensional layered Co-MOF precursor; g-j) Co_{1-x}S synthesized at sulfurization temperature of 500, 600, 700, 800°C.

4.3 Transmission electron microscope (TEM)

Interfacial morphology of Co_{1-x}S was further analyzed by TEM at higher resolution.

Figure 4.5: Co_{1-x}S synthesized at sulfurization temperature of 700°C : a-d) TEM images, e) HRTEM images, f) SEAD pattern, g-j) The SEM and elemental mapping images of Co_{1-x}S synthesized at sulfurization temperature of 700°C

The TEM image which low magnification shown in Figure 4.5 a), b) demonstrate similar lateral sizes of different pieces of Co_{1-x}S composites synthesized under 700°C , the shape of a single layer is rectangle alike.

The magnified TEM image in Figure 4.5 c), d) further revealed that the two-dimensional layered structure was porous. Nanoparticles (black dots) were homogeneously observed in grey area (carbon matrix).

High resolution images presented in figure 6e indicated that instead of being exposed on outer surface, Co_{1-x}S nanoparticles were wrapped homogeneously by graphitic carbon layers.

The lattice fringes has 0.25nm d-spacing. This is related to cobalt sulfide (CoS)'s (101) lattice plane. Series of bright concentric rings in SAED (figure 6f) showed cobalt sulfide's polycrystalline property. Miller indexes from inner and out are (100), (101), (102), (110), corresponding to CoS (JCPDS no. 65-3418), which is the hexagonal phase, space group was P63/mmc. The analysis of SAED pattern was consistent with the XRD results [5].

The elemental mapping of a piece of two dimensional layered Co_{1-x}S composites synthesized under 700°C was shown in figure 4.5 g-j). The EDX result proves the coexistence of cobalt, sulfur, and carbon elements. They are homogeneously dispersed within the two-dimensional layered framework.

4.4 Brunauer-Emmett-Teller (BET)

Porosity property of the Co_{1-x}S sulfurized at 500, 600, 700, 800°C could be reflected by BET results. Isotherm curves of nitrogen adsorption or desorption, and the respective pore size distribution diagram are introduced, as shown in figure 4.6.

The isotherm curves of composites at four sulfurization temperatures showed distinct mesopore hysteresis loops. The BET surface areas of Co_{1-x}S sulfurized at 500, 600, 700, 800°C , are 34.76, 37.97, 63.37, $73.95\text{ m}^2\text{g}^{-1}$, respectively. The BET surface areas of Co_{1-x}S sulfurized at 700°C , 800°C appear to be the largest. Large surface area could provide excess active sites, so that electrolyte could better contact with the electrodes [2][6].

Based on the nitrogen adsorption data, the Barrett-Joyner-Halenda (BJH) calculations gave the results of the average pore sizes, which were 77.67, 106.45, 86.20, $76.32\text{ \AA}$ for Co_{1-x}S sulfurized at 500, 600, 700, 800°C .

Figure 4.6: Nitrogen sorption isotherms of Co_{1-x}S at sulfurization temperature of: a-d) 500, 600, 700, 800°C, respectively. Inset curves are respective BJH pore size distribution diagrams.

The pore size distributions of 500, 600, 700, 800°C are very similar, pore diameter: 3-45 nm. BET pore size of Co_{1-x}S sulfurized at 600°C appears to be the largest. The BJH calculations also gave average volume sizes of 0.1035, 0.1096, 0.1266, 0.1077 cm^3g^{-1} for Co_{1-x}S sulfurized at 500, 600, 700, 800°C. The BET volume size of Co_{1-x}S sulfurized at 700°C appears to be the largest. The data is shown below:

Table 4.1: The BET surface area, pore size, volume size of Co_{1-x}S sulfurized at 500, 600, 700, 800°C.

Co_{1-x}S	Surface area (m^2g^{-1})	Pore size ($\text{\AA}$)
Precursor	0.1448	588.88
500°C	34.76	77.67
600°C	37.97	106.45
700°C	63.37	86.20
800°C	73.95	76.32

4.5 V-Profile

The galvanostatic charge-discharge cycling test needs to be conducted at 25°C between 0.01V and 3.0V vs. Li under various current densities with Neware battery testing system (Neware, BTS-5V 10mA, China). The specific capacities are to be calculated based on the total mass of the composites.

Figure 4.7: Galvanostatic charge-discharge voltage profiles of Co_{1-x}S at sulfurization temperature of: a) 500°C , b) 600°C , c) 700°C , d) 800°C .

Figure 4.7 shows the typical galvanostatic charge/discharge curves for Co_{1-x}S in first five cycles between 0.01 and 3V at a current density of 100mAh g^{-1} . It should be noted that all the current densities and specific capacities here are calculated based on the total mass of the composite to avoid the overestimation.

The Co_{1-x}S sulfurized at 500°C is shown in Figure 4.7 a). The initial discharge/charge capacity of Co_{1-x}S is 1439.26mAh g^{-1} , 820.69mAh g^{-1} , respectively. The initial coulombic efficiency is 57.0%. The large initial capacity may benefit from the full utilization of Co_{1-x}S particles and the irreversible formation of a solid-electrolyte interphase (SEI).

During the second cycle, the discharge/charge capacity decreased to 833.43mAh g^{-1} , 718.11mAh g^{-1} , respectively, leading to a high coulombic efficiency of 86.2%. This

coulombic efficiency indicates the better reversibility of the lithiation/delithiation processes.

The first discharge curves were composed of two slopes and one platform. The first slope from 1.9V to 1.3V was assigned to the insertion of a small amount of lithium. The platform observed at 1.2V could be attributed to the displacement reaction of $\text{Li}_2\text{S} + \text{Co}$. Another slope from 0.8V to 0.01V is due to the formation of a surface polymeric layer, which in general contributes to additional capacity.

The CoS sulfurized at 600°C is shown in Figure 4.7 b). The initial discharge/charge capacity of Co_{1-x}S is 1085.49 mAh g⁻¹, 748.36 mAh g⁻¹, respectively. The initial coulombic efficiency is 68.9%. The large initial capacity may benefit from the full utilization of Co_{1-x}S particles and the irreversible formation of a solid-electrolyte interphase (SEI).

During the second cycle, the discharge/charge capacity decreased to 1056.25 mAh g⁻¹, 895.01 mAh g⁻¹, respectively, leading to a high coulombic efficiency of 84.7%. This coulombic efficiency indicates the better reversibility of the lithiation/delithiation processes.

The first discharge curves were composed of two slopes and one platform. The first slope from 2.0V to 1.2V was assigned to the insertion of a small amount of lithium. The platform observed at 0.9V could be attributed to the displacement reaction of $\text{Li}_2\text{S} + \text{Co}$. Another slope from 0.7V to 0.01V is due to the formation of a surface polymeric layer, which in general contributes to additional capacity.

The Co_{1-x}S sulfurized at 700°C is shown in Figure 4.7 c). The initial discharge/charge capacity of Co_{1-x}S is 1238.35 mAh g⁻¹, 809.80 mAh g⁻¹, respectively. The initial coulombic efficiency is 65.4%. The large initial capacity may benefit from the full utilization of Co_{1-x}S particles and the irreversible formation of a solid-electrolyte interphase (SEI).

During the second cycle, the discharge/charge capacity decreased to 826.84 mAh g⁻¹, 773.59 mAh g⁻¹, respectively, leading to a high columbic efficiency of 93.6%. This columbic efficiency indicates the better reversibility of the lithiation/delithiation processes.

The first discharge curves were composed of two slopes and one platform. The first slope from 1.9V to 1.4V was assigned to the insertion of a small amount of lithium. The platform observed at 1.3V could be attributed to the displacement reaction of Li₂S + Co. Another slope from 0.9V to 0.01V is due to the formation of a surface polymeric layer, which in general contributes to additional capacity.

The CoS sulfurized at 800°C is shown in Figure 4.10 d). The initial discharge/charge capacity of Co_{1-x}S is 1214.76 mAh g⁻¹, 783.55 mAh g⁻¹, respectively. The initial columbic efficiency is 64.5%. The large initial capacity may benefit from the full utilization of Co_{1-x}S particles and the irreversible formation of a solid-electrolyte interphase (SEI).

During the second cycle, the discharge/charge capacity decreased to 795.44 mAh g⁻¹, 723.25 mAh g⁻¹, respectively, leading to a high columbic efficiency of 90.9%. This columbic efficiency indicates the better reversibility of the lithiation/delithiation processes.

The first discharge curves were composed of two slopes and one platform. The first slope from 1.9V to 1.4V was assigned to the insertion of a small amount of lithium. The platform observed at 1.34V could be attributed to the displacement reaction of Li₂S + Co. Another slope from 1.2V to 0.01V is due to the formation of a surface polymeric layer, which in general contributes to additional capacity.

4.6 Cyclic voltammetry (CV) test

Cyclic voltammetry is one of the most important electrochemical analysis methods. It is widely used in the fields of electrochemistry, inorganic chemistry, organic chemistry and

biochemistry, for it is efficient and simple to characterize a redox system. It is used to study the properties, mechanism and kinetic parameters of electrode reaction. Moreover, it can also be utilized to study the side chemical reactions in the process of electrode reaction, as well as SEI film formation.

CV test can be measured on Autolab, PGSTAT302N, which is an electrochemical workstation. From cycling and rate results, samples which sulfurized at 700°C showed an advantage in capacity retention and cyclic stability.

Figure 4.8: Cyclic voltammograms of Co_{1-x}S at sulfurization temperature of: a) 500°C, b) 600°C, c) 700°C, d) 800°C.

To evaluate the Li ion storage electrochemical reactions of Co_{1-x}S composite, CV curves of the initial five cycles were performed. A sweep rate of 0.1mV s^{-1} and a voltage range from 0.01-3.0V were used.

For Co_{1-x}S sulfurized at 700°C shown in Figure 4.8 c), four reduction peaks centered at 0.42V, 0.67V, 0.99V and 1.28V were observed in the first cathodic sweep. A small peak at about 1.28V can be assigned to an initial process of Li insertion reaction:

The broad peak centered at 0.99V was related to the electrochemical reduction reaction:

The peak at about 0.42V was attributed to the formation of the solid electrolyte interphase (SEI) film.

In the first anodic scan, a very weak peak at about 0.98V may be ascribed to the partial decomposition of SEI film. This peak is disappeared in the subsequent second to fifth cycles. There is an oxidation peak at 1.34V, which can be assigned to the initial process of Li extraction reaction:

The strong oxidation peak at 2.08V was related to the oxidation reaction:

In the second cathodic sweep, the peak centered at 0.67V in the first cycle shifted to 0.68V, the peak centered at 0.99V shifted to 1.29V, the peak centered at 1.28V shifted to 1.71V. In the second anodic sweep, the peak centered at 1.34V shifted to 1.35V, the peak centered at 2.08V shifted to 2.07V. The shifting of peaks could due to that the electrode underwent minor structural rearrangement in the few cycles. The peaks are in good agreement with the plateaus in the galvanostatic discharge curves.

From the second cycle onwards, the sweeps were largely overlapped, implying the good cycling stability. The peak intensity decreased from the first to fifth cycle.

For Co_{1-x}S sulfurized at 500°C shown in Figure 4.8 a), three reduction peaks centered at 0.68V, 0.90V and 1.20V were observed in the first cathodic sweep. A small peak at about 1.20V can be assigned to an initial process of Li insertion reaction:

The peak centered at 0.90V was related to the electrochemical reduction reaction:

The peak at about 0.68V was attributed to the formation of the solid electrolyte interphase (SEI) film.

In the first anodic scan, a very weak peak at about 1.00V may be ascribed to the partial decomposition of SEI film. This peak is disappeared in the subsequent second to fifth cycles. There is an oxidation peak at 1.35V, which can be assigned to the initial process of Li extraction reaction:

The strong oxidation peak at 2.07V was related to the oxidation reaction:

The peak at 2.34V could be assigned to the formation of $\text{Co}_{2.67}\text{S}_4$.

In the second cathodic sweep, the peak centered at 0.68V in the first cycle shifted to 0.70V, the peak centered at 0.90V shifted to 1.23V, the peak centered at 1.20V shifted to 1.58V.

In the second anodic sweep, the peak centered at 1.35V shifted to 1.38V, the peak centered at 2.07V shifted to 2.10V, the peak centered at 2.34V shifted to 2.40V. The shifting of peaks could due to that the electrode underwent minor structural rearrangement in the few cycles. The peaks are in good agreement with the plateaus in the galvanostatic discharge curves.

From the second cycle onwards, the sweeps were not as overlapped as comparing to CVs of 600°C , 700°C and 800°C , the area became smaller and smaller, implying the capacity

was fading and the cycling stability was not as good. The peak intensity substantially decreased from the first to fifth cycle, indicating poor reversibility.

For Co_{1-x}S sulfurized at 600°C shown in Figure 4.8 b), four reduction peaks centered at 0.49V, 0.68V, 0.94V and 1.12V were observed in the first cathodic sweep. A small peak at about 1.12V can be assigned to an initial process of Li insertion reaction:

The peak centered at 0.94V was related to the electrochemical reduction reaction:

The peak at about 0.49V was attributed to the formation of the solid electrolyte interphase (SEI) film.

In the first anodic scan, a very weak peak at about 0.99V may be ascribed to the partial decomposition of SEI film. This peak is disappeared in the subsequent second to fifth cycles. There is an oxidation peak at 1.34V, which can be assigned to the initial process of Li extraction reaction:

The strong oxidation peak at 2.09V was related to the oxidation reaction:

In the second cathodic sweep, the peak centered at 0.68V in the first cycle shifted to 0.69V, the peak centered at 0.94V shifted to 1.29V, the peak centered at 1.12V shifted to 1.80V.

In the second anodic sweep, the peak centered at 1.34V shifted to 1.36V, the peak centered at 2.09V shifted to 2.10V. The shifting of peaks could due to that the electrode underwent minor structural rearrangement in the few cycles. The peaks are in good agreement with the plateaus in the galvanostatic discharge curves.

From the second cycle onwards, the sweeps were not as overlapped as comparing to CVs of 700°C and 800°C, implying the cycling stability was not as good. The peak intensity decreased from the first to fifth cycle.

For Co_{1-x}S sulfurized at 800°C shown in Figure 4.8 d), three reduction peaks centered at 0.69V, 1.08V and 1.30V were observed in the first cathodic sweep. A small peak at about 1.30V can be assigned to an initial process of Li insertion reaction:

The broad peak centered at 1.08V was related to the electrochemical reduction reaction:

The peak at about 0.69V was attributed to the formation of the solid electrolyte interphase (SEI) film.

In the first anodic scan, a very weak peak at about 0.96V may be ascribed to the partial decomposition of SEI film. This peak is disappeared in the subsequent second to fifth cycles. There is an oxidation peak at 1.33V, which can be assigned to the initial process of Li extraction reaction:

The strong oxidation peak at 2.06V was related to the oxidation reaction:

In the second cathodic sweep, the peak centered at 0.69V in the first cycle shifted to 0.70V, the peak centered at 1.08V shifted to 1.34V, the peak centered at 1.30V shifted to 1.73V.

In the second anodic sweep, the peak centered at 0.96V shifted to 1.34V, the peak centered at 1.33V shifted to 2.04V. The shifting of peaks could due to that the electrode underwent minor structural rearrangement in the few cycles. The peaks are in good agreement with the plateaus in the galvanostatic discharge curves.

From the second cycle onwards, the sweeps were largely overlapped, implying the good cycling stability. The peak intensity decreased from the first to fifth cycle.

Overall speaking, samples synthesized at 700°C have the best cyclic stability as the sweep curves from the first to the fifth cycle is the most overlapped.

4.7 Cycling

The cyclic performance of Co_{1-x}S sulfurized at 500, 600, 700 and 800°C was tested through galvanostatic cycling under 100mA g^{-1} current density [7]. Results were presented in figure 4.7.

Figure 4.9: Cycling performance under 100mA g^{-1} of Co_{1-x}S at sulfurization temperature of: 500, 600, 700, 800°C.

For CoS , $\text{Co}_{2.67}\text{S}_4$ sulfurized at 500°C, the initial discharge specific capacity was $1440.15\text{ mAh g}^{-1}$, the second cycle was 834.89 mAh g^{-1} . Capacity decreased from the second cycle onwards, and became stable 50th cycle later, the average specific capacity after stabilization was 228.18 mAh g^{-1} . After cycle 100th, the specific capacity was 179.29 mAh g^{-1} .

mAh g^{-1} , which was 21.5% of the original capacity. Overall speaking, the specific capacity for CoS and $\text{Co}_{2.67}\text{S}_4$ sulfurized at 500°C was the lowest among the four sulfurization temperatures.

For CoS sulfurized at 600°C , the initial discharge specific capacity was $1085.74 \text{ mAh g}^{-1}$, the second cycle was $910.02 \text{ mAh g}^{-1}$. Capacity decreased from the second cycle onwards. At cycle 100^{th} , the specific capacity drop to $244.06 \text{ mAh g}^{-1}$. Retention rate of capacity was 26.8%.

For CoS sulfurized at 800°C , the discharge specific capacity of the 1^{st} cycle was $1214.77 \text{ mAh g}^{-1}$, the second cycle was $794.99 \text{ mAh g}^{-1}$. Specific capacity decreased from the second cycle onwards. At cycle 100^{th} , capacity drop to $250.85 \text{ mAh g}^{-1}$. Retention rate of capacity was 31.6%.

For CoS sulfurized at 700°C , the initial discharge specific capacity was $1240.67 \text{ mAh g}^{-1}$, the second cycle is $828.10 \text{ mAh g}^{-1}$. Specific capacity decreased from the second cycle onwards, and became stable after the 10^{th} cycle, the average specific capacity after stabilization was $633.39 \text{ mAh g}^{-1}$. 50 cycles later, specific capacity decayed. At cycle 100^{th} , the specific capacity maintained at $421.50 \text{ mAh g}^{-1}$, 50.9% of the initial capacity. Overall speaking, the specific capacity for CoS sulfurized at 700°C was the highest and the most stable among the four sulfurization temperatures.

For CoS sulfurized at 700°C , the first fifty cycles maintained an average discharge specific capacity of about $633.39 \text{ mAh g}^{-1}$, higher than CoS (590 mAh g^{-1})'s theoretical capacity. After 50 cycles, sample gave reversible capacities of 228.18, 360.38, 621, 400 mAh g^{-1} for Co_{1-x}S sulfurized at 500, 600, 700, 800°C . 100 cycles later, the discharge specific capacities almost keep at 179.29, 255.80, 421.50, 255.80 mAh g^{-1} for Co_{1-x}S sulfurized at 500, 600, 700, and 800°C , respectively.

The Co_{1-x}S composite with a sulfurization temperature at 700°C has superior cyclic stability and discharge specific capacity retention compared with other three products sulfurized under 500, 600 and 800°C .

4.8 Rate

The high rate performance of Co_{1-x}S sulfurized at 500, 600, 700, and 800°C was reflected by cycling the battery under increasing current densities ranging from 100mA g^{-1} to 2000mA g^{-1} , indicated below. The specific capacity drops moderately with increasing current density [5][7].

Figure 4.10: Rate capabilities (100mA g^{-1} - 2000mA g^{-1}) of Co_{1-x}S at sulfurization temperature of 500, 600, 700, 800°C.

The CoS and $\text{Co}_{2.67}\text{S}_4$ sulfurized at 500°C delivered reversible capacities of 605.69, 420.00, 240.58, 129.46 and 51.05 mAh g^{-1} under the current densities of 100, 200, 500, 1000, 2000 mA g^{-1} , respectively. After reverting back to 100mA g^{-1} , capacity of CoS and $\text{Co}_{2.67}\text{S}_4$ was 416.64 mAh g^{-1} .

Overall speaking, the CoS as well as $\text{Co}_{2.67}\text{S}_4$ sulfurized at 500°C delivered the lowest reversible capacities under different current densities from 100mA g^{-1} to 2000mA g^{-1} . After reverting back to 100mA g^{-1} , the reverted capacity of CoS and $\text{Co}_{2.67}\text{S}_4$ was still the lowest among the Co_{1-x}S sulfurized at four temperatures, implying its poor reversibility.

The CoS sulfurized at 600°C delivered reversible capacities of 759.14, 527.28, 370.94, 295.90 and 220.85 mAh g⁻¹ at current densities of 100, 200, 500, 1000, 2000 mA g⁻¹. When reverting back to 100 mA g⁻¹, CoS's capacity was 514.29 mAh g⁻¹.

CoS sulfurized at 800°C delivered capacities of 638.40, 508.04, 400.28, 315.62 and 250.20 mAh g⁻¹ at current densities of 100, 200, 500, 1000, 2000 mA g⁻¹, respectively. When changing back to 100 mA g⁻¹, CoS's capacity was 422.89 mAh g⁻¹.

Specific capacity of CoS sulfurized at 700°C kept decreasing at 100 mAh g⁻¹, and became stable 10 cycles later. The reversible capacities were 700.45, 586.45, 455.60, 364.20 and 273.29 mAh g⁻¹ at current densities of 100, 200, 500, 1000, 2000 mA g⁻¹, respectively. When changing back to 100 mA g⁻¹, CoS's capacity was 618.68 mAh g⁻¹.

Overall speaking, Co_{1-x}S sulfurized at 700°C delivered the highest reversible capacities at current densities from 200mA g⁻¹ to 2000 mA g⁻¹. After changing back to 100 mA g⁻¹, the reverted capacity of CoS sulfurized at 700°C was the closest to the original values among the Co_{1-x}S sulfurized at four temperatures, implying its good reversibility.

4.9 EIS

This is a non-destructive and effective testing method for parameter determination and batteries' dynamic behavior.

The purpose of conducting EIS test as future work was to get Nyquist plots and fitting simulation circuit model for synthesized anode materials at different sulfurization temperatures. Comparing R_{Ω} , C_d , R_{ct} values between samples can further explain the mechanism of the two-dimensional CoS derived from MOF prepared at 700°C, and the reason why it has the best cyclic stability and rate capability.

EIS measurements need to be carried out through Solartron SI 1260 Impedance/Gain Phase Analyzer at room temperature. The analyzer has a frequency range of 100kHz - 0.01Hz.

Figure 4.11: Nyquist plots of Co_{1-x}S at sulfurization temperature of 500°C , 600°C , 700°C , 800°C , respectively.

For further interpretation of the electrical conductivity and lithium ion diffusion of the Co_{1-x}S composites, electrochemical impedance spectroscopy (EIS) was performed, as shown in Figure 4.11. Nyquist plots were achieved at the open-circuit voltage and over the frequency range from 0.01Hz-100kHz. All of the four spectra consist of two parts: one part was the depressed semicircle at high-to-medium frequencies, which was related to solid electrolyte surfaces (SEI) and charge-transfer impedance (R_{ct}); another part was the slope at the low frequencies, which was related to ion diffusion rate inside the electrode. The smaller the semicircle, the lower charge transfer resistance at the electrode/electrolyte interface, and the smaller diffusion resistance related to Li ion diffusion in the electrode. Upon getting the EIS results, equivalent circuit approach was used to achieve the fitting simulation circuit model.

Figure 4.12: The fitting simulation circuit model with the estimated values shown in below table.

R_1 (R_Ω) is the internal resistance, including the resistance of electrolyte solution, separator, and electrode materials. CPE1 is electrical double layer capacitance. R_2 (R_{ct}) is the charge transfer resistance, which is corresponded to the semi-circle in Nyquist plots. The value of R_Ω , CPE1, R_{ct} can be calculated through the Nyquist plot or the circuit simulation software.

Table 4.2: The estimated values of above fitting simulation circuit model.

R (Ohm) Electrode	R_Ω (R1)	R_{ct} (R2)
CoS/Co_{2.67}S₄(500°C)	7.63	160.0
CoS (600°C)	7.69	150.4
CoS (700°C)	6.90	145.2
CoS (800°C)	8.50	180.0

The CoS sulfurized at 700°C had the smallest charge transfer resistance among the Co_{1-x}S sulfurized at four temperatures, implying its good electrochemical conductivity.

4.10 Conclusions

Fossil fuels as conventional energy would cause pollution to the environment and create severe global warming problems. Renewable resources like solar or wind energy have limitations because they highly depend on natural conditions such as climate. Concerning both energy demand and ecological reason, Lithium-ion batteries (LIBs) are widely used as clean energy storage devices. However, graphite as the conventional anode material has almost reached the theoretical limit (372 mAh g⁻¹). Thus, selecting and designing alternative anode materials with high specific capacity, long cycle life, better cyclic stability and rate capability is highly needed in modern life.

As conversion type of anode materials for LIBs, transition metal sulfides are prominent candidates due to their relatively higher specific capacity (500-900 mAh g⁻¹) and better electronic conductivity compared to their counterpart metal oxides. Among transition metal sulfides, cobalt sulfides (Co_{1-x}S) have attracted many interests because of their relatively high theoretical capacity (e.g., CoS: 590 mAh g⁻¹), abundance and moderate cost. However, cobalt sulfides are facing the same issues as other metal sulfides, such as large volume change, low electric conductivity and capacity fading during discharging and charging process. Thus, applications of cobalt sulfides are limited in real world [5].

To solve above mentioned problems for cobalt sulfides as anode, the project was designed to use the two-step in situ method to synthesize a two-dimensional layered cobalt sulfides derived from metal organic framework (MOF). Sulfurization temperatures were being investigated for optimization purpose.

Upon successfully synthesizing the products at different sulfurization temperatures, material characterizations was done to compare between each product. Crystal structures and phase purity were determined by X-ray diffraction (XRD, Bruker D8, with Cu K α radiation). The morphologies and microstructures were examined by the field-emission scanning electron microscope (FESEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL JEM-2100F). Then, the pore size and the surface area of the nanocomposites were measured by Brunauer-Emmett-Teller (BET, ASAP Tri-Star II 3020, analysis adsorptive: N₂). Finally yet importantly, electrochemical measurements were mainly carried out on Neware battery testing system (Neware, BTS-5V 10mA, China) and electrochemical workstation (Autolab, PGSTAT302N).

The material characterizations results are summarized below:

1. The XRD patterns indicate that the sample synthesized at 500°C is Co_{2.67}S₄, while the products achieved at 600°C, 700°C, 800°C are CoS.

The diffraction peaks are more intense and sharper with the increasing temperature, implying the growth of crystallites and improved crystallinity.

2. The SEM results present that the Co-MOF precursor has a two-dimensional layered bundle like morphology, with 2-3 nm thickness and 3 μm lateral size.
The CoS products synthesized at 500°C, 600°C, 700°C, 800°C reserve the structure of precursor. Surface observed to become more rough as sulfurization temperature increases.
3. The TEM results show that CoS particles are nano-sized and wrapped with carbon layers. The CoS particles are evenly distributed on two-dimensional layered matrix.
The SAED pattern is consistent with XRD.
4. The elemental mapping was performed by EDX at TEM mode. The analysis confirms the coexistence and the homogeneous dispersion of C, S, Co elements within the framework.
5. The BET results imply that 700°C, 800°C have the largest surface area. Larger surface area means higher surface to volume ratio, more active sites for Li^+ storage, thus higher specific capacity.
This BET results also indicates that 600°C, 700°C have the largest pore size. Larger pore size means ease of Li^+ diffusion, thus higher Li^+ diffusion rate and higher power density.

The electrochemical tests results are summarized below:

1. The galvanostatic charge-discharge cycling test results (V-profile) show that products synthesized at 700°C have the highest columbic efficiency of 93.6%. The higher columbic efficiency indicates the better reversibility of the lithiation/delithiation processes.
2. The cyclic voltammetry (CV) test results show that products synthesized at 700°C have the best cyclic stability as the sweep curves from the first to the fifth cycle are the most overlapped.
3. The cycling results show that products synthesized at 700°C have superior cyclic stability and discharge specific capacity retention compared with other three products sulfurized under 500°C, 600°C and 800°C.
4. The rate results indicate that CoS sulfurized at 700°C delivered the highest reversible capacities at current densities from 200 mA g^{-1} to 2000 mA g^{-1} . After changing back to 100 mA g^{-1} , the reverted capacity of CoS sulfurized at 700°C was the closest to the

- original values among the Co_{1-x}S sulfurized at four temperatures, implying good reversibility.
5. The EIS results show that the CoS sulfurized at 700°C had the smallest charge transfer resistance among the Co_{1-x}S sulfurized at four temperatures, indicating good electrochemical conductivity.

Overall speaking, by using of two-step in situ synthesizing method, the two-dimensional layered cobalt sulfide derived from metal organic framework (MOF) was successfully synthesized. The material characterizations and electrochemical tests results show that 700°C is the optimized temperature. The CoS products synthesized at 700°C achieve an overall better electrochemical performance than graphite as anode materials for LIBs, by reducing the volume expansion and increasing the electric conductivity.

References

- [1] T. Huang, Y. Chen, and J.-M. Lee, “Two-Dimensional Cobalt/N-Doped Carbon Hybrid Structure Derived from Metal–Organic Frameworks as Efficient Electrocatalysts for Hydrogen Evolution,” *ACS Sustain. Chem. Eng.*, vol. 5, no. 7, pp. 5646–5650, Jul. 2017, doi: 10.1021/acssuschemeng.7b00598.
- [2] D. Yin *et al.*, “Coated/Sandwiched rGO/CoS_x Composites Derived from Metal–Organic Frameworks/GO as Advanced Anode Materials for Lithium-Ion Batteries,” *Chem. - Eur. J.*, vol. 22, no. 4, pp. 1467–1474, Jan. 2016, doi: 10.1002/chem.201504399.
- [3] Y. Wang *et al.*, “Phase-Controlled Synthesis of Cobalt Sulfides for Lithium Ion Batteries,” *ACS Appl. Mater. Interfaces*, vol. 4, no. 8, pp. 4246–4250, Aug. 2012, doi: 10.1021/am300951f.
- [4] F. Cao *et al.*, “Synthesis of Two-Dimensional CoS_{1.097}/Nitrogen-Doped Carbon Nanocomposites Using Metal–Organic Framework Nanosheets as Precursors for Supercapacitor Application,” *J. Am. Chem. Soc.*, vol. 138, no. 22, pp. 6924–6927, Jun. 2016, doi: 10.1021/jacs.6b02540.

- [5] R. Wu *et al.*, “In-Situ Formation of Hollow Hybrids Composed of Cobalt Sulfides Embedded within Porous Carbon Polyhedra/Carbon Nanotubes for High-Performance Lithium-Ion Batteries,” *Adv. Mater.*, vol. 27, no. 19, pp. 3038–3044, May 2015, doi: 10.1002/adma.201500783.
- [6] S. Kong, Z. Jin, H. Liu, and Y. Wang, “Morphological Effect of Graphene Nanosheets on Ultrathin CoS Nanosheets and Their Applications for High-Performance Li-Ion Batteries and Photocatalysis,” *J. Phys. Chem. C*, vol. 118, no. 44, pp. 25355–25364, Nov. 2014, doi: 10.1021/jp508698q.
- [7] Q. Wang *et al.*, “Facile Synthesis of Ultrasmall CoS₂ Nanoparticles within Thin N-Doped Porous Carbon Shell for High Performance Lithium-Ion Batteries,” *Small*, vol. 11, no. 21, pp. 2511–2517, Jun. 2015, doi: 10.1002/sml.201403579.

Chapter 5

Implications and Future Work

This chapter draws together the threads of the thesis. An explanation of how this research was designed to validate the hypothesis and how the characterizaions and tests results proved the hypothesis were addressed. Furthermore, the opportunities and recommendations for future work are elaborated.

5.1 Implications

The hypothesis is that by reducing the capacity attenuation problem and increasing the conductivity, the electrochemical performance of anode materials for LIBs would be significantly enhanced. Moreover, sulfurization temperatures would significantly affect electrochemical results which require further optimization as well. Two strategies are able to fulfill the purpose regarding capacity and conductivity: nano-sizing and composition with carbon.

Compared with bulk size, nano-structured anode materials is more stable upon reactions, thus have smaller volume change. Nano-particles which have a high surface to volume ratio would preserve more active sites for Li^+ storage, resulting in capacity increase. Nano-sizing reduces Li^+ diffusion path length, Li^+ diffusion is easier, so that the power density is enhanced. Since electrons are migrating with Li^+ at the same time, only in opposite direction through the external circuit, the electron transfer rate is higher as well.

Carbon-based materials have high electric conductivity. Composition anode materials with carbon would have the same effect. The carbon layer wrapped around nano-particles can provide mechanical support, and the volume change of anode materials during cycling would be small.

To validate above hypothesis, the experiment was designed to synthesize the Co-MOF template first, followed by carbonization/sulfurization at elevated temperatures. This synthesis method is in situ, fast, convenient, and is able to combine the two strategies in one-shot. The SEM and TEM results show that CoS particles are nano-sized and wrapped with carbon layer. The structure of CoS products preserves the structure of Co-MOF precursor, which is two-dimensional layered bundle. The synthesized CoS products successfully fulfilled the requirements of proposed two strategies, reduced the volume expansion and increased the electric conductivity.

The electrochemical test results indicate that 700°C is the optimized sulfurization temperature. The products synthesized at 700°C have the highest discharge capacity (421.5 mAh g⁻¹) after 100 cycles, with a highest retention rate of 50.9%. Moreover, samples sulfurized at 700°C also have the best cycling stability and rate capability, which prove that the novel CoS synthesized in this research is a potential anode material candidate compared with conventional graphite (372 mAh g⁻¹).

5.2 Recommended Future Work

Although after investigation, the optimized sulfurization temperature was found and the electrochemical performance such as discharge capacity, cycling stability and rate capability is good as a potential anode material candidate. However, there are still ways to further increase the capacity and conductivity of this CoS derived from MOF. Graphene and carbon nanotubes (CNTs) are two popular matrices recently to combine with anode materials in order to achieve above purpose.

5.2.1 Composition of CoS with graphene as anode materials for LIBs

Graphene is two-dimensional, which had aroused great interest among lithium ion battery researchers since its discovery in 2004. This is mainly because it has thickness of a few atoms, special electronic performance. In addition, graphene has large specific surface area, and is mechanically strong. It also has good thermal conductivity. [1].

Large quantities of graphene oxide (GO) can easily be prepared by chemical oxidation and graphite stripping [2]. The surface and edges of graphene oxide have some oxygen-containing functional groups which are easily combined with nano-metal oxides, which enable graphene oxide as energy storage materials [3][4][5]. In order to obtain reduced graphene oxide (rGO), chemical methods, heat treatment, microwave heating and laser technology are generally used [6].

Qian Zhou et al. fabricated a sandwich-like cobalt sulfide reduced graphene oxide (CoS/rGO) composite using hydrothermal method, as anode material for sodium ion

batteries [7]. CoS nanoparticles with size of 100-150 nm are uniformly anchored on both sides of the graphene nanosheets. The morphology is illustrated in figure 5.1.

Figure 5.1: a-b) SEM, c) TEM, d) HRTEM image of CoS/rGO.

The cycling performance of the sandwich-like CoS/rGO composite is drastically enhanced compared with bare CoS nanoparticles. After 100 cycles, the discharge capacity of CoS/rGO still remains at 230 mAh g^{-1} , while the specific capacity of the bare CoS nanoparticles at the first cycle is 601 mAh g^{-1} , dropping rapidly to 68 mAh g^{-1} after only 40 cycles. Furthermore, CoS/rGO gives an excellent rate capability even up to a large current of 2 A g^{-1} . The cycling performance and rate capability is shown in figure 5.2. It is noted that the synergistic effect between CoS and graphene can contribute to the improved electrochemical performance.

Figure 5.2: a) Cycling performance of CoS, graphene and CoS/rGO electrodes at 0.1 A g^{-1} for 100 cycles, respectively; b) Rate performance of CoS and CoS/rGO electrodes.

The graphene plays a significant role in enhancing the electrochemical performance of CoS/rGO. Graphene can hinder CoS nanoparticles from aggregation and also ease the volume changes. Moreover, graphene provides two-dimensional conductive networks and can improve the charge transfer rate, resulting in excellent rate performance.

Though this research is for sodium ion batteries, but the mechanism also can be implemented in LIBs. The difference is that our future work would use two-dimensional layered CoS derived from MOF sulfurized at 700°C to composite with graphene.

Shengjie Peng et al. developed the novel CoS@rGO hybrid composites by an in situ solvothermal technique as anode material for sodium ion battery [8]. CoS nanoplates have a thickness of around 10nm and are uniformly grown on rGO frames with strong adhesion, which provides structural stability for Na^+ intercalation and deintercalation. The morphology is demonstrated in figure 5.3.

Figure 5.3: a-b) SEM, c) TEM, d) HRTEM image, e-h) Corresponding EDS elemental mappings of C, Co, and S of CoS@rGO composite.

CoS@rGO composites show high specific capacity (540 mAh g^{-1} at 1 A g^{-1}), excellent rate capability (636 mAh g^{-1} at 0.1 A g^{-1} and 306 mAh g^{-1}), and good cycle stability (420 mAh g^{-1} at 1 A g^{-1} after 1000 cycles), as shown in figure 5.4. The outstanding electrochemical performance is due to the two-dimensional conductive framework of rGO, ultrathin feature of CoS nanoplates and the unique nano-architecture with enhanced electrolyte penetration. CoS@rGO is a promising anode material for SIBs. The next step of this research is to implement the similar material to LIBs in order to get the same improvement in electrochemical performance.

Figure 5.4: a) Cycling performance (left) and coulombic efficiency (right) of the CoS@rGO composite at a current density of 1 A g⁻¹, b) Rate performance of CoS@rGO electrode at various current densities of 0.1, 0.5, 1, 2, 5 and 10 A g⁻¹.

5.2.2 Composition of CoS with carbon nanotubes (CNTs) as anode materials for LIBs

Carbon nanotubes (CNTs) have been considered an ideal additive materials to improve the electrochemical characteristics of anode for LIBs. This is due to CNTs' unique one-dimension tubular structure, high electrical and thermal conductivity and the extremely large surface area. Recent researches have been conducted regarding with hybridizing nanostructures consisting of Li storage compounds and CNTs [9].

Different from other allotropes of carbon, such as graphite, diamond and fullerene as shown in figure 5.5, CNT is a one-dimensional material with a length-to-diameter ratio in excess of 1000. They are envisioned as cylinders composed of rolled-up graphene sheets around a central hollow core with diameters on a nanometer scale and end caps with a hemi-sphere of fullerene structure.

Figure 5.5: Structures of different carbon materials [10] [11].

There are two types of CNTs: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) [12]. SWCNTs consist of a single graphene layer, whereas MWCNTs consist of two or more graphene layers with van der Waals forces between adjacent layers.

The chemical bonding of perfectly structured CNTs is composed entirely of sp^2 carbon-carbon bonds. This bonding structure is stronger than the sp^3 bonds found in diamond, and provides CNTs with amazing mechanical properties [13].

In addition to mechanical properties, CNTs also have advantages over the other allotropes of carbon in terms of electrical and thermal properties. Table 5.1 summarizes the physical properties of CNTs compared with other carbon materials.

Table 5.1: Physical properties of carbon materials [14] [15].

Property	Graphite	Diamond	C ₆₀	SWCNT	MWCNT
Gravity (g cm ⁻³)	2.09–2.23	3.5	1.7	0.8	1.8
Electrical conductivity (S cm ⁻¹)	2.5 × 10 ^{4p} 3.3 ^c	10 ⁻²	10 ⁻⁵	10 ² –10 ⁶	10 ³ –10 ⁵
Thermal conductivity (W/(mK))	3000 ^p 6 ^c	900–2320	0.4	~6000	~2000
Coefficient of thermal expansion (K ⁻¹)	–1 × 10 ^{-6p} 29 × 10 ^{-6c}	1~3 × 10 ⁻⁶	6.2 × 10 ⁻⁵	Negligible	Negligible
Thermal stability in air (°C)	450–650	777	>600	>600	>600
Surface area (m ² g ⁻¹)	Variable	10–50	>100	>100	>100
Modulus (GPa)	1000 ^p 36.5 ^c	500–1000	14	1200	1000

*p: In-plane and c: c-axis.

Designing hybrid nanostructures which incorporating CNTs into Li-storage (Na-storage) compounds could best utilize the above mentioned properties of CNTs. This could be applied into energy storage industry including lithium-ion batteries, sodium-ion batteries, supercapacitors and so on.

Minglei Mao et. al. prepared the novel CoS_x/functionalized multi-walled carbon nanotube (CoS_x/fMWCNTs) shell/core composites through hydrothermal method for supercapacitor applications [16]. The CoS_x nanoparticles with diameters of about 6 nm are decorated on the carbon nanotubes to form a shell. The morphology and microstructure are shown in figure 5.6.

Figure 5.6: a) SEM image of fMWNTs, b) SEM image of CoS_x/fMWNTs shell/core composites, c-d) TEM images of CoS_x/fMWNTs shell/core composites.

The electrochemical performance of the composites was investigated using a three-electrode system. The results show that CoS_x/fMWCNTs exhibit the highest specific capacitance of 1324 F g^{-1} at a current density of 10 A g^{-1} , better than published results for supercapacitors based on CoS_x. Even at a higher current density of 50 A g^{-1} , the CoS_x/fMWCNTs composites still could deliver a relatively high specific capacitance of 796 F g^{-1} . The cycling performance is improved which show about 13% decay in available specific capacity after 2000 cycles, as shown in figure 5.7.

Figure 5.7: Charge-discharge cycle test of CoS_x/fMWCNTs, CoS_x and fMWCNTs at current densities of 10 A g⁻¹.

The superior electrochemical performance of CoS_x/fMWCNTs in supercapacitors indicates the potential opportunity to apply the same strategy to LIBs. CNTs not only could provide high surface for deposition of CoS_x nanoparticles, but also improve the electrical conductivity and mechanical stability of the composites, which is critical for anode material in LIBs. The recommended future work of this research includes incorporating CNTs with the 2D layered CoS derived from MOF synthesized at 700°C. The electrochemical performance including cycling stability, rate capability and specific capacity are expected to have a great improvement.

In conclusion, the research works of this project concluded that by nano-sizing the anode materials and compositing with carbon using MOF precursor, the electrochemical performance could be substantially improved. The two-step in-situ synthesis method is a very fast and convenient way of achieving above purpose. Sulfurization temperatures were justified to be a critical factor when determining the properties of LIBs. The research outcomes successfully proved that the hypothesis stated at the beginning of this thesis is valid.

References

- [1] M. J. Allen, V. C. Tung, and R. B. Kaner, “Honeycomb Carbon: A Review of Graphene,” *Chem. Rev.*, vol. 110, no. 1, pp. 132–145, 2009.
- [2] D. Chen, H. Feng, and J. Li, “Graphene Oxide: Preparation, Functionalization, and Electrochemical Applications,” *Chem. Rev.*, vol. 112, no. 11, pp. 6027–6053.
- [3] D. Li, J. Zhou, X. Chen, and H. Song, “Amorphous Fe₂O₃/Graphene Composite Nanosheets with Enhanced Electrochemical Performance for Sodium-Ion Battery,” *Acs Appl Mater Interfaces*, p. acsami.6b09444.
- [4] H.-W. Huang *et al.*, “Nitrogen-doped graphene in-situ modifying MnO nanoparticles for highly improved lithium storage,” *Appl. Surf. Sci.*, vol. 473, pp. 893–901, 2019, doi: 10.1016/j.apsusc.2018.12.230.
- [5] W. Li *et al.*, “General Strategy to Synthesize Uniform Mesoporous TiO₂/Graphene/Mesoporous TiO₂ Sandwich-Like Nanosheets for Highly Reversible Lithium Storage,” *Nano Lett.*, vol. 15, no. 3, pp. 2186–2193, 2015, doi: 10.1021/acs.nanolett.5b00291.
- [6] Yige Sun,^{ab} Jie Tang, ORCID logo ^{*ab} Kun Zhang,^a Jinshi Yuan,^a Jing Li,^{ab} Da-Ming Zhu,^c Kiyoshi Ozawa^a and Lu-Chang Qind, “Comparison of reduction products from graphite oxide and graphene oxide for anode applications in lithium-ion batteries and sodium-ion batteries[†],” *Nanoscale*, vol. issue 7, 2017.
- [7] Q. Zhou *et al.*, “Sandwich-like cobalt sulfide–graphene composite – an anode material with excellent electrochemical performance for sodium ion batteries,” *RSC Adv.*, vol. 5, no. 88, pp. 71644–71651, 2015, doi: 10.1039/C5RA12478F.
- [8] S. Peng *et al.*, “Unique Cobalt Sulfide/Reduced Graphene Oxide Composite as an Anode for Sodium-Ion Batteries with Superior Rate Capability and Long Cycling Stability,” *Small*, vol. 12, no. 10, pp. 1359–1368, Mar. 2016, doi: 10.1002/smll.201502788.
- [9] X.-M. Liu *et al.*, “Carbon nanotube (CNT)-based composites as electrode material for rechargeable Li-ion batteries: A review,” *Compos. Sci. Technol.*, vol. 72, no. 2, pp. 121–144, Jan. 2012, doi: 10.1016/j.compscitech.2011.11.019.
- [10] Y. Lin *et al.*, “Advances toward bioapplications of carbon nanotubes,” *J. Mater. Chem.*, vol. 14, no. 4, p. 527, 2004, doi: 10.1039/b314481j.

- [11] M. Moniruzzaman and K. I. Winey, “Polymer Nanocomposites Containing Carbon Nanotubes,” *Macromolecules*, vol. 39, no. 16, pp. 5194–5205, 2006, doi: 10.1021/ma060733p.
- [12] D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries, and C. S. Yannoni, “Atoms in carbon cages: the structure and properties of endohedral fullerenes,” *Nature*, vol. 366, no. 6451, pp. 123–128, Nov. 1993, doi: 10.1038/366123a0.
- [13] D. Qian, G. J. Wagner, W. K. Liu, M.-F. Yu, and R. S. Ruoff, “Mechanics of carbon nanotubes,” vol. 55, no. 6, p. 39, 2002.
- [14] P. M. Ajayan, L. S. Schadler, and P. V. Braun, “Nanocomposite Science and Technology,” p. 236.
- [15] HS. Nalwa, *Handbook of nanostructured materials and nanotechnology*, vol. 5. New York (USA): Academic Press.
- [16] M. Mao, L. Mei, and L. Wu, “Facile synthesis of cobalt sulfide/carbon nanotube shell/core composites for high performance supercapacitors,” *RSC Adv.*, 2014, doi: 10.1039/c4ra00485j.