Synthesis and electrochemical studies of nanostructured metal oxides for lithium ion batteries

Li, Linlin

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NANYANG
TECHNOLOGICAL
UNIVERSITY

**SYNTHESIS AND ELECTROCHEMICAL STUDIES OF
NANOSTRUCTURED METAL OXIDES FOR LITHIUM ION
BATTERIES**

LI LINLIN

School of Materials Science and Engineering

2016

SYNTHESIS AND ELECTROCHEMICAL STUDIES OF NANOSTRUCTURED METAL OXIDES FOR LITHIUM ION BATTERIES

LI LINLIN

School of Materials Science and Engineering

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Abstract

The key to optimize lithium ion batteries (LIBs) for future advanced application is to develop novel electrode materials with outstanding electrochemical properties. Nanomaterials with precisely designed configurations provide one of the most desirable ways. As one of the most studied candidates, metal oxides, especially Sn-based and Co-based oxides, are currently extensively exploited as anode for LIBs. Nevertheless, several issues need to be addressed that handicap the commercial application of these metal oxides. So, scientific research and breakthroughs are imperative to meet the requirements for real use.

With this in view, a series of one-dimensional (1D) Sn-based (ASnO_3) and Co-based (ACo_2O_4) ternary oxides with various nanoarchitectures has been prepared by simple and versatile electrospinning techniques. In this thesis, one major aim is to investigate the effect of different nanostructures on the electrochemical performance of LIBs. Meanwhile, the possible formation mechanism for the unique structure will be studied to shed some light on the controllable fabrication of other metal oxides with similar morphology. Benefiting from their unique structural features, eggroll-like CaSnO_3 nanotubes (CSO-NT), hierarchical CaCo_2O_4 nanofibers (CCO-NF), and porous NiCo_2O_4 nanotubes (NCO-NT) demonstrate superior electrochemical performance compared to their corresponding counter-parts, respectively.

To gain deep understanding on the enhanced batteries performance, by comparing the lithium storage capability of as-prepared different nanostructures, the effect of counter ions substitution, especially A-site substitution, in ASnO_3 and ACo_2O_4 systems has been systematically discussed. By virtue of excellent properties of the active matrix elements Ni, porous NCO-NT with large capacity and remarkable cycling stability is identified as the most potential anode materials for LIBs.

As the electrochemical reaction mechanisms and capacity degradation is critical for the rational design of advanced LIBs, this thesis performed fundamental investigation for the

structure evolution of eggroll-like CSO-NT, hierarchical CCO-NF, and porous NCO-NT. The origin of the capacity degradation and lithium storage mechanisms have been proposed and discussed. Moreover, the reaction kinetics and lithium diffusion coefficients were also analyzed in depth. Lastly, it is hoped that all of studies could shed more light on the fundamental science.

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constant phase element (*CPE*) to replace the pure capacitance due to the depressed semicircle, Warburg impedance (*W*); (c) Fitted impedance data obtained from Nyquist plots utilizing the circuit in Figure 6.20b.

Abbreviations

LIBs	Lithium Ion Batteries
SnO ₂	Tin Oxide
Co ₃ O ₄	Cobalt Oxide
NiO	Nickel Oxide
CaSnO ₃	Calcium Tin Oxide
SrSnO ₃	Strontium Tin Oxide
BaSnO ₃	Barium Tin Oxide
CaCo ₂ O ₄	Calcium Cobalt Oxide
NiCo ₂ O ₄	Nickel Cobalt Oxide
SnCl ₂ ·H ₂ O	Tin Chloride Dihydrate
DMF	N, N-dimethylformamide
NMP	N-methylpyrrolidinone
PVDF	Poly (vinylidene difluoride)
LiPF ₆	Lithium Hexafluorophosphate
PVP	Poly(vinylpyrrolidone)
PAN	Polyacrylonitrile
CSO-NT	CaSnO ₃ Nanotubes
CSO-NF	CaSnO ₃ Nanofibers
CSO-NB	CaSnO ₃ Nanobelts
CSO-NR	CaSnO ₃ Nanorods
CCO-NF	CaCo ₂ O ₄ Nanofibers
NCO-NT	NiCo ₂ O ₄ Nanotubes
NCO-NF	NiCo ₂ O ₄ Nanofibers
NCO-NB	NiCo ₂ O ₄ Nanobelts
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional

Li ⁺	Lithium ion
SEI	Solid Electrolyte Interface
TMOs	Transition Metal Oxide
FESEM	Field Emission Scanning Electron Microscope
TEM	Transmission Electron Microscope
HRTEM	High Resolution Transmission Electron Microscope
SAED	Selected Area Electron Diffraction
BET	Brunauer-Emmett-Teller
XRD	X-Ray Diffraction
XPS	X-Ray Photoelectron Spectroscopy
EDX	Energy-Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy

Chapter 1 Introduction

1.1 Background

The growing appetite for energy, in tandem with the urgent need to minimize greenhouse gas emissions, has become one of the most critical challenges of our time. This challenge has brought about an unprecedented requirement for sources of renewable energy, as well as reliable and efficient devices for energy conversion and storage. Rechargeable batteries, also known as secondary batteries, appear to have certain characteristics which make them uniquely suited candidates for addressing this requirement.^[1-3] Compared with various established technologies like the nickel-metal hydride (Ni-MH) batteries, nickel-cadmium (Ni-Cd), or lead acid, the lithium ion battery (LIB) is considered the most promising system, with prominent advantages of greater cycling longevity, higher energy density, and light weight. At the time of writing, LIBs are almost ubiquitously used to power the current generation of portable consumer electronic devices, from laptop computers to cell phones and camcorders. They have also found applications in the medical industry, in devices such as defibrillators and cardiac pacemakers among others.^[4, 5]

With the aim to supplement, or even supplant the conventional internal combustion engine (ICE), it is expected use of LIBs for vehicular transport, which can be classified into pure electric vehicles (EV, requires > 40 kWh), plug-in hybrid (PHEV), and hybrid vehicles (HEV).^[6-8] However, such applications ideally required LIBs with much improved energy and power densities. Therefore, to satisfy the above requirements, vigorous efforts are underway to explore advanced LIBs.

Since the working principle behind LIBs is based on the reversible reaction between the anode and the cathode, the intrinsic characteristics of the electrode materials play a critical part in determining the electrochemical performance of LIBs.^[9-11] It is well known that commercial LIBs, which is developed by Sony Co. in 1990, use graphite as anode, which have the advantages of being non-toxic and relatively inexpensive. However, graphite anodes possess a low theoretical specific capacity (~ 372 mAh g⁻¹), severely limiting its potential application in electric automobiles. Additionally, the large volume variation

during Li ion intercalation/extraction, coupled with safety concerns resulting from the formation of lithium dendrite during overcharging, are two major drawbacks.^[12-14] Thus, these disadvantages directly push researchers to find substitutes to graphite to achieve safer LIBs with better energy and power density.

Currently, various transition metal oxides (TMOs) are being extensively investigated as promising alternative anodes for LIBs, mainly due to their superior properties compared with graphite anode.^[15-17] However, the employment of TMOs in LIBs is still limited by their poor cycling performance and intrinsic low charge/ions conductivity. Nanoarchitecture offers one of the most desirable approaches to alleviate these problems.^[18-20] Although TMOs with desirable nanoarchitectures possess many attractive features, achieving its practical application in LIBs still remains great challenges.

1.2 Motivation

Along with the rapid development of nanotechnology, electrode materials with suitable nanoarchitectures provide new opportunities to achieve high-performance LIBs for future applications. Up to date, numerous examples have indicated that the lithium storage properties of electrode materials could be tailored and remarkably improved by designing proper nanostructures. Therefore, the fabrication of nanostructured electrode materials has already been a fertile and attractive research field.

It is worth mentioning that over the past 15 years, there has only been one successfully commercialized alternative anode – a Sn/Co/C amorphous/ nanocrystalline composite developed by Sony Co. in 2005.^[15, 21] Sn, acts as the electrochemical active material and reacts with Li ions to form intermetallic alloy, whereas Co and carbon, act as electrochemical inactive matrix to accommodate the volume variation during cycling process, thereby resulting in good long-term cyclability.^[22] Benefiting from the inactive buffer “matrix”, Sn/Co/C could obtain a reversible and stable capacity of around 350–450 mAh g⁻¹. Inspired by this concept of electrochemical active/inactive matrix, it is anticipated that the combination of one or more metal oxides as active/inactive matrix elements will be a desirable way to enable alternative anodes with better cycling performance and large capacity. Besides, compared to mechanical mixing of inactive and

active metal oxides, complex or ternary oxides are convinced to be an ideal way to incorporate these matrices. So far, although some results are encouraging, there is still no adequate research and available theory to demonstrate the detailed interaction between counter ions in ternary or composites TMOs, as well as how the nanostructures affect the batteries performances. Hence, this thesis will focus on this direction to gain further understanding.

1.3 Overall Objective and Scope of Research

The main research scope and objective of this thesis is to develop metal oxide nanocomposites (AB_xO_y nanostructures) as advanced anode for LIBs with large capacity, high energy density, and excellent safety. The detailed goals are listed below:

1.3.1 Investigation of the impact of nanoarchitecture on the electrochemical properties of AB_xO_y

Nanoarchitecture offers one of the best available ways to design and tune high-performance electrode materials for LIBs. Actually, lithium storage capabilities of nanostructured electrode largely depend on their structural properties. Different nanostructures exhibit their unique features.^[23-25] Specifically, electrode materials with flexible nanostructures could provide sufficient free spaces to alleviate the huge volume variation during cycling process. Moreover, compared with microscale materials, nanostructured materials have an inherently large surface area that could not only enlarge the contact area between the electrolyte and active material, but also result in short diffusion lengths, thus rendering the material with good electrode kinetics, enhanced capacity and rate capability.

With this in view, a series of AB_xO_y nanomaterials with various nanostructures, especially one-dimensional (1D) shapes has been prepared by facile and versatile electrospinning technique. In this thesis, one major aim is to examine the influence of different nanostructures on the LIBs's electrochemical performance. Meanwhile, the possible mechanisms for the formation of the unique structure will be studied to shed some light on

the controlled fabrication of other metal oxides with similar morphologies. Various characterization techniques will be utilized to evaluate the composition and structural features of the as-prepared samples.

1.3.2 Study the effect of counter ions substitution in AB_xO_y system on electrochemical performance of LIBs

As mentioned above, the combination of one or more metal oxides as active/inactive matrix elements will be a desirable way to enable alternative anodes with better cycling performance and large capacity. Moreover, it is found that distinguishable electrochemical performance could be achieved by simply adjusting the counter ions in some ternary metal oxides such as $NiCo_2O_4$,^[26, 27] $MgCo_2O_4$,^[28] $Ca_3Co_4O_9$,^[29] $MnCo_2O_4$,^[30, 31] $NiSnO_3$,^[32] $CoSnO_3$,^[33, 34] $CaSnO_3$,^[35, 36] $CuFe_2O_4$.^[37] Nevertheless, there is no systematic research about the impact of counter ion within AB_xO_y nanostructures on the electrochemical performance. Hence, this thesis devotes to investigate the substitution of counter ion, especially A-site substitution, in AB_xO_y nanostructures. By proper selection of the starting materials composition and morphology, the effect of active or inactive matrix within AB_xO_y nanostructures will be conducted to contribute a comprehensive understanding of metal oxides nanocomposites as anode for LIBs. Significantly, by comparing the lithium storage capability of different AB_xO_y nanostructures, the effect of counter ion substitution in AB_xO_y nanostructures will be discussed and the most potential anode materials will be identified.

1.3.3 Fundamental studies the reaction mechanism of AB_xO_y nanostructures towards lithium ions during cycling process

Understanding the electrochemical reaction mechanisms and capacity degradation is critical for the rational design of advanced LIBs.^[38, 39] Although the electrochemical reaction is so complex and the materials characterizations of cycled electrode are always intricate, some *ex-situ* techniques including *ex-situ* TEM, *ex-situ* XRD, and *ex-situ* XPS, have also been proved as powerful tool to offer valuable information about morphology

evolution, and phase transformation during lithiation/delithiation process.^[40] With these in mind, the aim of this thesis is to deep understand the structural features of AB_xO_y nanostructures after cycling and further improve battery performance. Specifically, the fundamental study for the structure evolution of AB_xO_y during charge/discharge process is performed. The origin of the capacity degradation mechanism of AB_xO_y will be proposed and discussed. Moreover, the reaction kinetics and lithium diffusion coefficients will also be analyzed and discussed by using EIS and CV. Last, it is hoped that all of investigations could shed light on the fundamental science.

1.4 Thesis Organization

The layout of this thesis is listed as below:

Chapter 1 provides the introduction of the research background and motivation, as well as defines the scope and objectives of the project.

Chapter 2 briefly introduces the basic configuration and operating principles of LIBs. In term of lithium storage mechanisms, a series of representative anode materials are reviewed.

Chapter 3 describes the various techniques, which are used in this thesis, such as materials characterization tools, synthesis methodology for metal oxides nanocomposites, and electrochemical measurement procedures.

Chapter 4 investigates the electrochemical properties of $ASnO_3$ ($A = Ba, Sr, \text{ and } Ca$) and summarizes the influence of morphology modification and A-site substitution in $ASnO_3$.

Chapter 5 investigates the electrochemical properties of ACo_2O_4 ($A = Ca \text{ and } Ni$) and summarizes the influence of morphology modification and A-site substitution in ACo_2O_4 .

Chapter 6 carry out a series of fundamental studies on $ASnO_3$ and ACo_2O_4 , such as lithium diffusion studies, electrochemical Li storage mechanism, as well as the importance of ternary metal oxides.

Chapter 7 reaches the conclusion of the whole research project, together with the proposed future studies in Chapter 7.

Chapter 2 Literature Review

Figure 2.1 The gravimetric energy density and volumetric energy density for commonly used batteries systems. Reproduced with permission from reference ^[41].

Among the most successful technologies, LIBs, originally commercialized by Sony Co. in 1990, have revolutionized portable electronic devices. As shown in Figure 2.1,^[41] it seems that LIBs possess competitive advantages for electric vehicles (EVs) and grid applications because of its significantly higher energy density and lighter weight than that of other energy storage devices, including lead-acid, Ni-Cd, and Ni-MH. However, these applications commonly require LIBs with high power/energy densities, low cost, good safety, thermal stability, and excellent cycling performance. To realize large energy/power densities, further breakthroughs in electrode materials lies at the heart of next-generation LIBs. So in other words, innovative materials chemistry holds the key to the advances in LIBs.^[42]

2.1 Basic Principles of LIBs

Undoubtedly, LIBs represents one of the most prospective technologies with a variety of advantages, including low maintenance, high energy density, and no memory effect. The conventional LIBs consist of a layered-oxide cathode (generally the lithium metal oxide, LiCoO_2), an anode (generally graphite), and a porous membrane separator soaked in non-aqueous electrolyte (LiPF_6 in ethylene carbonate/diethylcarbonate), which not only enable ion transfer but also prevent directly contact between the two electrodes.

Figure 2.2 Schematic illustration of LIBs, comprising a graphite anode, LiCoO_2 cathode, and a non-aqueous liquid electrolyte separating the electrodes. Reproduced with permission from reference [20].

Figure 2.2 shows the basic LIBs system. During charging, Li ions deintercalate from the cathode and are inserted into the anode, in the process transferring electrons via the external circuit from cathode to the anode. Conversely, the anode releases Li ions which then intercalate back into cathode during discharging. During charge/discharge cycling, lithium ions are transported backwards and forwards between the electrodes through the organic electrolyte, which reversibly converts the chemical energy into electricity and stores the electrical energy within the battery. The chemical reactions can be summarized as follows:[43]

Since the performance of LIBs is heavily dependent on active materials utilized for Li storage, hence the prudent selection of electrode materials is critical. The ideal electrode material should possess a large reversible capacity, excellent conductivity, good cycle life, enhanced safety, and be both inexpensive and environmental friendly. Currently, the dominant commercial LIB anode material is graphite, which has several advantages, including a flat and low working potential, favorable cycling stability, and is relatively cheap. Nevertheless, the theoretical capacity of around 372 mAh g^{-1} could be provided by graphite, which corresponds to a stoichiometry of LiC_6 . Such low capacity is no longer satisfying for high energy applications. Moreover, the Li ion transport rate of graphite is lower than $10^{-6} \text{ cm}^2 \text{ s}^{-1}$, leading to a low power density of battery as the power density associates with the chemical diffusion coefficient of Li ions. Furthermore, another limitation arises from the safety concerns because of lithium dendrite formation during the overcharge process, coming from the low Li intercalation voltage of the graphite (almost approaching 0 V vs. Li/Li^+). Therefore, there is an urgent need to find advanced anode materials for high-performance LIBs.^[44] Although undeniable obstacles ahead, noteworthy efforts have been paid by researchers to explore alternative commercial LIBs anode.

2.2 Metal Oxides-based Anode Materials

In terms of obtaining a large power and energy density, a wide variation of metal oxide-based materials has been regarded as promising prospective anodes for LIBs. Research into innovative anode materials can be classified into three main types depending on their reaction mechanism – intercalation/deintercalation anode materials, alloy/dealloy anode materials, and conversion reaction anode materials.^[15, 43, 45] In this section, the state of the art of metal oxides-based anode materials for LIBs will be discussed, with emphasis on the recent outcomes and outstanding results in the domain of nanotechnology.

2.2.1 Anodes : Intercalation/deintercalation reaction

According to the definition, intercalation mechanism refers to the electrochemical insert/de-insert of lithium ions into/out the host's crystal lattice without destroying the major structural features. By virtue of the excellent stability of crystal structure, the reversibility of intercalation electrode materials are always favorable. However, the lower specific capacity and poor electrical conductivity of these materials largely limit their widespread use.^[46]

In addition to graphite, various other intercalation materials have drawn attention as possible alternative anodes for LIBs, for example, metal oxides, polymers and chalcogenides. Among all of these candidates, Ti-based oxides (TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) are particularly attractive. Firstly, taken TiO_2 as an example, several polymorphs including anatase, rutile, and $\text{TiO}_2\text{-B}$ has been extensively studied as anode for LIBs. Commonly, the intercalation/de-intercalation reaction between Li and TiO_2 can be described as

In fact, the value of x depends on the morphology, crystallographic orientation, polymorphs of TiO_2 . Typically, this electrochemical reaction takes place at 1.5 – 1.8 V vs. Li. The relatively high insertion potential makes the TiO_2 electrode fairly safe and ensures fewer reactions on the electrode/electrolyte interface. However, low electronic conductivity, which is a common phenomenon for metal oxides, and poor Li ion transport kinetics are two major drawbacks for TiO_2 as anodes. To achieve fast Li^+ insertion/extraction, TiO_2 polymorphs with varied nanostructures such as nanowires, nanoribbons, nanotubes, and nanosheets, has been fabricated and demonstrated enhanced Li storage properties.^[25, 43, 47]

Ternary titanium oxides, especially spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), have also been investigated comprehensively for Li storage through the intercalation/de-intercalation reactions. Generally, a formula unit of LTO can accommodate 3 mol of Li in the spinel structure (at approximately 1.5 V vs. Li^+/Li), yielding a 175 mAh g^{-1} theoretical capacity. Crucially, a negligible change of cubic lattice parameter is induced during Li cycling, making LTO a “zero-strain” material possessing remarkable cycling stability. Besides, the Li^+ diffusion is fairly high (around $1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 300 K), thereby achieving high Coulombic

efficiency at high rate. However, the low specific capacity compared to graphite and poor electronic conductivity of LTO strongly restricts its widespread utilization. Nowadays, by using nanotechnology, a variety of strategies has been developed to overcome these problems, including tailoring particle size, and coating with conductive materials, which vastly improved its reversibility and rate capability.^[8, 15, 48]

2.2.2 Anodes: Alloying/dealloying reaction

Figure 2.3 Gravimetric and volumetric capacities for selected anode elements. Reproduced with permission from reference ^[49].

Recently, a range of metallic or semi-metallic elements (e.g., Si, Ge, Sn, Sb, Al, Mg, and Bi) and various compounds have been demonstrated to possess an ability to alloy with lithium at a low potential ($V \leq 1$ V vs. Li). Figure 2.3 shows the gravimetric and volumetric capacities of selected anode elements.^[49] Representatively, Si and Sn, which could be lithiated up a stoichiometry of $\text{Li}_{4.4}\text{M}$, corresponding to a large theoretical capacities as high as 4200 and 933 mAh g⁻¹, respectively, are the main focus as Li alloying metals over the last two decades. Unfortunately, the huge volume variation during electrochemical lithiation/delithiation process, severely handicapped their practical

utilization as LIBs anodes. This phenomenon is deleterious to the long term cycling stability because it results in the active material experiencing cracking and subsequent pulverization leading to electrode disintegration and the rapid decline in capacity. Another issues concomitant with the Si anode is its limited electrical conductivity which hampers rapid lithiation.^[50, 51] To mitigate these obstacles, considerable effort has been focused on utilizing nanosized particles, nanostructured materials, and/or composite structures that incorporate active components within a rigid matrix.

2.2.2.1 *Sn-based binary oxides*

Sn-based binary oxides, including SnO and SnO₂, have drawn much attention as potential high-capacity anodes for LIBs. Take SnO₂ as example, the basic reaction mechanism is shown as below:^[15, 25]

The alloying/dealloying reaction endows SnO₂ with theoretical reversible capacity of ~ 782 mAh g⁻¹, equivalent to accommodate 4.4 Li per Sn. Generally, the cycling stability of Sn-based oxides is superior to metallic Sn, owing to the electrochemically formation of amorphous or nanosized Li₂O which acted as a matrix to inhibit the aggregation of Sn. Nevertheless, the Li cycling properties and the critical factors determining the reversibility of SnO₂ have been investigated by a lot of research groups. It was discovered that a reversible capacity of around 300 mAh g⁻¹ up to 25 cycles could be achieved at 37.2 mA g⁻¹ in the voltage range of 0.3 – 1.0 V. However, acute capacity fading has been observed when the cut-off voltage was increased to 1.3 V, highlighting the importance of controlling the cut-off voltage of Sn oxides.^[52] Therefore, it is crucial to control the cutoff voltage of Sn oxides. This improved cycling performance is attributed to the effective suppression of Sn particle coarsening that occurs primarily during the delithiation process,

from an intermetallic Li-Sn phase to Sn. Such restriction of delithiation is also accompanied by the decrease of energy density.

Nowadays, various strategies have been proposed to enhance the capacity retention of Sn oxides, and two of them are widely used. One effective way is to build novel SnO₂ nanoarchitecture, involving of 1D nanofibers/nanotubes/nanorods, 2D nanosheets, and 3D hierarchical structures. The other approach is to introduce electrochemical active/inactive elements or oxides, such as carbon and metal oxides, to buffer the fluctuations in volume during charge/discharge process. Although the preparation of nanostructured SnO₂ or composites are promising methods, there remain nontrivial challenges of scaling-up the elaborate configurations that give satisfactory Li cycling properties.

2.2.2.2 *Sn-based ternary oxides*

A variety of Sn-based ternary oxides (M_xSnO_y) with varying crystal structures have been investigated in the past. The lithium storage mechanism for these ternary oxides invariably entails the destruction of the ordered crystal structure accompanied by the generation of metal oxides (MO_y) or metal (M), and formation of nanosized Sn metal in amorphous Li₂O, and subsequently, by the reversible alloying of the Li⁺ into Sn metal. In this case, only metal oxides (MO or MO_y) are observed during initial discharge, where M is rare earth metal, alkaline earth, or alkali. Whereas the respective M nanoparticles is generated along with the formation of Li₂O, where M is Cd, Cu, Ni, Co, Zn, or Fe.

Recently, the group of Chowdari reported that Li cycling behavior of ASnO₃ (A = Ca, Sr, Ba, and Cd).^[35, 36, 53, 54] Best reversibility is noted for CaSnO₃. They found that the excellent cycling performance of CaSnO₃ is likely ascribed to the better buffering ability of electrochemically inactive CaO matrix, which is formed during first discharge. In addition, there are also some other reports about Li cycling performance of ASnO₃, A = Co, Mn, and Mg.^[55] However, it is hardly to synthesize such well-defined compounds, and the composites might mainly exist in the form of AO·SnO₂ or SnO₂ + A₂SnO₄. Although the reversible capacity up to 800 – 1200 mAh g⁻¹ has been obtained for A = Co in the range of 0 – 3.0 V^[56] and for A = Mn^[57] and Mg^[58] between 0 – 2.0 V, respectively, a severe capacity fading still can be noted for all cases.

A summary of selected Sn-based ternary oxides are shown in Table 2.1. Although it does not include all the research related to Sn-based anodes, it is sufficient to indicate that the starting crystal structures, morphology, particle size, play key role to control the electrochemical performance of Sn-based ternary oxides. According to the comparison in Table 2.1, all listed ASnO_3 present enhanced Li storage properties, especially operated in the voltage range of 0 – 1.0 V. Moreover, it is obvious that the electrochemical performance is critically influenced by substituting cation A. Although ASnO_3 with different structures has been fabricated and investigated as anode materials, the cyclability definitely does not reach the requirement for real use in LIBs. Therefore, continuing studies on ASnO_3 with improved electrochemical performance are still needed.

Table 2.1 Electrochemical performance of selected Sn-based ternary oxides (ASnO_3).

Formula	Morphology	Reversible Capacity/ N^{th} Cycle (mAh g^{-1})	Voltage Range (V)	Current Density
Mg_2SnO_4	Microparticle ^[58]	700/20 th	0.0 – 2.0	50 mA g^{-1}
CoSnO_3	Nanoparticle ^[56]	850/20 th	0.0 – 3.0	100 mA g^{-1}
CdSnO_3	Nanocube ^[53]	475/40 th	0.005 – 1.0	60 mA g^{-1}
CaSnO_3	Nanoparticle ^[35]	445/50 th	0.005 – 1.0	60 mA g^{-1}
	Nanoflower ^[59]	547/50 th	0.005 – 1.0	60 mA g^{-1}
	Nanotubes ^[60]	256/20 th	0.005 – 1.3	60 mA g^{-1}
SrSnO_3	Nanoparticle ^[54]	222/20 th	0.005 – 1.0	30 mA g^{-1}
BaSnO_3	Nanoparticle ^[54]	156/20 th	0.005 – 1.0	30 mA g^{-1}

2.2.3 Anodes: Conversion reaction

The dawn of the 21st century invigorates interest in a new concept of lithium storage mechanism in LIBs – so-called conversion reaction. Distinguishing from the intercalation-deintercalation and alloying-dealloying reaction, it refers to the reversible electrochemical reaction between lithium and interstitial-free active electrode materials, M_aX_b , where M

represents transition metal, X is anion.^[17, 61, 62] Although some transition metal sulphides, nitrides, fluorides, and phosphides have been found to react with Li by conversion reaction, transition metal oxides (TMOs), as one of the family of compound, deserves the most attention.

TMOs (M_xO_y , $M = \text{Ni, Co, Fe, Cu, Mn, etc.}$) with no interstitial sites for lithium intercalation/deintercalation undergo reversible reduction in the presence of Li ions based on the following equation^[15, 18]:

Figure 2.4 Schematic demonstration of the conversion reaction process. Reproduced with permission from reference ^[63].

Normally, the first discharge reaction causes destruction of crystal structure or amorphization of M_xO_y . This is followed by the generation of highly reactive metallic nanodomains embedded into the Li_2O matrix. The in-situ electrochemically formed Li_2O that is commonly considered as electrochemically inert, could participate in reactions during cycling. Moreover, a polymer-like film appears around metal nanograins in the

fully discharge state, which is supposed to deriving from the catalytic degradation of the solvents of electrolyte.^[63] and then it completely disappears when charged to 3.0 V.^[15] In the subsequently charging process, the re-generation of metal oxides is regarded as a consequence of decomposition of Li_2O . Overall, the conversion reaction associated with binary transition metal oxides can be vividly displayed in Figure 2.4.

In principle, TMOs are able to incorporate two or more Li per 3D metal in conversion reaction, thereby giving rise to significantly higher capacities and energy densities compared to graphite anodes. However, several fundamental obstacles, such as large volume variation during electrochemical cycling, poor Coulombic efficiency observed at the initial cycle, large voltage hysteresis, and low capacity retention, make these materials far from commercial implementation. Conceptually, reducing particle size or using nanocomposites are believed to be efficient approaches towards improve the electrochemical performance of TMOs anode. Since there exists a wealth of documentation on the progress of nanostructured TMOs as electrodes for LIBs in the scientific literature, this thesis will focus solely on the performance of nanosized cobalt oxides.

2.2.3.1 *Co-based binary oxides*

Co-based binary oxides such as Co_3O_4 and CoO are among the most explored high capacity LIB anode materials. Specifically for cobalt oxides, Co_3O_4 and CoO can, via conversion reaction, deliver theoretical capacities of up to 890 and 715 mAh g^{-1} ,^[64] respectively. Since Poizot et al. published their original work, CoO with various nanostructures, or in the form of composites with graphene/carbon, have been successfully demonstrated as anode materials for LIBs. Outstanding reversible capacities of between 750 – 1000 mAh g^{-1} have been recorded for CoO fabricated with different particle sizes and morphologies, as shown in Table 2.2.^[62, 65, 66] Besides, considering the kinetic limitation of CoO , very good rate capacity retention of around 400 – 600 mAh g^{-1} can be obtained, even at relatively high current rates from 0.5 – 2 C.^[67] Moreover, studies show that a polymeric gel layer of between 50 to 100 nm thickness forms on the surface of Co metal particles when discharged to 0 V, and disappears when charged to 3 V.

Significantly, it is found that this polymeric gel film is beneficial to the capacity retention of LIBs. Indeed, if the discharge voltage limit is raised from 0 to 0.4 V, capacity decay is obvious. Figure 2.5 confirms the existence of polymeric gel film^[68].

Figure 2.5 TEM images (bright field) of a CoO-based electrode (a) after its initial discharge to 0.02 V, (b) at 0.02 V after 10 cycles from 0.02 - 1.8 V, (c) at 1.8 V after 10 cycles from 0.02 - 1.8 V (d) after cycling and full reoxidization up till 3 V. Note the disappearance of the polymeric layer and the visible 30 Å thick inorganic layer on the fully-charged sample (d). Reproduced with permission from reference.^[68]

In spite of the early attention on CoO, far more interest has been attracted by Co₃O₄ recently, owing mainly to its higher theoretical capacity of approximately 890 mAh g⁻¹, and easier preparation compared with CoO.^[17] Up to now, a whole slew of techniques employed in nanotechnology such as decomposition of precursors, hydrothermal synthesis, coprecipitation method, and electrospinning synthesis,^[69] have been extensively used to prepare Co₃O₄ in the form of flowerlike,^[70] nanotubes,^[71] nanospheres,^[72] and thin films

on conductive substrates^[73, 74]. Meanwhile, the performance of resulting materials as anode for LIBs has been studied. It is found that the reversible capacity of Co₃O₄/graphene composite is much higher than that of pure Co₃O₄ nanostructures, as shown in Table 2.2.

In addition, the majority of the literatures report that the initial reversible capacities of nanostructured Co₃O₄ exceed its theoretical values. The observed extra capacity leads to various explanations, but the most common is the ‘polymeric layer’s’ reversible formation/decomposition during deep discharge and the presence of nano- or micropores leading to the storage of Li⁺ interfacially.^[15] Moreover, another obvious disadvantage for Co₃O₄ as anode is the large voltage hysteresis. For example, the average discharge plateau is in the range of 0.75 – 1.0 V vs. Li, in contrast the average charge plateau is between 1.5 and 2.0 V vs. Li.^[75]

Table 2.2 Electrochemical performance of selected Co-based binary oxides. 1C = 890 mAh g⁻¹.

Formula	Morphology	Reversible Capacity/N th Cycle (mAh g ⁻¹)	Voltage Range (V)	Current Density
CoO	Platelet ^[66]	800/100 th	0.01 – 3.0	100 mA g ⁻¹
	Nanoparticle ^[67]	850/100 th	0.01 – 3.0	1 C
	Film on Ni ^[65]	877/100 th	0.01 – 3.0	1 C
Co ₃ O ₄	Nanotube ^[71]	1220/20 th	0.01 – 3.6	50 mA g ⁻¹
	Flowerlike ^[70]	1226/350 th	0.0 – 3.0	0.5 C
	Nanosheet/Ni ^[74]	1058/30 th	0.02 – 3.0	0.2 C
Graphene/Co ₃ O ₄	Nanosphere ^[72]	700/200 th	0.01 – 3.0	1 A g ⁻¹

2.2.3.2 Co-based ternary oxides

Co-based ternary oxides with varying crystal structures, in particular spinel and CaFe₂O₄-type structures, have been rigorously investigated as anode materials for LIBs. Generally,

Table 2.3 Electrochemical performance of selected Co-based ternary oxides (ACo_2O_4) with different morphologies and counter ions A.

Formula	Morphology	Capacity/ N^{th} Cycle (mAh g^{-1})	Discharge Voltage	Charge Voltage	Current Density
CuCo_2O_4	Nanoparticle ^[76]	740/40 th	0.96 V	2.1 V	60 mA g^{-1}
CuCo_2O_4	Nanoparticle ^[77]	755/20 th	0.95 V	2.1 V	60 mA g^{-1}
$\text{CuCo}_2\text{O}_4/\text{rGO}$	Nanocube ^[78]	570/350 th	0.88 V	2.11 V	1 A g^{-1}
MgCo_2O_4	Needlelike ^[79]	102/50 th	1.1 V	2.0 V	60 mA g^{-1}
FeCo_2O_4	Microparticle ^[79]	747/50 th	0.9 V	1.75 V	60 mA g^{-1}
FeCo_2O_4	Nanoflake/Ni ^[80]	905/170 th	0.72/1.57 V	1.69/2.2 V	200 mA g^{-1}
FeCo_2O_4	Nanoparticle ^[81]	458/60 th	0.95 V	1.79 V	64 mA g^{-1}
MnCo_2O_4	Nanowire ^[82]	1194/50 th	0.84/1.65 V	1.56/2.25 V	100 mA g^{-1}
MnCo_2O_4	Core-shell ^[83]	900/60 th	0.85 V	2.27 V	100 mA g^{-1}
MnCo_2O_4	Microsphere ^[84]	722/25 th	0.86/1.15 V	1.49/1.98 V	200 mA g^{-1}
NiCo_2O_4	Microsphere ^[85]	1198/200 th	1.0 V	1.6/2.1 V	200 mA g^{-1}
NiCo_2O_4	Nanoflake ^[86]	884/100 th	1.17 V	2.16 V	500 mA g^{-1}
NiCo_2O_4	Nanobelt ^[7]	981/100 th	1.18 V	2.1 V	500 mA g^{-1}
$\text{NiCo}_2\text{O}_4/\text{C}$	Nanoparticle ^[87]	715/50 th	0.83 V	1.74/2.33 V	40 mA g^{-1}
$\text{NiCo}_2\text{O}_4/\text{rGO}$	Nanoplate ^[88]	816/70 th	0.9 V	1.6/2.2 V	100 mA g^{-1}
$\text{NiCo}_2\text{O}_4/\text{rGO}$	Nanosheet ^[89]	954/50 th	1.2 V	1.88/2.1 V	200 mA g^{-1}
$\text{NiCo}_2\text{O}_4/\text{Au}$	Nanotube ^[90]	732/200 th	0.94 V	1.67/2.19 V	100 mA g^{-1}

Co metal ions coupled with one or more ions (which can be electrochemically active or inactive) constitute the ternary oxide. The lithium storage mechanism refers to the electrochemically active (such as Ni or Mn) or inactive metal ions (such as Ca or Mg) forming metal or metal oxides by the conversion reaction. Large capacity and good reversible stability Co-based ternary oxides have been reported through the rational control of the crystal structure, particle size, morphology, and the active/inactive metal ions.

Next, some of the latest studies on Co-based ternary oxides (ACo_2O_4) have been summarized in Table 2.3. By comparing these results, it is found that the effect of the counter ion (A^{2+}) in ACo_2O_4 is distinctly felt in the working voltage and capacity retention. Meanwhile, the morphology also has profound effect on the electrochemical performance of ACo_2O_4 anodes. Besides, compounds with $\text{A} = \text{Ni}$ perform better than those with $\text{A} = \text{Cu}$, Mg , Mn , and Fe . Therefore, it may be concluded that Ni is a good “matrix” elements to enhance the battery performance of ACo_2O_4 . Nevertheless, it must be mentioned that the reversible capacity degradation still can be observed for almost all cases. Although, it is clear that the morphology is governed by the techniques used for synthesis, and that the counter ions fulfill a key part in deciding the Li cyclability of ACo_2O_4 , the reasons for the observed capacity fading and conversion reaction mechanism remain unclear and necessitate deeper research in the future.

2.3 Representative Ternary Oxides (AB_xO_y)

A variety of ternary oxides (AB_xO_y) with different crystal structures, including perovskite (ASnO_3), spinel (ACo_2O_4), brownmillerite, and so on, have been reported as anode for LIBs. Certain improvements in the cyclability of these materials have been achieved by tuning the morphology, the size of particles, and the nanoarchitecture. Generally, at least one electrochemically active metal element along with one or more other metal ions (active or inactive), constitute these novel structures. Due to the combination of two metal elements, they not only possess new physicochemical characteristic but also offer the possibility for various application. All of these endow them more competitive advantages than that of simple oxides.

Despite the desirable properties of ternary metal oxides, their commercial application in LIBs is still handicapped by some basic issues which have been discussed in section 2.2.2 and 2.2.3. Since the electrochemical properties of ternary oxides have been published in a wealth of literatures, some of the latest studies on ASnO_3 with perovskite structure and ACo_2O_4 with spinel structure are discussed in this section.

2.3.1 Perovskite structure (ABO_3)

Ternary metal oxides with perovskite structure (general formula ABO_3) have given rise to great interests in solid-state physics and chemistry, mainly because of their large variety of intriguing properties, which render them promising application in magnetic and electronic devices. Usually, the simple perovskite-type structure (Figure 2.5a) refers to a 3D framework, which is constructed by corner-sharing BO_6 octahedra with A cations in 12-fold-coordinated sites. The ideal ABO_3 structure (Figure 2.5b) is cubic, but distortions are often introduced. The most frequently seen distortion is tilting of the BO_6 octahedra, which mainly induced by the mismatch between the cavity and the sizes of the A-site cations.^[91-93] A-site cation with relatively large size often refers to alkaline metal, alkaline-earth metals and lanthanide ions, while B generally represents transition-metal ions. Other species such as ASnO_3 perovskite were also important. Clearly, the A-site is a key factor in tailoring the properties by modifying the size of perovskite structure and affecting the states of the B-site cations, mainly because of the chemical and physical properties of these oxides are largely dependent on the degree of tilting. So it opens up more possibilities for fabricating compounds with novel functional features by substituting A-site cations.

Figure 2.6 (a) Crystal structures of simple ABO_3 perovskite; (b) Ideal cubic ABO_3 perovskite structure. Reproduced with permission from reference ^[91].

Recently, ASnO_3 perovskites are receiving plenty of research interest as anodes for LIBs and Chowdari's group reported the introducing alkaline-earth metal elements ($\text{A} = \text{Ba}$, Sr , and Ca) in the structure of ASnO_3 . Taking CaSnO_3 as an example, the mechanism behind Li cycling encompasses the alloying-dealloying reaction of Sn-based oxides to yield CaO

as an inactive matrix during the first discharge. Enhanced electrochemical performance (capacity and cyclability) have been observed for CaSnO_3 . Although further research is needed to verify the detailed reaction mechanism during cycling process, these instances illustrate the diversity of strategies undertaken by researchers to develop and fabricate advanced electrode materials with desirable properties.

2.3.2 Spinel structure (AB_2O_4)

Figure 2.7 Crystal structures of AB_2O_4 spinel-type structure. The AO_4 tetrahedra are shown in blue, BO_6 octahedra in grey, and oxygen anions in red. Reproduced with permission from reference.^[94]

Ternary spinel oxides (AB_2O_4) are a large class of compounds and have been extensively studied in scientific fields including solid-state physics, optical science and electrochemistry. The ideal AB_2O_4 spinel structure is based on cubic close-packed oxygen with one eighth of the tetrahedral voids occupied by a divalent A cation, and one quarter of

the octahedral voids occupied by the trivalent B cation.^[94] While in an inverse spinel, the tetrahedral holes filled with B atoms and the octahedral holes filled with both A and B atoms. As the physical and chemical properties of these oxides is largely determined by cations on the A and B-sites, the various combinations on the cations sites bring in more chances to gain desirable properties.

AB₂O₄ spinel structure forms an important class of electrode materials for LIBs due to their 3D diffusion network. Depending on the choice of metal ions, the capacity and voltage plateaus of the corresponding spinel-based electrodes can be easily tuned and excellent Li cycling stability and reversibility can be obtained.^[95, 96] Since Co can exist in both divalent and trivalent states, Co-based spinel oxides with the formular ACo₂O₄ have been wide reported and their electrochemical performances are summarized in Table 2.3. Despite the attracting properties of ACo₂O₄, continuous capacity loss can be found in all cases upon long-term cycling, which rooted from the inefficient Li⁺ reaction route. Thus, fully understanding of their origins is urgent and necessary.

2.4 Importance of Nanoarchitected Materials

It is well established that the cyclability and reversibility of ternary metal oxides still could not satisfactory for commercial LIBs. The undesirable performance can be ascribed to the sluggish electronic/ionic transport, poor structural stability and massive structural reorganization that lead to the pulverization and fail to accommodate the fluctuations in volume during cycling. The tremendous progresses in nanotechnology have suggested that these issues can be well circumvented by making nanoarchitected electrode materials. In general, the intriguing advantages associated to nanostructured materials could greatly improve the electrochemical performance of LIBs. Specifically, nanomaterials usually possess large specific surface area, thus increasing electrochemical active sites in the electrode/electrolyte interfaces and leading to large capacity. Moreover, the reduced dimensions and particle size significantly short path way for electron/ions transportation, thereby enhancing the kinetics of lithium ions diffusion and resulting in higher rate capability. Furthermore, making electrode materials in nanosize could boost the structural

stability and better alleviate the volume expansion and contraction during cycling, therefore achieving excellent cycling stability.^[97]

Figure 2.8 Schematic illustration of a conventional electrospinning process. Reproduced with permission from reference ^[98].

Considering these appealing perspectives of nanostructuring, numerous ternary metal oxides with diverse nanoarchitectures, including nanofibers, nanotubes and nanosheets, have been prepared and used for advanced LIBs electrode materials. Nevertheless, some drawbacks of nanomaterials, including undesirable side reactions with electrolyte owing to the increased surface areas, large tendency to agglomerate because of the excess surface free energy, and low packing density leading to reduced volumetric energy density, could not be overlooked and serious limits its practical use in LIBs. Therefore, several strategies have been addressed to overcome the above mentioned shortcomings. One

policy is to engineer electrode materials into special dimensions (1D, 2D, and 3D) to lower the excess surface free energy. Particularly, to use as anodes in LIBs, 1D nanostructures need only a few points of contact to ensure efficient electron transport with the 3D network of the electrode, whereas nanoparticles may easily become electrically isolated as they expand and contact upon cycling. Besides, 1D nanostructures are more stable and suitable to overcome the aggregation of active materials and facile strain relaxation upon electrochemical cycling owing to the existence of many open space among interwoven 1D nanostructures, which would result in enhanced capacity and cycle life of LIBs.^[99, 100] Another way is to prepare highly organized hierarchical structures, where generally consist of secondly building blocks to form the whole structures. By using such unique structures, the as-prepared materials could take the advantages of both secondary superstructures and elegant hierarchical assemblies. In this regards, it is anticipated that desirable electrochemical performance would be achieved by introducing secondary nano-building block in 1D micro-/nano-structures. For example, the formation of ZnCo_2O_4 hollow nanotubes^[101] and hierarchical V_2O_5 nanofibers^[102, 103] by their respective secondly nano-building block has been illustrated and further confirm our hypothesis.

Targeted to synthesis 1D nanostructures with novel morphologies is now essential. Conventionally, the synthetic techniques for 1D structure such as advanced nanolithographic techniques and chemical synthesis based on templating method, are either sophisticated or involve multiple steps, which strongly restrict their large and rapid produce. Meanwhile, it is very difficult to well control the uniformity of the final product including size, shape, and chemical composition in large scale. In contrast, electrospinning, as an outstanding facile and versatile technique to fabricate well-organized 1D nanostructured materials with diameters ranging from a few hundred micrometers to several nanometers, exhibits noticeable advantages.^[104]

Figure 2.8 displays a schematic of a conventional electrospinning process, which consists of a spinneret, collector and high voltage power supply. Essentially, the technique relies on applying a strong electric field between the spinneret's tip (containing a melt or blended polymer solution) and a collector. As the electric field increases, a tremendous electrostatic force stretches the flowing fluid into a Taylor cone. At a critical voltage, the

repulsion from the electrostatic forces exceeds the polymer drop's surface tension, and then the fibrous structure is generated. In addition, the creation of fine electrospun samples need to careful adjust many operating parameters, including applied voltage, working distance, solution feed rate, and the viscosity or concentration of polymer solution. Thus, the morphologies and properties of final products can be easily controlled.

2.5 Summary

A detailed literature survey shows that ternary metal oxides (AB_xO_y) with two different metal cations, are emerging as prospective electrode materials for LIBs. By virtue of the complex chemical compositions and synergetic effects arising from both metal elements, exceptional electrochemical behavior could be obtained. Significantly, AB_xO_y systems provide more possibility and feasibility to tailor the working voltages, and capacity retention by rationally substituting cations. Moreover, engineering the nanostructure of AB_xO_y has also been illustrated as an efficient approach to optimize the battery performance of such systems. Nevertheless, facile and controllable synthesis of AB_xO_y with purposefully designed nanoarchitectures still remains great challenges. Besides the correlation of the different metal cations and nanostructures with lithium reaction route in AB_xO_y systems is not yet fully understood. Therefore, this thesis aims to fabricate various 1D AB_xO_y with novel morphologies using electrospinning method. Considering the influence of morphology modification and counter ion substitution, the electrochemical properties of AB_xO_y , especially $ASnO_3$ and ACo_2O_4 , would be investigated in depth. Then, the detailed reaction mechanism with lithium ions of AB_xO_y would also be discussed.

Chapter 3 Experimental Methodology

This section is a general overview of materials synthesis procedures, structural characterization, and electrochemical testing methodologies employed for nanostructured ternary metal oxides (AB_xO_y) as anode for LIBs.

3.1 Synthesis of 1D Ternary Metal Oxides (AB_xO_y)

As a remarkably versatile and facile method for producing diverse 1D nanostructured materials, electrospinning, has been widely used to develop 1D functional material for a variety of applications. Particularly, in order to obtain 1D metal oxides for LIBs, electrospinning is usually coupled with thermal treatment to make these metal oxides suitable for real use. By rationally tuning the selected experimental parameters, for instance the applied voltage, viscosity of precursor solution, and flowing rate during electrospinning process, as well as heating rate and temperature during thermal treatment, 1D metal oxides with controlled textures and novel morphologies, could be easily obtained.

3.1.1 Fabrication of $CaSnO_3$ nanofibers, nanotubes, and nanobelts

In a representative fabrication for the precursor solutions, firstly, 5 mL of absolute ethanol (Sigma Aldrich) was used to dissolve poly (vinylpyrrolidone) (PVP) with molecular weight of 360, 000 with vigorous stirring to form a 20 wt% PVP solution. Simultaneously, 5 mL of DMF was used to dissolve stoichiometric amounts of $SnCl_2 \cdot 2H_2O$ (Sigma Aldrich) and $Ca(NO_3)_2 \cdot 4H_2O$ (Sigma Aldrich) with vigorous stirring. The N,N-dimethylformamide (DMF) solution was then poured into the ethanol/PVP solution combined with vigorous stirring for 24 h at room temperature, forming a homogenous solution for the subsequent electrospinning (Figure 3.1).

A single-spinneret electrospinning setup was utilized to electrospin the precursor solution. The voltage used between the aluminium foil collector and the tip of the needle was 16kV; the distance between the collector and the needle was kept at 15cm; and the flow rate was

maintained at 1 mL h^{-1} (Figure 3.1). In the subsequent thermal treatment procedure, the as-spun fiber were sintered in air atmosphere with a ramping and cooling rate of $1 \text{ }^{\circ}\text{C min}^{-1}$ and maintained at $800 \text{ }^{\circ}\text{C}$ for 5 h, $700 \text{ }^{\circ}\text{C}$ for 5 h, and $600 \text{ }^{\circ}\text{C}$ for 24 h, respectively. The sample annealed at $800 \text{ }^{\circ}\text{C}$ for 5 h, $700 \text{ }^{\circ}\text{C}$ for 5 h, and $600 \text{ }^{\circ}\text{C}$ for 24 h, would be denoted as CSO-NF, CSO-NT, CSO-NB, respectively.

Figure 3.1 Schematic demonstration for the preparation procedure of CaSnO_3 nanotubes by electrospinning.

3.1.2 Fabrication of eggroll-like CaSnO_3 nanotubes, and nanorods

Initially, Polyacrylonitrile (PAN) was dissolved in 5 mL of DMF with vigorous stirring to yield a 20 wt% solution. Next, stoichiometric amounts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in another 5 mL of DMF. This DMF solution was then poured into the PAN/DMF solution while maintaining constant stirring for 24 h at room temperature to homogenize the solution. To investigate the influence of reactant concentrations on the morphologies of nanofibers, we prepared two types of precursor solutions which have different weight ratio of metallic precursor concentration over PAN concentration from 0.65 : 1 (CSO-NR) to 1.30 : 1 (CSO-NT) (The weight of PAN was kept constant). A high potential of 15 kV was utilized between the aluminum collector and needle tip. The distance from the collector to the needle tip was 14 cm, as shown in

Figure 3.2. Finally, sintering of the as-spun precursor fibres was conducted at 600 °C for 24 h in air.

Figure 3.2 Schematic demonstration for the preparation procedure of eggroll-like CaSnO_3 nanotubes by electrospinning.

3.1.3 Fabrication of 1D ASnO_3 (A = Sr and Ba) nanostructures

All chemical reagents were used as received. Similar experimental procedures with section 3.1.1 were applied to fabricate 1D SrSnO_3 (SSO-NF), BaSnO_3 (BSO-NF), nanostructures, simply substituting $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ by using corresponding $\text{Sr}(\text{NO}_3)_2$ (Sigma Aldrich), $\text{Ba}(\text{NO}_3)_2$ (Sigma Aldrich). In order to get the crystallized 1D ASnO_3 nanostructures, suitable thermal treatment was performed to obtain the single phase of ASnO_3 accordingly.

3.1.4 Fabrication of hierarchical CaCo_2O_4 hierarchical nanofibers and nanoplates

We used all chemical reagents as received. In a representative fabrication procedure, the viscous hybrid solution for electrospinning was prepared by dissolving 1 g PVP ($M_w=360,000 \text{ g mol}^{-1}$) in a mixed solution of 5 mL ethanol and 5 mL DMF and maintained constant stirring until thoroughly dissolve of PVP, and then, 1 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mmol $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were added into the mixed solution. After stirring for 24 h at room

temperature, a pink, viscous, clear solution was achieved. Next, the as-obtained precursor solution was drawn into a plastic syringe equipped with a stainless steel nozzle. The solution was then electrospun by applying a 16 kV DC voltage between the collector (aluminium foil) and the needle tip, at a flow rate of 1.0 mL h^{-1} , with a distance of 15 cm. Ultimately, sintering of the as-obtained precursor fibres was conducted at different temperatures with a ramping rate of 1°C min^{-1} in air atmosphere. The as-spun samples, annealed at 650°C and 750°C for 2 h, were labelled as hierarchical CCO-NF and CCO-NP, respectively.

3.1.5 Fabrication of NiCo_2O_4 nanofibers, nanotubes and nanobelts

We used all chemical reagents as received. In a representative preparation procedure, PVP ($M_w=360,000 \text{ g mol}^{-1}$) was dissolved in a mixed solvent comprising of 5 mL ethanol and 5 mL DMF, together with vigorous stirring to achieve a homogeneous solution of 10 wt% PVP. Stoichiometric amounts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a Co/Ni molar ratio of 2 : 1 were then added into the solution in order to achieve a homogenous pink and viscous solution, followed by continually stirring at room temperature for 24 h. In order to investigate the impacts of reactant concentrations on the morphologies of as-obtained fibrous structure, we prepared three different precursor solutions, which possess various weight ratio of PVP over metallic precursor (denoted as M) concentration. The PVP concentration hold constant. Samples were labeled as NiCo_2O_4 nanofibers (denoted as NCO-NF) with M : PVP = 0.44 : 1, NCO-NT with M : PVP = 0.61 : 1 and NiCo_2O_4 nanobelts (denoted as NCO-NB) with M : PVP = 0.87 : 1. Then, the precursor solution was transferred into a plastic syringe equipped with a stainless steel nozzle, which was connected to a high voltage power supply. The flow rate was set to 1 mL h^{-1} and a voltage of 12 kV was applied between the aluminum collector and the needle tip, separated by a 14 cm distance. The as-obtained solution was electrospun into nanofibres, which were then annealed at 450°C for 2 h in air.

3.2 Materials Characterizations

3.2.1 Powder x-ray diffraction (XRD)

The crystallite structures were determined through the use of a Shimadzu X-ray diffractometer (Cu-K α) with step scanning (40 kV, 0.5 s dwell time, 0.01°) over a 2 θ range between 10 and 80°. Rietveld refinement, carried out using the fundamental parameters peak shape profile contained within the software TOPAS, was then used to analyse the x-ray diffraction patterns.^[105]

3.2.2 Thin film x-ray diffraction (XRD)

The crystalline components of electrode were identified by using thin film XRD (Shimadzu, Cu K α radiation, with step scanning over a 2 θ range between 10 and 80°).

3.2.3 Field emission scanning electron microscope (FESEM)

The morphologies of the as-prepared samples were studied using FESEM (JEOL JSM-7600F) a 5 kV acceleration voltage and working distance of around 7 cm. Prior to capturing the images, the sample should be stabilized using carbon tapes and then pasted onto the stainless steel holder. To avoid the charging effect, the as-prepared samples were usually coated with around 10 – 15 nm of platinum using a sputtering coater (JEOL JFC-1600).

3.2.4 Transmission electron microscope (TEM)

Morphological and crystallographic information were characterized by TEM microscope (JEOL 2100F), which was performed at 200 kV. By analyzing the image and the corresponding diffraction pattern, some valuable information including grain sizes, the orientation of nanostructures, and the appearance of superstructures, can be identified. With the aid of the energy dispersive X-ray attachment, qualitative and quantitative measurements for the concentration and elemental compositions can be achieved by utilizing the characteristic X-ray spectra.^[106]

3.2.5 Energy dispersive x-ray spectroscopy (EDX)

Elemental composition of the samples was studied using the EDX attachment of the FESEM (Section 3.1.3), while elemental mapping was performed using the EDX equipped on the TEM (Section 3.1.4). For the sample using EDX attached on FESEM, the working distance of 15 cm was used. To avoid charging of sample and gain appropriate spectrum, the accelerating voltage of 15 kV was selected. EDX, as a non-destructive technique, could qualitative, semi-quantitative, quantitative determine the composition of samples. In addition, the spatial distribution of elements could also be obtained by using mapping.

3.2.6 X-ray photoelectron spectroscopy (XPS)

XPS is a surface-sensitive and quantitative spectroscopic technique which gives critical information on the electronic state, chemical state, and elemental composition of the elements. The XPS spectrum is obtained by using a beam of x-rays to irradiate the material. By analyzing the number of electrons which escape from the top surface (around 10 nm) and measuring the kinetic energy, a variety of information on the material's surface chemistry can be deduced. Being a non-destructive characterization tool, XPS can also be used to determine a metal ion's valency even within complex compounds. The characteristic binding energy peaks of ions, either metal or non-metal, are correlated to their crystal lattice coordination and oxidation state. Therefore, XPS, as a powerful tool, has been extensively applied to analyze functional materials for energy-related applications.^[107]

Herein, the surface chemical states of as-prepared samples are characterized by XPS, using a Kratos AXIS Ultra spectrometer with the monochromatic Al K α x-ray. Survey scans were performed from 0 to 1200 eV, which was calibrated by referring to adventitious carbon at 284.8 eV. Peak fitting and deconvolution were conducted with XPS surface analysis software by applying a Voigt function with 30% Lorentzian character and a Shirley background.

3.2.7 Fourier transform infrared spectroscopy (FTIR)

FTIR is an effective analytical tool to elucidate the functional groups and covalent bonding information of a molecule. By detecting the infrared absorption and spectrum of materials, FTIR gives quantitative and qualitative information of organic and inorganic materials. Thus, this instrument was used to analyze the transformation of functional group of electrospun products before and after thermal treatment at different conditions. In order to obtain the FTIR spectrum, the sample was incorporated in translucent pellets of KBr and placed in a Perkin-Elmer Spectrum GX FTIR and subjected to 16 scans at a 2 cm^{-1} resolution over the range of 4000 – 400 cm^{-1} .

3.2.8 Nitrogen adsorption/desorption isotherm

The nitrogen adsorption/desorption isotherms were recorded by applying Micromeritics, ASAP 2020 at 77 K. Prior to measurement, the samples were degassed at 393 K under nitrogen flow for 2 – 4 h. According to the obtained nitrogen adsorption/desorption isotherms, the Brunauer-Emmett-Teller (BET) method was applied to ascertain the surface area of the electrospun products. A Barrett-Joyner-Halenda (BJH) analysis was then conducted to determine the pore size distributions.

3.2.9 Thermogravimetric analysis (TGA)

Commonly, TGA is used to identify the mass loss or gain owing to decomposition, oxidation, or loss of volatiles. It provides information about the organic and inorganic content of the sample, especially useful in predicting the material's structure. Herein, TGA was applied on electrospun precursor nanofibers to determine the temperature and weight change of decomposition reaction by using TA instrument Q500 apparatus. The samples were heated to the target temperature from room temperature, at a ramping rate of 5 $^{\circ}\text{C min}^{-1}$ under air flow.

3.3 Electrochemical Studies

3.3.1 Coin cell fabrication

Fabrication of the electrodes for electrochemical investigations was achieved through the mixing of Super P carbon (Timcal), a polyvinylidene fluoride (PVDF) binder (Kynar 2801) and active materials in a weight ratios of 20 : 20 : 60, 15 : 15 : 70 and 10 : 10 : 80 in N-methylpyrrolidinone (NMP, Sigma Aldrich) to achieve a homogenous, viscous slurry. An approximately 21 μm thickness of this slurry was then coated by doctor blade on an etched copper foil, combined with drying in an vacuum oven for 12 h at 80 $^{\circ}\text{C}$ in air. Twin rollers were used to press the samples to enable close contact with the current collector. Then, the sample was cut into 16 mm diameter discs (with active material of $\sim 3 - 4$ mg). Because of the intrinsic electronic conductive behaviour of the AB_xO_y electrode, we optimized the electrode composition containing the binder, super P carbon, and active material in a weight ratio 20 : 20 : 60 to realize high performance composition. The lithium storage properties of as-prepared ternary metal oxides (AB_xO_y) were evaluated by using a CR 2016 coin cell assembled in a glovebox filled with argon. The metallic lithium was used as counter electrode, the separator used was Celgard 2400, and the electrolyte employed was 1 M LiPF_6 in diethylene carbonate/ethylene carbonate (DEC : EC = 1 : 1)

3.3.2 Galvanostatic charge/discharge (GCD)

According to the convention of the LIBs research community, all the potential/working voltages mentioned in this thesis use lithium metal as reference and counter electrode (Li^+/Li_0 , E_0 with respect to H^+/H_0 (SHE) = - 3.04 V), which were investigated in a half-cell configuration using a two electrode coin cell setup. Galvanostatic discharge/charge cycling was conducted at room temperature by using a multichannel battery testing system (Neware) in the potential range from 0.005 to 3.0 V, using a constant current mode. In this thesis, it is to be note that the discharge profile refers to the lithium insertion behavior, whereas the lithium extraction process is expressed by charge profile.

3.3.3 Cyclic voltammetry (CV)

Cyclic Voltammetry (CV) tests were performed using a Solartron 1470E within a 0.005 – 3.0 V voltage range at room temperature under a constant scanning rate. Different scanning rates were selected depending on the respective purposes. In this thesis, cathodic peaks represent the occurrence of the reduction reaction (lithium insertion process) using lithium metal as reference electrode, while anodic peaks indicate the presence of the oxidation reaction (lithium extraction behavior).

3.3.4 Impedance spectroscopy (EIS)

EIS has been demonstrated as one of the most useful and important tools for evaluating the electrochemical processes and investigating the kinetics of the electrochemical Li insertion/extraction behavior. Generally, EIS realizes the qualitative comparisons of the charge transfer process and diffusion controlled reactions before or after lithium insertion process. By altering the applied frequency, the electrical and ionic resistance of the sample can be obtained.

In this thesis, EIS was carried out on equilibrated cell before cycling and cycled electrodes at different voltage and then equilibrated for 2 – 3 h. Next, EIS was measured by using 10 mV bias voltages from a 100 kHz to 0.1 Hz frequency range at room temperature. The data were recorded as the Nyquist plots $-Z''$ vs. Z' , which could be evaluated by utilizing software, specifically, Zview and Zplot (version 2.2, Scribner Associates Inc., U.S.A.).

3.3.5 *Ex-situ* electrode preparation

With regard to *ex-situ* XRD characterization, duplicated cells were charged and discharged to various voltages, and relaxed for around 3 h at that voltage. Subsequently, the electrodes were retrieved by dismantling the coin cells and washed using DEC to eliminate the organic electrolyte. Next, the electrodes were left in a glovebox for at least 2 days until dry. Prior to taking measurement, the electrodes were sealed using parafilm “M” to ensure the minimal contact with air during transportation.

3.3.6 Lithium diffusion coefficient by Randles-Sevcik equation

The lithium diffusion coefficient could be calculated from the Randles-Sevcik equation, which describes the influence that the scan rate has on the peak current in CV. Generally, the peak current of diffusion-controlled reversible electrochemical reaction follows the below equation:

$$I_p = 2.687 \times 10^5 n^{3/2} \nu^{1/2} D_{Li}^{1/2} A C_{Li} \quad (3.1)$$

Where I_p represents the peak current, n refers to the number of electrons per reactive species, ν denotes the scan rate, D_{Li} is the Li^+ diffusion coefficient, A refers to the surface area of working electrode and C_{Li} is the concentration of Li^+ in electrolyte.^[108]

To determine the D_{Li} values, CV measurements were conducted on ternary metal oxides (AB_xO_y)-based half-cell at various scan rates. The peak currents of the main oxidation peaks were selected to perform the calculations.

Chapter 4 Electrospun 1D ASnO_3 (A = Ca, Sr, Ba) Nanostructures with High Lithium Storage Properties

4.1 Introduction

As an important power source, Lithium-ion batteries (LIBs), is becoming increasingly pervasive in our daily life. Along with the rapid evolution of nanotechnologies, high energy LIBs that hold great potentials for application in electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs), become the research focus.^[2, 18] However, to achieve such applications, LIBs with high power and energy density, large capacity, excellent cycling stability, good safety, low toxicity, and cost-effective are required. In order to realize high power/energy density, novel electrodes are needed to substitute currently applied anodes (graphite with theoretical capacity only 372 mAh g^{-1}). Up to now, a variety of transition metal oxides (TMOs) are being widely investigated as promising candidates as anode for LIBs mainly because of their large theoretical capacity (around $400\text{--}900 \text{ mAh g}^{-1}$).^[17]

In all kinds of TMOs, binary and ternary oxides, especially Sn-based composites, enjoy a place of pride due to their large theoretical capacity (782 mAh g^{-1}) that as high as twice times capacity of commercial used graphite anode and low operating potential versus Li.^[109-114] Unfortunately, the poor capacity retention upon long-term cycling greatly hampers their real application of Sn-based oxides in LIBs. The uneven and large volume changes (almost up to 300%) of Sn-based oxides which occur during lithium insertion and extraction processes, could account for the above problems, then resulting in the pulverization and cracking of the electrode and ultimately leading to loss of contact between individual active materials.^[58, 115] One generally accepted approach to alleviate these problems is to design various Sn-based nanostructures with interior hollow structures and enlarged specific surface areas, which could enable fast lithium ions and electron transportation, thereby improving the capacity retention and rate capability. This is because the void space would not only significantly alleviate the stress relaxation that caused by high volume variation but also shorten the pathway of lithium ions

diffusion.^[116-123] In addition to this strategy, another commonly used way is to build delicate Sn-based metal oxides in a confining matrix, in which the homogeneous electrochemical active or inactive matrix, such as carbonaceous and MO_x where $M = \text{Ca}, \text{Mn}, \text{Zn}, \text{Sr}, \text{Co}$ etc. may effectively buffer the volume changes and prevent the aggregation of active materials during charge-discharge process, thus prolonging the cycling life of the electrodes.^[35, 60, 124-129] More importantly, the detailed structure, sizes, and morphologies of Sn-based oxides also have significantly influence on the lithium storage properties.

Therefore, considerable attention has been paid to various kinds of stannates including M_2SnO_4 ($M = \text{Zn}, \text{Mg}, \text{Mn}, \text{Co}, \text{Ca}$),^[124, 127, 128, 130, 131] ASnO_3 ($A = \text{Cd}, \text{Sr}, \text{Co}, \text{Ba}, \text{Ca}$)^[35, 36, 53, 54, 56, 57, 59, 132, 133] and $\text{K}(\text{M}, \text{Sn})_8\text{O}_{16}$ ($M = \text{Fe}, \text{Mg}, \text{Mn}, \text{Li}$) because of their large lithium storage capacity and improved cycling performance, which originate from the generation of electrochemical active or inactive MO_x matrix taking place in the initial discharge process. Currently, research interests mainly focus on M_2SnO_4 (Zn_2SnO_4 , Mn_2SnO_4 , Co_2SnO_4) and ASnO_3 based anodes (CaSnO_3 , CoSnO_3 , SrSnO_3). With all this in mind, alkali earth elements such as Ca , Sr , and Ba , as electrochemically inactive matrix were considered as a good candidate among the variety of matrix elements which have been investigated in conjunction with Sn oxides. Take CaSnO_3 as example, although various CaSnO_3 with different morphologies have been synthesized by different techniques such as solid-state, hydrothermal, and sol-gel methods, all of these CaSnO_3 electrodes are evaluated in a relatively narrow potential range, including 0.005 – 1.0 V and 0.005 – 1.3 V. Importantly, it is well-accepted that the electrochemical performance of Sn-based ternary composites are significantly influenced by the operating voltage. So there still exists a scope to improve the electrochemical properties of ASnO_3 electrode in a larger and wider potential range. Since elaborately morphology modification could remarkably enhance the electrochemical performance, it is critical to prepare unique ASnO_3 nanostructures through effective and facile preparation strategy to enhance electrochemical properties.

It is well-accepted that electrochemical properties of electrode materials strongly depend on a variety of factors such as preparation condition, morphology, particle size, and measurement techniques, and others.^[20, 102, 134, 135] In many previous reports, 1D

nanostructure, including nanofibers, nanowires, nanotubes, and nanobelts, have been identified as one of the most important functional nanoarchitectures for potential use in many fields. When used as LIBs anode, 1D nanostructured electrodes possess a variety of advantages because of extremely reduced pathway for mass transport, effectively accommodating the structure strain, ensuring facile Li^+ ion diffusion, increased specific surface areas, and better electrolyte penetration, which definitely lead to enhanced capacity retention and cycle stability of LIBs.^[136, 137] Thus, various 1D nanostructure fabrication techniques have been applied. In these techniques, as an extraordinary simple and efficient strategy for synthesizing well-organized 1D configuration with rationally controlled diameters, electrospinning, are now intensively utilized to prepare various electrodes for LIBs. In other words, 1D Sn-based ternary oxide with various nanostructures could be obtained by adjusting the electrospinning parameters.

Up to date, it is found that there is few report on the preparation of 1D ASnO_3 nanostructures using electrospinning technique and their application as electrode for LIBs. In this work, we propose a new type CaSnO_3 1D nanostructure including CaSnO_3 nanotubes (denoted as CSO-NT), eggroll-like CSO-NT, and ASnO_3 ($\text{A} = \text{Sr}, \text{Ba}$) 1D nanostructures as high-performance anodes for LIBs, in which two design principles are well incorporated. The superior CaSnO_3 architecture, which benefits of 1D hollow interior structure and generated inactive matrix during first discharge, is anticipated to manifest remarkable electrochemical performance as anode for LIBs. The strategy for synthesizing ASnO_3 ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) 1D nanostructures is based on an efficient electrospinning technique combined with thermal treatment in air. The impact of sintering temperature and metal precursor concentration on the electrical properties, morphology evolution, and phase transition of ASnO_3 has been studied in detail. More significantly, the formation mechanism of CaSnO_3 1D nanostructures is proposed. In addition, the effect of A-site substitution in ASnO_3 ($\text{A} = \text{Ba}, \text{Sr}, \text{and Ca}$) on the battery performance has also been systematically discussed.

4.2 CaSnO_3 Nanotubes (CSO-NT)[†]

[†] Reproduced in part and modified from [L. L. Li, S. J. Peng, M. Srinivasan, et. al. *ACS Applied Materials & Interfaces*, 2012, 4, 6005-6012] by permission from *The American Chemical Society*. Copyright 2012.

Herein, we firstly prepare CaSnO_3 1D nanostructures using a simple single spinneret electrospinning strategy combined with thermal treatment in air. By rationally adjusting sintering temperature, a series of CaSnO_3 with different morphologies, including CaSnO_3 nanofibers (CSO-NF), CaSnO_3 nanotubes (CSO-NT), and ruptured CaSnO_3 nanobelts (CSO-NB), can be obtained.

4.2.1 Structure and morphology analysis

Figure 4.1 XRD patterns of CaSnO_3 sintered at different times and various temperatures.

Firstly, XRD analysis was conducted to study the phase purity, composition, and crystalline structure of the electrospun products sintered at specific temperatures, as shown in Figure 4.1. When the thermal treatment condition is 600 °C for 5 h, all the peaks belonged to the as-prepared sample could be assigned to SnO_2 phase (JCPDS 41–1445). While CaSnO_3 phase can not be identified under this condition, suggesting that Ca^{2+} is

hardly embedded into the lattice at such condition. Further increasing sintering duration to 24 h (at 600 °C) leads to the generation of pure CaSnO_3 with perovskite structure (JCPDS 31–0312, SG: P212121 (19), $a_0 = 5.6615 \text{ \AA}$, $b_0 = 7.8825 \text{ \AA}$, $c_0 = 5.5162 \text{ \AA}$).^[138] Any other impurity phase could not be observed, demonstrating the formation of single-phase CaSnO_3 . As anticipated, increasing the sintering temperature to 700 °C and 800 °C for 5 h, respectively, the as-prepared final products are CaSnO_3 with high phase purity and the intensity of all diffraction peaks increase accompanied by the increase of sintering temperature due to the improvement in crystallinity.

Figure 4.2 TGA curve of the as-spun precursor for CaSnO_3 nanotubes measured from room temperature to 900 °C in air.

The thermogravimetric analysis also supported the XRD results (Figure 4.2). It can be observed that before 200 °C, the weight loss of around 11% correspond to the crystal water in the metallic precursor, absorbed moisture, and volatile solvent. The decomposition of metallic precursor and the removal of PVP could be related to the large weight loss of around 67%. After 600 °C, there is no more weight loss, suggesting that organic species have been completely removed. Therefore, the sintering temperature of 600 °C, 700 °C, 800 °C was employed.

Figure 4.3 FT-IR spectra of (a) PVP; (b) as-spun precursor nanofibers; (c) CaSnO_3 products sintered at 700 °C for 5 h.

Figure 4.3 presents the FT-IR spectra of CaSnO_3 products, as-spun precursor nanofibers and the PVP polymer sintered at 700 °C for 5 h, respectively. The prominent broad absorption band centred at 3436 cm^{-1} could be assigned to the $-\text{OH}$ group symmetric stretching vibration due to the existence of ethanol solvent and adsorbed moisture. The peak observed at 2930 cm^{-1} and 1427 cm^{-1} could be ascribed to the bending and symmetric stretching of C-H group because of the existence of PVP polymer. The representative peaks located at around 1661 cm^{-1} could be interpreted as C=O functional group of PVP polymer.^[139] The peaks centred at 1288 cm^{-1} correspond to the absorption of tertiary amine group of PVP polymer. The as-spun precursor nanofibers possess similar peaks with PVP polymer apart from the new peaks that presented at $\sim 1384\text{ cm}^{-1}$, suggesting the appearance of trapped ethanol solvent. After sintered at 700 °C for 5 h, the peaks belonged to organic components disappears completely because of the decomposition of PVP, meanwhile the new peak located at around 643 cm^{-1} appears which is related to Sn-O-Sn symmetric and antisymmetric vibrations,^[140] demonstrating

the beginning of crystallization. Hence, the FT-IR results further confirm the formation of single phase CaSnO_3 nanocrystallites and the thoroughly removal of PVP polymer after thermal treatment.

Figure 4.4 XPS spectra of CaSnO_3 sintered at 700 °C for 5 h (a) survey scan; (b) high resolution Ca 2p scan; (c) high resolution Sn 3d scan; (d) high resolution O 1s scan.

Figure 4.4 shows XPS pattern of CaSnO_3 sintered at 700 °C for 5 h, which gives the information of the surface valence states and chemical composition of the as-obtained sample. Generally, XPS is extensively used to characterize electrode materials and other metal oxides to investigate the valence states of the non-metal or metal ions. According to the survey XPS spectrum in Figure 4.4a, it can be clearly seen the existence of O, Sn and Ca elements accompanied by adventitious carbon. Figure 4.4b exhibits that the doublet

peaks with binding energy (BE) at 349.8 eV and 346.3 eV can be related to Ca $2p_{1/2}$ and $2p_{3/2}$ spin-orbit splitting peaks with a BE separation of around 3.5 eV, respectively. This BE values observed in this work is consistent with previously reported.^[54] Figure 4.4c presents the Sn 3d spectrum with BEs at 494.4 and 486.0 eV, corresponding to $3d_{3/2}$ and $3d_{5/2}$, respectively. The BE separation of Sn 3d spectra is around 8.4 eV. These results obviously demonstrate that Sn and Ca possess +4 and +2 oxidation state in CaSnO_3 , respectively. Figure 4.4d gives O1s spectra with the BE at 531.5 and 529.6 eV, which correspond to the adsorbed oxygen and lattice oxygen. Moreover, the atom ration of O : Sn : Ca is around 60.49% : 19.93% : 19.58% on the basis of the quantification of XPS spectra, matching well with the stoichiometry of CaSnO_3 . Furthermore, the XPS investigation is also in agreement with the above XRD and FT-IR observations, further proving the formation of single-phase CaSnO_3 .

To deep understand the microstructures and morphologies of as-spun 1D nanostructures sintered at various temperatures ranging from 600 °C to 800 °C, FESEM and HRTEM were performed, as shown in Figure 4.5, 4.6, and 4.7. It should be noted that the diameter and morphology of 1D nanomaterials could be changed by rationally adjusting the electrospinning parameters and will play a critical part in determining the properties of the final products. By tuning the electrospun parameters, including the feeding rate of electrospun precursor solution, the weight ratio of inorganic salt and the applied voltage, we can obtain continuous nanofibers, which possess uniform diameter of around 250 nm and smooth surface, as shown in Figure 4.5a. Besides, the as-spun precursor nanofiber could form a polymer film on the surface of aluminum substrate, which can be easily collected (inset in Figure 4.5a). To gain single-phase CaSnO_3 1D nanomaterials, PVP was eliminated by sintering in a high temperature in air. Obviously, we can see that the morphology of the as-spun product changed from nanofibers to nanotubes after sintered at 700 °C for 5 h. The tube-like morphology is clearly presented in Figure 4.5b and c. Moreover, due to the generation of single phase CaSnO_3 and the decomposition of PVP, the surface roughness of CSO-NT increase and the average diameter of CSO-NT decrease to around ~180 nm. Furthermore, the EDX analysis was carried out to examine the elemental composition of CSO-NT. Figure 4.5d indicates that the strong signals, which can be indexed to O, Sn and Ca, can be identified, further suggesting the generation of

CSO 1D nanostructure. Thus, all of these results verify the generation of CSO-NT nanocrystalline, agreeing well with the XRD and SEM observation.

Figure 4.5 FESEM images of (a) as-spun precursor nanofibers; (b, c) sintered CaSnO_3 at 700 °C for 5 h; (d) EDX spectra of sintered CaSnO_3 at 700 °C for 5 h. The photo of the electrospun precursor film is inset in (a).

Next, TEM and HRTEM were further used to characterize the crystalline structures of CSO-NT. The tube-like structure of CSO-NT, which is constructed by numerous nanocrystallites with individual crystallite size of around 10 nm, can be clearly seen in Figure 4.6a and b. In addition, the middle and edge part of nanotubes exhibit different colour, corresponding to interior hollow structure (~ 90 nm) and the wall (~ 40 nm), respectively. Figure 4.6c shows the HRTEM images of CSO-NT. It can be observed that well-defined lattice fringes with interplanar distance of around 0.281 nm could be assigned to the (121) plane of CaSnO_3 . Figure 4.6d exhibits the SAED pattern of CSO-NT with well-defined diffraction rings, illustrating the polycrystalline feature of CSO-NT. EDX elemental mapping further identify the composition distribution of CSO-NT. The uniform distribution of O, Sn and Ca can be seen from Figure 4.6f – h and meanwhile the same tube-like shape can be clearly observed (Figure 4.6e). These results further confirm

the tube-like morphology as well.

Figure 4.6 (a – c) TEM and HRTEM images; (d) the SAED pattern; and (e – h) TEM image and the EDX elemental mappings of O, Sn, and Ca (as labelled) for sintered CaSnO_3 at 700 °C for 5 h.

It is found that both the size and morphology of the final product are dramatically influenced by the sintering temperature in present synthesis. For instance, after calcinated at 600 °C for 24 h, the conventional electrospun fibrous morphology of CSO-NF could be perfectly maintained (Figure 4.7a, b). The diameter of CSO-NF is around $\sim 150 \text{ nm}$, which is much smaller compared to that of CSO-NT. Figure 4.7c reveal the TEM images of CSO-NF sintered at 600 °C for 24 h. Clearly, the interconnected fibrous morphology consists of numerous nanocrystals, which agrees well with the SEM observations. The

HRTEM image (inset in Figure 4.7c) proves the presence of CaSnO_3 phase. Nevertheless, the 1D CaSnO_3 nanoarchitectures collapse at 800 °C for 5 h and finally exhibit ruptured nanobelts structure, as shown in Figure 4.7d and e. Similarly, the TEM image in Figure 4.7f further confirms the ruptured nanobelts morphology of CSO-NB which is sintered at 800 °C for 5 h. Significantly, Figure 4.7f shows the nanoparticles around the nanobelts, indicating the collapse of nanobelts. Again, the HRTEM image inset in Figure 4.7f supports the formation of CaSnO_3 phase.

Figure 4.7 FESEM images with different magnification of sintered CaSnO_3 at (a, b) 600 °C for 24 h; (d, e) 800 °C for 5 h. TEM and HRTEM images (inset) of sintered CaSnO_3 at (c) 600 °C for 24 h; (f) 800 °C for 5 h.

BET analysis was carried out to study the porosity of the 1D CaSnO_3 nanostructures. Figure 4.8 depicts the N_2 adsorption/desorption isotherm and the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curves of the as-prepared samples. All of the isotherm correspond to the type IV isotherm with H3 hysteresis loops in the pressure range of around 0.6 – 1.0, indicating the existence of mesoporous structures. CSO-NT with BET surface area of around $33.99 \text{ m}^2 \text{ g}^{-1}$, can be identified, which is larger than that of CSO-NF ($10.87 \text{ m}^2 \text{ g}^{-1}$) and ruptured CSO-NB ($18.56 \text{ m}^2 \text{ g}^{-1}$). Besides, the pore size distributions (Figure 4.8b) suggest that the size of most of the pores is less than 50 nm, which is consistent with the TEM results. Remarkably, it is well-known that porous

features and the relatively high specific surface area are crucial to facilitate the electron and Li^+ transportation in the electrode/electrolyte interface and ensure more active sites for fast electrochemical reactions, leading to greatly improved lithium storage properties.

Figure 4.8 (a) N_2 adsorption/desorption isotherms; (b) corresponding pore-size distribution of CSO-NF, CSO-NT, ruptured CSO-NB.

4.2.2 Formation mechanism of CSO-NT

It is well-accepted that the sintering temperature plays a critical role to determine the morphologies of electrospun products such as nanofibers or nanotubes. The high sintering temperature is suitable to create spaces between neighbouring nanocrystals. However, the specific temperature should be kept between a proper range, too low or too high would affect the morphology of as-prepared samples. The formation process of electrospun CSO-NT is identical to that of ceramic powders during spray drying process.^[141] During thermal treatment, with the increase of sintering temperature, PVP will be gradually removed. Various gases are generated including gaseous solvent molecules, carbon oxides, and other gases because of the solvent evaporation and decomposition of PVP. Therefore, these results in the difference in the pressure between the external and internal of the nanofibers and the swelling of the electrospun nanofiber takes place. In addition, the primary nanocrystals of CaSnO_3 initially generated in both inner and outside sites of the precursor fibers. Many factors including the diffusion rate of gases, CaSnO_3 nanoparticles, the evaporating rate, and composition of fibers, determined

Figure 4.9 Schematic demonstration for the formation process of CSO-NF, CSO-NT, ruptured CSO-NB.

the formation of hollow structures. When the temperature is relatively low (600 °C), the reaction speed in the inner is smaller compared to that of the outside because of thermal non-equilibrium, while the difference of concentration gradient in the inner sites and the outside are so small and the pressure in the inside is smaller than that of outside of the fiber due to the evaporating speed of gases inside the fibers smaller than the diffusion speed of gases through the fiber surface, ultimately resulting in the shrinkage of the outside nanocrystals and generation of CSO-NF. While further increasing the sintering temperature to 700 °C, both the gases evaporation rate and the reaction rate in the inner sites fast raised. Herein, the relatively large strain strength promotes the expansion of the inner nanocrystals and meanwhile, the pressure in the outside of the fiber is smaller

compared to that of inside, thus leading to the generation of CSO-NT, as shown in the Figure 4.9. Finally, when the sintering temperature is further raised to 800°C , the ruptured nanobelts structure formed due to the collapse of CSO nanotubes.

4.2.3 Electrochemical studies

Figure 4.10 Cycling performance of CSO-NT with active material, PVDF binder and super P carbon in various weight ratios at the current density of 60 mA g^{-1} in the voltage range of $0.005 - 3.0 \text{ V}$.

Firstly, we evaluated how the morphologies of CaSnO_3 1D nanostructures affect the battery performance. It is well-accepted that both the current rate and voltage window strongly influence the electrochemical performance of LIBs.^[142, 143] The relatively broad potential window provides harsher condition for the lithium ions extraction/insertion. Hence, a broad voltage range of $\sim 0.005 - 3.0 \text{ V}$ was used in this work. Besides, due to the intrinsic electronic conductivity of CaSnO_3 electrode, it can be observed that the electrode with the highest carbon content exhibits the best cycling performance (Figure 4.10). Therefore, in the following experiments, in order to gain high electrochemical performance, the electrode composition was optimized to be $60 : 20 : 20$ (the weight ratio

of active material, binder and super P carbon).

Figure 4.11 (a) Cycling stability of the electrospun 1D CaSnO_3 nanostructures (at current density = 60 mA g^{-1}); (b) rate properties of 1D CaSnO_3 nanostructures at different current density.

Figure 4.11a displays the cyclability of CaSnO_3 1D nanostructures sintered at various conditions. As compared to the two counterparts, CSO-NT exhibits improved capacity retention. Specifically, CSO-NT possess a higher capacity retention of around 565 mAh g^{-1} even after 50 cycles, compared to that of 401 mAh g^{-1} for CSO-NF and 330 mAh g^{-1} for ruptured CSO-NB. In addition, after the second cycle, CSO-NT remains the coulombic efficiency at about 97.5%. Herein, the superior cycling stability of CSO-NT can be attributed to the unique tube-like structure, which can efficiently buffering the huge volume variation and enhance cycling stability. Figure 4.11b presents the rate performance of CaSnO_3 with three unique morphologies, which are evaluated at different current rates. Benefiting from the enlarged specific surface area (Figure 4.8) and the reduced Li^+ diffusion pathway, the best rate capability can be observed from CSO-NT even at various current densities. Besides, at a high current density of as large as 2 A g^{-1} , CSO-NT still can deliver a high capacity of around 400 mAh g^{-1} , while CSO-NF and ruptured CSO-NB can deliver only 331 mAh g^{-1} and 241 mAh g^{-1} , respectively. Importantly, a reversible capacity of 510 mAh g^{-1} , still can be obtained by CSO-NT, at the current density reduced to 500 mA g^{-1} . In addition, it can be seen that cycle stability of the sample sintered at $600 \text{ }^\circ\text{C}$ for 5 h is poorer compared to CSO-NT (Figure 4.12). The FESEM image manifests that the fibrous morphology still can be maintained in the

sample sintered at 600 °C for 5 h (inset in Figure 4.12).

Figure 4.12 Capacity versus cycle number of 1D Sn-based nanostructures calcined at 600 °C for 5 h (at current density = 60 mA g⁻¹). The inset is the FESEM image of calcinated 1D Sn-based nanostructures at 600 °C for 5 h.

In order to deeper understanding the influence of morphology modification on the electrochemical properties of CaSnO_3 , electrochemical impedance spectroscopy (EIS) analysis is performed. Figure 4.13a shows the representative Nyquist plots, which is constructed by an inclined line at low frequency (at 10 Hz – 0.1 Hz) and a semicircle at high frequency (at 100 kHz–10 Hz). The high frequency semicircle refers to the surface film resistance and charge transfer impedance that take place in the following chemical and electrochemical reaction on the interface. It is clearly seen that the diameter of semicircle of CSO-NT displays the lowest value, implying the best battery performance. The impedance value are obtained by fitting to an equivalent electrical circuit (Figure 4.13b), which is composed of electrolyte resistance (R_e), surface film and charge transfer resistance ($R_{(sf+ct)}$), polarization impedance (R_f), intercalation capacitance (C_1), Warburg impedance (W_{ol}) and constant phase element (CPE_1), and Figure 4.13c shows the fitting impedance values according to the equivalent circuit. On the basis of the shape of the

curves and the impedance values, CSO-NT shows the lowest value of $R_{\text{sf+ct}}$ of 42.3 Ω , compared to that of CSO-NF (90.1 Ω) and ruptured CSO-NB (161.3 Ω). All of these imply that the excellent electrochemical properties of CSO-NT can be related to its continuous hollow tubular structures, which not only shorten the pathway for electron transfer but also facilitate Li^+ diffusion rapidly. Besides, the EIS results also confirm that the interior hollow tubular configuration is a key factor to enhance the battery properties of CaSnO_3 .

Figure 4.13 (a) Nyquist plots for 1D CaSnO_3 nanostructures at fresh state under OCV; (b) The equivalent circuit applied to fit the experimental impedance spectra; (c) Fitted impedance data acquired from Nyquist plots by using the circuit in figure 4.13 (a).

Subsequently, we studied the electrochemical properties of CSO-NT. In order to clearly understand the electrochemical reaction processes, CV analysis was performed, as shown in Figure 4.14a. Obviously, we could distinguish the initial curve from the later ones. It should be noted that some cathodic peak at high voltage disappeared, possibly because of the formation of the solid-electrolyte interface film (SEI) on the surface of electrode and the original structure of CSO-NT are destructed or being amorphous, leading to the generation of electro-inactive CaO matrix embedded into active materials. Thus, in the initial cycle, the cathodic peak located at ~ 1.24 V corresponds to the formation of Li_2O and the irreversible electrolyte decomposition. In addition, two small cathodic peaks centred at ~ 0.8 V and ~ 0.67 V, respectively, might correspond to the irreversible reduction of tin oxides to generate Sn metal.

Figure 4.14 (a) Cyclic voltammograms (CV) of CSO-NT electrode for the initial three cycles at scan rate of 0.1 mV s^{-1} in the potential window of $0.005 - 3.0 \text{ V}$. The inset is the CV curves of the fourth to sixth; (b) Discharge and charge profiles of CSO-NT for the initial three cycles at the current density of 60 mA g^{-1} in the potential window of $0.005 - 3.0 \text{ V}$.

In addition, at the low voltage closing to 0 V , the pronounced cathodic peak appears, possibly deriving from the reversible reaction of Sn and Li to form alloy. The correspondingly dealloy reaction occurs at around 0.58 V . The other anodic peak centred at $\sim 1.26 \text{ V}$ could be related to the partly reversible oxidation of the metallic tin particles to tin oxide. In other words, this means that the reduction of the tin oxide to metallic Sn takes place at around 0.60 V . In the subsequent cycles, the redox couples at around $0.2 - 0.048/0.58 \text{ V}$ and $\sim 0.60/1.26 \text{ V}$ maintain rather stable. Due to the generation of various Li_xSn , the cathodic peak observed at lower potential splits into a doublet (0.2 V and 0.048 V) in the subsequent cycles.^[35] Next, we need to point out that the anodic peak centred at $\sim 0.58 \text{ V}$ appears significantly intensity increase, implying the existence of probably occurred activation process in the electrode. Moreover, from the second cycle onwards, the anodic and cathodic peaks perfectly overlaid, demonstrating the excellent reversibility of the alloying-dealloying reactions (the inset of Figure 4.14a).

Figure 4.14b presents the discharge and charge profiles of CSO-NT at a current density of 60 mA g^{-1} . Significantly, an identical lithium storage mechanism could be identified from discharge/charge curves of CSO-NF and ruptured CSO-NB (Figure 4.15), confirming that

different morphology have no influence on the redox reactions. In consistent with the above CV results, four voltage plateaus located at ~ 1.24 V, ~ 0.8 V, ~ 0.67 V, and ~ 0.2 V could be observed in the initial discharge profile, and a very high discharge capacity of 1168 mAh g^{-1} can be gained. Clearly, the theoretical value of 1089 mAh g^{-1} is slightly lower than that of observed value, which could be related to the generation of SEI film deriving from the reaction between Li^+ and the electrolyte. Subsequently, in the charge process, a charge capacity of around 741 mAh g^{-1} can be obtained. The initial irreversible reactions result in a low initial coulombic efficiency (only 63%). The discharge and charge capacities still could reach 759 mAh g^{-1} and 739 mAh g^{-1} , respectively, in the second cycle, which result in the efficiency value increased up to 97.3%. Besides, the coulombic efficiency as high as $\sim 97.5\%$ could maintain in the subsequent cycles, which imply that lithium storage properties of CSO-NT could be greatly enhanced. Surprisingly, the CSO-NT 1D nanostructures could be perfectly retain even after 50 cycles (Figure 4.16). The strong tenacity of CSO-NT could definitely contribute to the improved electrochemical properties, especially capacity retention during high rate testing.

Figure 4.15 Discharge/charge profile of (a) CSO-NF (b) ruptured CSO-NB electrodes for the initial three cycles at the current density of 60 mA g^{-1} in the voltage range of $0.005 - 3.0$ V.

Figure 4.16 FESEM images of (a) fresh CSO-NT electrode; (b) electrode of CSO-NT after 50 cycles.

Therefore, in view of the relatively broad potential range used in our work, all of these results definitely demonstrate that CSO-NT manifest improved cyclability and rate performance, which are related to the below reasons (i) the continuous hollow tubular structures could benefit the penetration of electrolyte and facilitate the Li^+ diffusion and (ii) the interior void space of CSO-NT could efficiently buffer the dramatic volume variation during cycling process and offer a enlarged electrolyte/electrode interface, that provide a decreased diffusion times of ions and possibly promote transition of phases. In addition, the inactive matrix, which formed during first discharge process, have an important influence on minimizing the aggregation of active material by virtue of the even distribution of the whole electrode and meanwhile the mechanical stress deriving from volume variation during cycling process could be effectively alleviated.

4.2.4 Summary

We have successfully prepared CSO-NT using a facile single-spinneret electrospinning technique. By simply tuning the sintering temperature, we can easily control the morphologies of CSO-NT, CSO-NF and ruptured CSO-NB. Electrochemical measurements show that CSO-NT possesses remarkable cyclability and rate performance compared with CSO-NF and ruptured CSO-NB. After 50 cycles, a reversible capacity of around 565 mAh g^{-1} (the coulombic efficiency of around 97.5%) can be obtained by CSO-

NT at a current of 60 mA g^{-1} . The unique interior hollow tubular structure could account for its remarkable lithium storage performance. In other word, CSO-NT exhibits its huge potential as anode in LIBs and meanwhile, this work provides a deeper insight to further understand the impact of sintering temperature on electrospun nanofibers and the importance of hollow tubular structure on 1D nanostructure electrode.

4.3 Eggroll-like CaSnO_3 Nanotubes (CSO-NT)[†]

As the CSO-NT electrode has demonstrated a good electrochemical performance, further research to improve its electrochemical performance is crucial and necessary. Since section 4.2 has presented the influence of sintering condition on CaSnO_3 1D nanostructures. In this section, we will mainly investigate the relationship between the viscosity of precursor solution and the morphologies of novel eggroll-like CSO-NT. Significantly, such novel morphology has not been reported in the literature. Meanwhile, it is known that the morphologies of the materials are a key issue for LIBs applications. Therefore, our work about the novel morphologies is important and necessary. Besides, we have investigated the evolution of the morphologies from CaSnO_3 nanorods (CSO-NR) to eggroll-like CSO-NT in detail by adjusting the concentrations of the reactants. More importantly, eggroll-like CSO-NT exhibits improved cyclability and rate performance compared to the above work. Therefore, we believe that this work has high novelty, and it is the deepening research on CaSnO_3 .

4.3.1 Structure and morphology analysis

Figure 4.17 shows the SEM images of as-spun nanofibers, which are prepared by using different weight ratios of polyacrylonitrile (PAN) polymer and metallic precursor. We can see that the two different samples compose of uniform nanofibers with smooth surfaces. To determine the thermal decomposition temperature of the as-spun precursor nanofibers, thermogravimetric analysis (TGA) analysis was carried out. As shown in

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Figure 4.17 FESEM images of as-spun precursor nanofibers with various weight ratios of the metal precursor over PAN polymer: (a) 1.30 : 1, (b) 0.65 : 1.

Figure 4.18 (a) TGA curve of as-spun precursor nanofibers with weight ratios of the metal precursor over PAN polymer around 1.30 : 1; (b) FTIR spectra of egg-roll like CSO-NT , as-spun precursor nanofibers, and PAN.

Figure 4.18a, there is a large weight loss between 300 °C to 400 °C, and it remains at around 53 wt% after 600 °C, implying the completely elimination of PAN and decomposition of the metal precursor. Therefore, the as-spun precursor nanofibers are sintered at 600 °C, which is expected to form CaSnO_3 pure phase at such temperature. In addition, according to the FTIR results, we can see that all the peaks which are belonged to PAN, completely disappeared and only Sn-O-Sn vibrations could be identified after thermal treatment (Figure 4.18b), suggesting the thoroughly elimination of PAN polymer

and the formation of CaSnO_3 .^[144, 145]

Figure 4.19 (a) Crystal structure of eggroll-like CSO-NT and (b) Rietveld refined XRD pattern.

Figure 4.20 XPS spectra of eggroll-like CSO-NT (a) survey scan; (b) high resolution Ca 2p scan; (c) high resolution Sn 3d scan; (d) high resolution O 1s scan.

Figure 4.19a shows that the as-prepared CaSnO_3 adopts an orthorhombic perovskite

structure with space group Pbnm .^[146] It is distorted from cubic symmetry by an octahedral tilting distortion. Basically, a variety of distorted SnO_6 octahedral build a complex network with the Ca^{2+} ions located in the octahedral cavities. The as-prepared CaSnO_3 , which is constructed from corner-sharing distorted SnO_6 octahedrons, possess a 3D framework of tunnels for Li diffusion. According to the XRD pattern of eggroll-like CSO-NT in Figure 4.19, all the well-defined peaks can be indexed to orthorhombic CaSnO_3 . From the Rietveld refinement results, we can see the calculated lattice parameters of CaSnO_3 are $c = 7.894 \text{ \AA}$, $b = 5.669 \text{ \AA}$, and $a = 5.523 \text{ \AA}$, which is coincident with JCPDS data (Card No. 77 - 1797, $c = 7.906 \text{ \AA}$, $b = 5.681 \text{ \AA}$, $a = 5.532 \text{ \AA}$). Moreover, XPS results confirms that the oxidation state of Sn and Ca is + 4 and + 2, respectively, and the atom ratio of O : Sn : Ca is around 60.60% : 20.04% : 19.36% (Figure 4.20). Therefore, these results suggest that pure phase CaSnO_3 can be easily prepared through a simple thermal treatment in air ($600 \text{ }^\circ\text{C}$ for 24 h).

Figure 4.21 (a and b) FESEM images in different magnification of eggroll-like CSO-NT and (c) magnified FESEM image, which is taken from the square area in (b). (The inset is the photograph of eggroll.) (d and e) TEM images, (f) HRTEM image, and (g) SAED pattern (h) EDX image of eggroll-like CSO-NT.

Next, FESEM is used to characterize the morphology of eggroll-like CSO-NT, as shown in Figure 4.21a. The fibrous morphology of CSO-NT can be maintained very well after annealed at $600 \text{ }^\circ\text{C}$ for 24 h. From the corresponding magnified FESEM images in Figure

4.21b and c, the rough surfaces and uniform hollow tubular structures can be clearly identified from eggroll-like CSO-NT. The average length of eggroll-like CSO-NT is more than $\sim 20\ \mu\text{m}$ and the diameter is around 560 nm (Figure 4.21b). Interestingly, eggroll-like CSO-NT looks the same with egg-rolls and not only has similar channel-like surface but also possess identical tubular structure (Figure 4.21c and the inset in Figure 4.21b). Then, TEM was carried out to demonstrate the unique structural feature. Figure 4.21d clearly reveals the hollow tubular structure with the wall thickness of around 109 nm, matching well with above FESEM results. In addition, the HRTEM image displays that numerous of nanoparticles with size around 12 nm constitute the whole eggroll-like CSO-NT structure (Figure 4.21e). The lattice fringe is found to be $\sim 0.278\ \text{nm}$, corresponding to the (112) plane of eggroll-like CSO-NT (Figure 4.21f). The corresponding SAED pattern indicates the polycrystalline nature of eggroll-like CSO-NT (Figure 4.21g). The well-defined rings are in good agreement with the (002), (112) and (132) planes of CaSnO_3 . Moreover, EDX spectra with a O: Sn : Ca ratio of 3.16 : 1.07 : 1 further corroborate the XRD analysis (Figure 4.19b). Thus, egg-roll like CSO-NT has been successfully fabricated using a facile electrospinning method.

As we all know, various factors including electrospinning parameters, viscosity of precursor solution, metal precursor (denoted as M) concentration, and so on, play an critical role to determine the morphologies, size distributions, and diameters of 1D CaSnO_3 .^[104, 147] In the present study, we found that M concentration have an important influence on the morphologies of the final 1D CaSnO_3 nanostructures. To clearly demonstrate the influence of M concentration on 1D CaSnO_3 nanostructures, CSO-NR and eggroll-like CSO-NT were synthesized by precisely adjusting the weight ratios of M over PAN from 0.65 : 1 (CSO-NR) to 1.30 : 1 (CSO-NT).

Figure 4.22a and b show that CSO-NR with length up to several micrometers can be obtained and possesses uniform diameter of around 380 nm. The dense nanorod structure of CSO-NR can be obviously seen from the TEM image in Figure 4.22c. Meanwhile, there is no obvious colour change between the central and the edge part, indicating the solid inner structure of CSO-NR. Moreover, no detectable impurity phase could be identified from EDX and XRD patterns of CSO-NR (Figure 4.22d and its inset), which illustrates that the changes of M concentration could not influence the generation of single

phase CaSnO_3 . Furthermore, the lattice spacing of 0.278 nm is consistent with the (112) plane of CaSnO_3 , confirming its orthorhombic structure (inset in Figure 4.22c).

Figure 4.22 (a and b) FESEM images (c) TEM images and (d) XRD pattern of CSO-NR.

It is worth pointing out that CSO-NR also has a channel-like surface structure, which is similar with that of eggroll-like CSO-NT. Thus, BET analysis was further performed to characterize the surface feature of eggroll-like CSO-NT and CSO-NR in order to obtain the detailed structure information. Figure 4.23a exhibits that both samples show identical nitrogen adsorption/desorption isotherms, implying the characteristic of type IV isotherms with a type H3 hysteresis loop that is a representative feature for mesoporous structure. Figure 4.23b shows the pore size distributions of both samples, which is calculated by using the Barrett-Joyner-Halenda (BJH) method according to the desorption branch of the isotherms, indicating a relatively broad size distribution. Benefiting from unique surface feature and hollow tubular structure, eggroll-like CSO-NT have a larger BET specific

surface area ($37.8 \text{ m}^2 \text{ g}^{-1}$) compared to that of CSO-NR ($14.2 \text{ m}^2 \text{ g}^{-1}$).

Figure 4.23 (a) N_2 adsorption/desorption isotherms; (b) corresponding pore-size distribution of CSO-NR and eggroll-like CSO-NT.

4.3.2 Electrochemical studies

We further studied the lithium storage properties of both samples as anode for LIBs. Figure 4.24a shows the Coulombic efficiency of eggroll-like CSO-NT and the comparative cycling stability of both samples at a current rate of 60 mA g^{-1} in the potential window of $0.005 - 3 \text{ V}$. Apparently, eggroll-like CSO-NT could deliver a reversible capacity of around 648 mAh g^{-1} even up to 50 cycles, which is almost 1.6 times of that of CSO-NR (only 410 mAh g^{-1}). Although eggroll-like CSO-NT shows a relatively low Coulombic efficiency at the first cycle, it rapidly increases in the following cycles and maintains at around 98.1% after 50 cycles. In addition, Figure 4.24b also indicates that the rate performance of CSO-NR is also poorer than that of eggroll-like CSO-NT. Eggroll-like CSO-NT can deliver a capacity of 416 mAh g^{-1} even at current density as high as 2 A g^{-1} , while CSO-NR possesses a capacity of only 271 mAh g^{-1} , demonstrating the superior high-rate capability of eggroll-like CSO-NT. Subsequently, when a lower current density of 500 mA g^{-1} is used, a reversible capacity of 513 mAh g^{-1} still can be obtained by eggroll-like CSO-NT, further confirming the stability of electrode structure. Moreover, the significantly decreased charge transfer impedance (40Ω) for eggroll-like CSO-NT

towards CSO-NR ($87\ \Omega$) further demonstrate the superior electrochemical performance of eggroll-like CSO-NT (Figure 4.24c – e).

Figure 4.24 Electrochemical properties of CSO-NR and eggroll-like CSO-NT (a) at a current density of $60\ \text{mA g}^{-1}$ (b) at different current densities (c) Nyquist plots of eggroll-like CSO-NT and CSO-NR at fresh state under OCV (d) Equivalent circuit applied to fitting the experimental data (e) Fitted impedance data gained from Nyquist plots using the circuit in (d).

To deeper insight into the effect of the tube-like structure and channel-like surface structure on the lithium storage properties of the as-obtained samples, CV was performed to evaluate the eggroll-like CSO-NT, as shown in Figure 4.25a. In the initial cycle, the broad cathodic peak at around $1.21\ \text{V}$ could be clearly seen and vanished in the subsequent cycles, which corresponds to the structure destruction or crystal lattice amorphization, along with the generation of electro-inactive CaO matrix and active metallic Sn (eq 4.1). The broad cathodic peak located at around $0.76\ \text{V}$ could be attributed to the generation of the solid electrolyte interphase (SEI) film and, meanwhile, to the start

generation of Li-Sn alloys.^[129] The typical pair of peaks located at cathodic and anodic potential of ~ 0.07 and ~ 0.6 V can be related to the alloying-dealloying reaction between Sn and Li (eq 4.2), respectively. Additionally, the observed anodic peak at around 1.28 V corresponds to the oxidation of metallic Sn to Sn oxides. Surprisingly, in the second cycle, the cathodic peak centred at around 0.07 V splits into a doublet, locating at ~ 0.07 and ~ 0.22 V, which indicate Li-Sn alloying reaction taking place in two stages in the following cycles.^[35] Simultaneously, it can be clearly seen that the intensity of the cathodic peak located at 0.65 – 1.10 V shows remarkable increase, and another small cathodic peak at 1.35 – 1.55 V appears, further indicating that partly reversible reactions between metallic Sn and Sn oxides occurs.^[119] Additionally, in the second cycle, the anodic peak at around 0.6 V significantly increases in intensity, implying that there is a possible activation process in the electrode. More importantly, the anodic and cathodic peaks perfectly overlay in the following 5th, 10th, and 15th cycle, indicating that the electrochemical reactions possess excellent reversibility (inset in Figure 4.25a).

Figure 4.25 (a) CV curves of eggroll-like CSO-NT in the potential window of 0.005 – 3.0 V at a scan rate of 0.1 mV s^{-1} for the first two cycles. Inset shows the 5th, 10th, 15th cycles. (b) The discharge-charge curves of eggroll-like CSO-NT.

Figure 4.25b shows the discharge-charge curves of eggroll-like CSO-NT at a current density of 60 mA g^{-1} . The voltage profiles match well with the previous report.^[35] The first discharge/charge capacity of eggroll-like CSO-NT is $1149/738 \text{ mAh g}^{-1}$, resulting in

a huge first irreversible loss of around 38%. Because there are huge irreversible reduction between Sn oxides and metallic Sn and the generation of the SEI film during first cycle, the irreversible loss is unavoidable. At the second cycle, eggroll-like CSO-NT can deliver a discharge/charge capacity of around 772/737 mAh g^{-1} , demonstrating a relatively large Coulombic efficiency of 95.4%. Hence, it is clear that eggroll-like CSO-NT possess superior cycling performance and rate capability compared to CSO-NR. Importantly, nanofibrous morphology of eggroll-like CSO-NT electrode still can be identified after 50 cycles (Figure 4.26). This also confirms the remarkable lithium storage properties of CSO-NT.

Figure 4.26 SEM images of (a) raw eggroll-like CSO-NT electrode (b) eggroll-like CSO-NT electrode after 50 cycles. (It should be noted that the particles around the nanofibers are PVDF binder and conductive carbon black).

Both the unique tubular structure and channel-like surface feature of eggroll-like CSO-NT could account for its superior electrochemical properties. Specifically, the interior hollow tube-like structure of eggroll-like CSO-NT not only facilitate the rapidly diffusion of lithium ion but also possess sufficient space to accommodate the volume variation during lithiation/delithiation process. Moreover, by virtue of the relatively thick wall (109 nm) and channel-like surface feature, eggroll-like CSO-NT is equipped with excellent structural stability, which would benefit to buffer the electrode pulverization. Furthermore, the relatively high specific surface area of eggroll-like CSO-NT enables a variety of

reactive sites and thus results in enlarged contact area between the active materials and electrolyte.

4.3.3 Summary

In summary, eggroll-like CSO-NT has been successfully fabricated by using a versatile electrospinning technique. The reactant concentration have significant impact on the morphology and final structure of CaSnO_3 1D nanostructures. When served as anode in LIBs, eggroll-like CSO-NT presents more superior electrochemical properties compared to CSO-NR. Our work is anticipated to not only provide deep insight in fabrication of binary or ternary metal oxides with unique tube-like structures using the facile electrospinning technique, but also finding promising use in energy related devices.

4.4 SrSnO_3 and BaSnO_3 Nanostructures

Figure 4.27 XRD patterns of SrSnO_3 sintered at various temperatures.

Apart from the nanostructure design aspects, the lithium storage properties of Sn-based ternary oxides (ASnO_3) are sensitive to the selection of counter ions in A-sites. As eggroll-like CSO-NT demonstrate good battery performance, a simple substitution Ca by other alkali earth elements including Sr and Ba as inactive matrix elements, was carried out to construct SrSnO_3 and BaSnO_3 using electrospinning method. The effect of A-site substitution is evaluated by comparing the electrochemical properties of SrSnO_3 and BaSnO_3 with CaSnO_3 , respectively.

4.4.1 Structure and morphology analysis

Figure 4.28 XRD patterns of BaSnO_3 sintered at various temperatures.

Firstly, the phase purity and crystallinity of final electrospun samples sintered at various temperatures were evaluated by XRD, as shown in Figure 4.27 and 4.28, respectively. For the both sample sintered at 700°C for 5h, although slight SrSnO_3 and BaSnO_3 phase can be found, respectively, the main phase of the products is composed by Sn-based oxides, indicating that Sr^{2+} and Ba^{2+} are hardly embedded into the lattice at these condition,

respectively. As expected, increasing the sintering temperature to 900 °C for 5h resulted in the formation of SrSnO_3 and BaSnO_3 , respectively. However, slight SnO_2 still could be founded in the system, which agrees well with previous reported.

Figure 4.29 SEM images of (a) electrospun precursor nanofiber (b) sintered at 700 °C (c) sintered at 900 °C of Sr-Sn-O oxides.

Figure 4.30 SEM images of (a) electrospun precursor nanofiber (b) sintered at 700 °C (c) sintered at 900 °C of Ba-Sn-O oxides.

To further elucidate the microstructures and morphologies feature, FESEM was performed. Figure 4.29a presents the uniform and continuous Sr-Sn-based as-spun precursor composites nanofibers with smooth surface and average diameter around 170 nm. After sintered at 700 °C for 5h, the typical 1D electrospun structures can be maintained (Figure 4.29b). As observed, increasing the sintering temperature to 900 °C for 5h, the 1D nanostructures of SrSnO_3 crack and ultimately present randomly distributed nanorods structures (Figure 4.29c). Similarly, Figure 4.30 presents the SEM images of BaSnO_3 nanostructures sintered at various temperatures. It is found that the 1D nanostructures of Ba-Sn-O composites could also be maintained after sintered at 700 °C

for 5 h (Figure 4.30b). Apparently, further increasing the temperature to 900 °C for 5 h, a large amount of nanoparticles interconnected to form the 1D BaSnO₃ nanostructures (Figure 4.30c).

4.4.2 Electrochemical studies

Figure 4.31 (a) CV curves in the voltage window of 0.005 – 3.0 V at a scan rate of 0.1 mV s⁻¹ for the first three cycles; (b) the discharge/charge profiles of electrospun SrSnO₃ sintered at 900 °C for 5 h.

Next, we investigated the electrochemical properties of electrospun SrSnO₃ sintered at 900 °C for 5 h as anode in LIBs. Figure 4.31a gives the typical first three consecutive CV curves of electrospun SrSnO₃ sintered at 900 °C for 5 h in the voltage range of 0.005 – 3.0 V at a scan rate 0.1 mV s⁻¹. All the CV curves of SrSnO₃ are similar except for the slight shift of peak position and the difference in the intensity. Apparently, the feature of these CV curves looks quite like that of eggroll-like CSO-NT. In accordance with previous report, the three peaks centred at around 1.3, 0.6, and 0.2 V, can be identified in the first cathodic scan, corresponding to the multi-step electrochemical reactions. Specifically, the small cathodic peaks located at around 1.3 V can be ascribed to the structure destruction or crystal lattice amorphization process, accompanying by the generation of active metallic Sn and electrochemical inactive SrO matrix. Moreover, the cathodic peak at ~ 0.6 V corresponds to the decomposition of electrolyte and the formation of SEI film. Notably, the intense peak below 0.2 V could be related to the generation of Li-Sn alloys. The

representative peaks centred at potential of ~ 1.3 and ~ 0.6 V can be related to the oxidation of Sn metal to Sn oxides and dealloying reaction of Li-Sn alloys, respectively. Figure 4.31b shows the discharge/charge curves of electrospun SrSnO_3 at current density of 60 mA g^{-1} . Clearly, the voltage plateau is consistent with CV results. Significantly, the electrospun SrSnO_3 deliver a relatively high first discharge/charge capacity of $985/568 \text{ mAh g}^{-1}$. The first irreversible capacity loss is around 42%, which is mainly induced by the generation of SEI film. This is a common drawback for metal oxides anode materials and required further research to solve this issue.

Figure 4.32 Cycling performance of electrospun SrSnO_3 sintered at 900°C for 5 h at a current density of 60 mA g^{-1} .

In addition, the cycling stability and coulombic efficiency of SrSnO_3 anode are displayed in Figure 4.32. A reversible capacity of 302 mAh g^{-1} is delivered after 50 cycles, only corresponding to around 29% of its theoretical value of 885 mAh g^{-1} . Meanwhile, it is found that the coulombic efficiency stabilized at around 98.6%.

Figure 4.33a displays the CV curves of electrospun BaSnO_3 sintered at 900°C for 5 h at a scan rate 0.1 mV s^{-1} in the voltage range of $0.005 - 3.0 \text{ V}$. It is found that BaSnO_3 shows similar electrochemical reaction mechanism with both CaSnO_3 and SrSnO_3 , apart from

Figure 4.33 (a) CV curves in the voltage window of 0.005 – 3.0 V at a scan rate of 0.1 mV s^{-1} for the first three cycles; (b) the discharge/charge profiles of electrospun BaSnO_3 sintered at 900°C for 5 h.

Figure 4.34 Cycling performance of electrospun BaSnO_3 sintered at 900°C for 5 h at a current density of 60 mA g^{-1} .

the irreversible structure destruction during initial cathodic scan moving to the lower cut-off potential. The representative pair of peaks occurs at anodic and cathodic potential of ~ 0.6 and $\sim 0.1 \text{ V}$ could be related to the alloying/dealloying reaction between Sn and Li, respectively. Notably, the area underneath CV curves of electrospun BaSnO_3 is smaller

than both CaSnO_3 and SrSnO_3 , implying poorer lithium storage capability. Besides, the peaks position observed from the CV curves is in consistent with the plateau region in the discharge/charge curves shown in Figure 4.33b. Looking into its galvanostatic properties, the first discharge/charge capacity of electrospun BaSnO_3 achieves only $576/294 \text{ mAh g}^{-1}$ at current density of 60 mA g^{-1} . The reversible capacity of merely $\sim 109 \text{ mAh g}^{-1}$ can be retained after 50 cycles (Figure 4.34). From the perspective of lithium storage properties, electrospun BaSnO_3 is presumed to have negligible reaction with lithium by excluding the lithium ions consumption by electrolyte decomposition.

4.4.3 Summary

In summary, exploratory investigation has been performed on electrospun SrSnO_3 and BaSnO_3 , which simply replace Ca by Sr and Ba in ASnO_3 system. To elucidate their suitability as electrode for LIBs, their lithium storage properties are evaluated using CV and galvanostatic cycling. Although, the coulombic efficiencies are larger than 98% for the both cases, their reversible capacities are too low to be used as anode, which is even lower than graphite (372 mAh g^{-1}). Thus, these results indicate that both Sr and Ba are not suitable inactive matrix elements to enhance the electrochemical stability of Sn-based ternary oxides.

4.5 Effect of morphology modification in ASnO_3

Table 4.1 The comparison of electrochemical properties of CSO-NT with eggroll-like CSO-NT.

Sample	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Impedance (fresh electrode)	Initial discharge/charge capacity (mAh g^{-1})	50 th discharge capacity (mAh g^{-1})
CSO-NT	34	42.3	1168/741	565
CSO-NT (eggroll-like)	38	40	1149/738	648

To emphasize the importance of morphology modification in improving battery performance, a series CaSnO_3 with different morphologies, such as CSO-NF, CSO-NT, CSO-NB, eggroll-like CSO-NT, and CSO-NR, have been prepared using electrospinning technique. Their detailed electrochemical behaviors have been analyzed in Section 4.2.3 and Section 4.3.2, respectively. CSO-NT and eggroll-like CSO-NT illustrate better cycling stabilities than their corresponding counter-part, respectively. This mainly benefit from their hollow tubular-like 1D nanostructures, meanwhile implying that the battery performance is very sensitive to the morphologies of active materials. Based on the earlier discussion, the impact of morphology modification on the lithium storage properties of both CSO-NT and eggroll-like CSO-NT will be discussed in this section. The summary is tabulated in Table 4.1. Although, both CSO-NT and eggroll-like CSO-NT possess hollow interior 1D nanostructures, the sensitivity of electrochemical properties towards the morphology of active materials is evident from the slight difference in the cycling stability (Table 4.1). This can be ascribed to the difference in the unique surface structure (channel-like surface structure of eggroll-like CSO-NT), specific surface area, and internal impedance.

4.6 Effect of A-site substitution in ASnO_3

Table 4.2 The comparison of electrochemical performance of ASnO_3 (A = Ca, Sr and Ba).

Formular/ Molecular weight (g)	Initial theoretical discharge capacity (moles of Li) (mAh g^{-1})	Observed initial discharge capacity (moles of Li) (mAh g^{-1})	50 th discharge capacity (moles of Li) (mAh g^{-1})
$\text{CaSnO}_3/206.8$	1089(8.4)	1149(8.8)	648(5.21)
$\text{SrSnO}_3/254.3$	885(8.4)	985(9.3)	302(2.86)
$\text{BaSnO}_3/303.9$	741(8.4)	576(6.5)	109(1.24)

According to the plots in Figure 4.24a, 4.32, and 4.34, some selected data are listed in Table 4.2. The observed initial discharge capacities of CaSnO_3 and SrSnO_3 are higher than the corresponding theoretical capacity, which can be ascribed to the SEI formation

during first discharge.^[35, 36] While the initial discharge capacity of BaSnO_3 is lower than that of theoretical value, possibly due to the incomplete reaction. By comparing the cycling stability of BaSnO_3 , SrSnO_3 and CaSnO_3 , it is found that the reversible capacity decrease from Ca to Ba. Enhance in the ionic size and atomic weight in that order could be the main reasons. This is because the poorer conductivities between the inter particles and the increase of inactive matrix metal content per mole in the composite electrode would not in favor of electron transfer. Moreover, the difference in the counter ion, oxygen co-ordination, as well as the crystal structure of starting ASnO_3 , could also be important factors.^[54]

Chapter 5 Electrospun 1D ACo_2O_4 (A = Ca, Ni) Nanostructures with High Lithium Storage Properties

5.1 Introduction

In order to design advanced functional nanomaterials, a variety of techniques have been suggested to achieve desirable properties by precisely tailoring their various structural features.^[148, 149] With the aim to realize and enhance various structure-dependent characteristics in different applications, controllable fabrication of advanced nanomaterials with well-defined structures are becoming the main focus over the last couple of decades.^[150, 151] Exceptionally, for electrode materials in LIBs, 1D hollow or hierarchical configuration, which consist of secondary building blocks, can not only present superior ability for fast electron transportation and ion diffusion, but also enable an enlarged specific surface area for high electrochemical activity, that are two critical features to enhance the electrochemical properties of LIBs. More significantly, the secondary building block can shorten the diffusion pathway of the charge carriers, and meanwhile efficiently increase the interface between active materials and the electrolyte. Besides, the synergistic effect deriving from secondary building blocks and 1D nanostructure will greatly enhance the cycling stability and capacity of LIBs. Considering all of these advantages, it is anticipated that the preparation 1D configuration with unique morphologies and suitable compositions would possess great significance. However, even though many different methods have been report to synthesis these novel configurations, most of these are general in the formation of 1D heterostructures with hierarchical architectures by solution methods.^[102, 103, 152] Thus, the development of effective and facile strategy that is suitable for the synthesis of unique 1D nanoarchitectures still remains great challenges. Currently, electrospinning, as one of the most promising methods, has been extensively utilized as a remarkable cost-effective and convenient technique to produce various 1D nanoarchitectures with novel morphologies.^[143, 153] Remarkably, except to the uncomplicated setup, various 1D nanoarchitectures with

desirable lengths, morphology, diameters, compositions, and complex configuration could be simply achieved by rationally tuning the experimental parameters.

Considering various potential electrode materials, by virtue of their high theoretical capacity (up to around 890 mAh g^{-1}), controllable morphology and size, Co-based oxides is now intensively investigated for application in LIBs.^[154-156] However, the poor cycling stability and rapid capacity fading of Co-based oxides has become the main hindrance for their practical use. Part of the issues might be related to the aggregation of active materials and the prominent volume variation during lithium extraction-insertion process, which would cause of the loss of electrical contact and death area in the electrode. With the purpose to enhance the cycling stability of Co-based composites, the combination with active or inactive matrix element should be a promising solution.

Since electrospun eggroll-like CSO-NT (in section 4.3) presents promising electrochemical properties as LIBs anodes and Ca has also been demonstrated to be a good inactive matrix elements to enhance the batteries performance of Sn-based oxides. With this in mind, a simple replacement of Sn elements by Co at B-sites will be firstly carried out to construct 1D CaCo_2O_4 (CCO) nanostructures with novel morphologies. As a consequence, the effect of B-site substitution in ternary metal oxides will be systematically studied. Similarly, to identify the influence of counter ion A in Co-based ternary oxides, a series of 1D NiCo_2O_4 (NCO) with different morphologies, such as NiCo_2O_4 nanotubes (NCO-NT), NiCo_2O_4 nanofibers (NCO-NF), and NiCo_2O_4 nanobelts (NCO-NB), are prepared using electrospinning techniques. Remarkably, the possible formation mechanism and controllable fabrication process of both CCO and NCO with 1D nanostructure are also discussed.

5.2 Hierarchical CaCo_2O_4 Nanofibers (CCO-NF)[†]

Although the layered Ca-Co-based ternary oxides^[157-160] have been known owing to their high thermoelectric properties, up to now, it is rarely reported about their electrochemical properties. In addition, it is known that $\text{Ca}_3\text{Co}_4\text{O}_9$ ^[161, 162] has been prepared by

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electrospinning technique and shows enhanced thermoelectric properties. As far as we know, the synthesis of CaCo_2O_4 with 1D hierarchical nanostructure and their application as anode in LIBs are not reported. In the present work, we firstly illustrate the fabrication of 1D hierarchical CaCo_2O_4 nanofibers (denoted as CCO-NF), which is constructed by ultrathin nanoplates, through electrospinning technique and controlled thermal treatment. Remarkably, the morphologies of the as-obtained Ca-Co-O 1D nanostructure can be easily tuned from nanoplates-in-nanofibers structure, hierarchical nanofibers to nanoplates. Additionally, the impact of the sintering temperature on the crystallographic phase evolution and morphology is systematically discussed. Encouragingly, exceptional electrochemical properties with substantially enhanced cycling stability and rate performance has been demonstrated by the unique hierarchical CCO-NF, which is much better than that of nanoplates-in-nanofibers and nanoplates structure. More significantly, we believed that other structure-tunable metal oxides nanomaterials with improved electrochemical performance could be readily prepared by using the cost-effective and facile strategy we described here and would find potential application as high-performance electrode in LIBs.

5.2.1 Structure and morphology analysis

Figure 5.1 (a) Rietveld refined XRD pattern; (b) crystal structure of hierarchical CCO-NF after sintered at 650 °C for 2 h.

Figure 5.2 (a) EDX image of as-prepared hierarchical CCO-NF after sintered at 650 °C for 2 h; (b) TGA curve of as-spun precursor nanofibers.

Figure 5.3 (a) XRD patterns of final products sintered at different temperatures; (b) FTIR spectrum of PVP, as-spun precursor nanofibers, sintered CaCo_2O_4 at 650 °C for 2h.

The composition and phase purity of the as-prepared samples sintered at 650 °C for 2h were first evaluated by XRD analysis (Figure 5.1a). All diffraction peaks can be readily indexed to CaCo_2O_4 with monoclinic structure. The lattice parameters of CaCo_2O_4 calculated by Rietveld refinement are $a = 4.909 \text{ \AA}$, $b = 2.833 \text{ \AA}$, and $c = 5.634 \text{ \AA}$, in good agreement with JCPDS data (Card No. 51-1760, $a = 4.881 \text{ \AA}$, $b = 2.826 \text{ \AA}$, $c = 5.654 \text{ \AA}$). Figure 5.1b exhibits that CaCo_2O_4 possesses the monoclinic $P3$ structure, which is constructed from $[\text{CoO}_2]_n$ sheets of edge-sharing octahedra with Ca^+ ions between

layers.^[157, 162, 163] The unique layered structure of CaCo_2O_4 would make it beneficial for the Li diffusion.

Figure 5.4 SEM images (a) of as-spun precursor nanofibers (inset is large area view); (b and c) SEM and (d, e, and f) TEM images of hierarchical CCO-NF sintered at 650 °C for 2 h (inset is the corresponding SAED pattern).

In fact, EDX analysis further confirms the formation of single phase CaCo_2O_4 (Figure 5.2a). Moreover, TGA also demonstrates the completely formation of single phase CaCo_2O_4 occurring above 600 °C (Figure 5.2b).

Figure 5.5 (a) SEM images and inset shows the corresponding large-area view, (c and e) TEM images and the inset in e shows corresponding SAED pattern of as-obtained products sintered at 550 °C for 2 h; (b) SEM images and inset shows the corresponding large-area view, (d) TEM images and the inset in f shows corresponding SAED pattern of as-obtained CaCo_2O_4 sintered at 750 °C for 2 h.

Additionally, the XRD patterns of the as-prepared samples sintered at various temperatures indicate that CaCo_2O_4 with high phase purity can be generated at the sintering temperature above 600 °C. Actually only Co_3O_4 and CaCO_3 phase can be detected at 550 °C (Figure 5.3a), demonstrating that Ca^{+} is hardly efficient embedded into the lattice at this temperature.^[164] Moreover, FTIR spectra (Figure 5.3b) shows that after

sintered at 650 °C, all the bands belonged to PVP disappeared, which is in good agreement with the XRD results (Figure 5.1a).

In order to evaluate the microstructures and morphologies of the as-prepared samples, FESEM, and TEM were carried out. It can be clearly observed that continuous and uniform as-spun precursor nanofibers possess average diameter of ~ 240 nm and lengths could extend up to several micrometers, as shown in Figure 5.4a. Besides, the surface of as-spun nanofibers is relatively smooth and no secondary nanostructures can be identified (Figure 5.4a and its inset). Figure 5.4b shows that the continuous 1D nanostructures can be perfectly maintained whereas the diameter and morphology of the fibers vary significantly after sintered at 650 °C for 2 h. Figure 5.4c obviously shows that numerous of plate-like nanostructures stacked tightly each other to build the hierarchical fibrous nanostructures with a uniform diameter of ~ 170 nm. TEM result in Figure 5.4d further confirm this unique structure, which consist of tightly stacked nanoplates as secondary building blocks. Apparently, Figure 5.4e presents that the thickness of each nanoplate is around 6 nm. Moreover, HRTEM image displays the lattice fringes with spacing of 0.545 nm, matching well with the interplanar distance of (001) planes of CaCo_2O_4 (Figure 5.4f). Furthermore, the corresponding SAED pattern presents well-defined electron diffraction rings, obviously demonstrating the polycrystalline nature of CaCo_2O_4 (inset in Figure 5.4f).

As we all know, many factors including sintering temperature, properties of precursor solution, electrospinning parameters etc, have dramatic impact on the diameter and morphology of 1D nanomaterials fabricated by electrospinning method.^[102, 103] In the present work, by rationally changing some electrospinning parameters, we can obtain uniform 1D electrospun precursor (Figure 5.5a). Moreover, we can see that the thermal treatment procedure, which is used to remove organic PVP, is critical to fabricate hierarchical CCO-NF successfully. Thus, to pursue deep understanding on the formation mechanism of unique hierarchical 1D structures of CaCo_2O_4 , a series of temperature-dependent analysis is performed, as shown in Figure 5.5. Duo to the crystallization of metal oxides and the decomposition of PVP, the as-prepared nanofibers obviously present a rough surface and a variety of many nanoparticles with irregular shapes agglomerate on the surface after sintered at 550 °C for 2 h (Figure 5.5a and its inset). TEM image in

Figure 5.5c clearly shows the fibrous structure, which is in good agreement with the SEM analysis (Figure 5.5c). Interestingly, we found that many nanoplates with irregular shape are growing in the nanofibers, which is distinct from the hierarchical structure of CCO-NF. In addition, Figure 5.5e shows the HRTEM image, which suggests the crystalline feature of the as-prepared sample. Meanwhile, the interplanar distance of 0.244 nm is in consistent with the spacing of the (311) planes of Co_3O_4 (JCPDS card no.78-1969), matching well with the XRD analysis (Figure 5.3a). The SAED pattern in the inset of Figure 5.5e illustrates that the as-prepared sample is polycrystalline. Nevertheless, the sample obtained after sintered at 750 °C compose of many agglomerate nanoparticles and a variety of broken nanoplates, which is similar to previous report that fibers structure ruptures at elevated temperature (Figure 5.5b).^[103] Typically, the TEM image further verify the collapse of hierarchical 1D nanostructure of CaCo_2O_4 (Figure 5.5d). The corresponding SAED pattern and HRTEM image (Figure 5.5f and its inset) also suggest the generation of the CaCo_2O_4 phase (JCPDS card no. 51-1760). Hence, these analysis illustrates that the sintering temperature influence both the phase purity (Figure 5.1 and Figure 5.3a) the morphology (Figure 5.4 and 5.5).

Functional nanomaterials, especially electrode materials for LIBs, are expected to possess high specific surface area. Therefore, to more obviously depict their surface feature, Figure 5.6 gives the typical N_2 adsorption/desorption isotherms of the as-prepared samples, which is commonly used to demonstrate the surface properties. We can see that the as-prepared samples present almost identical similar adsorption/desorption isothermals, which correspond to type IV isothermal with H3 hysteresis loops, indicating the existence of a poor-defined mesoporous structure. Based on the Barrett-Joyner-Halenda (BJH) pore size distributions plots in the inset of Figure 5.6, most of the pores, mainly deriving from the interspaced pores between neighboring nanoplates, present a relatively wide size distribution. Benefiting from the unique hierarchical 1D nanostructure, hierarchical CCO-NF give rise to a larger BET specific surface areas ($35.7 \text{ m}^2 \text{ g}^{-1}$) and total pore volumes ($0.23 \text{ cm}^3 \text{ g}^{-1}$), than that of CaCo_2O_4 nanoplates structure ($25.1 \text{ m}^2 \text{ g}^{-1}$ and $0.14 \text{ cm}^3 \text{ g}^{-1}$) and nanoplate-in-nanofibers structure ($14.4 \text{ m}^2 \text{ g}^{-1}$ and $0.11 \text{ cm}^3 \text{ g}^{-1}$). In view of such interesting hierarchical 1D structures permitting facile electron transport and Li^+ ions diffusion, as well as enlarging the interface between electrode and electrolyte, we believe

that hierarchical CCO-NF possess promising potential to improve their electrochemical performance as electrode in LIBs.

Figure 5.6 N_2 adsorption/desorption isotherms of 1D CaCo_2O_4 nanostructures sintered at various temperature. Inset is the corresponding pore-size distribution.

5.2.2 Formation mechanism of hierarchical CCO-NT

As we all know, recent progress in nanotechnology have brought electrospinning to be a new technique to fabricate 1D nanostructures with unique morphologies, including hierarchical, porous, core/sheath or hollow structures. Besides, the preparation of these complex nanostructures commonly need to precisely control the spinning parameters or use specially designed spinnerets. Herein, we demonstrate that controlled thermal treatment and electrospinning can be combined to prepare hierarchical CCO-NF and the formation mechanism is systematically discussed, as shown in Figure 5.7. In this case, we noted that the composition of the fibers and thermal treatment procedure play a crucial role to determine the morphology of final products. The crystallization of metal oxides and decomposition of PVP simultaneously take place during calcination proceeded.

Moreover, the surface of the fibers begins to appear new features. When the sintering temperature is 550 °C, nanoplate-in-nanofiber structures can be generated because of the crystallization of metal oxides and the removal of PVP. Although, complete phase transition do not finish at this temperature, many nanoplate structures start to generate in the fibers due to the intrinsic platelike growth character of Ca-Co-based oxides, leading to the formation of nanoplate-in-nanofiber structures. Additionally, increasing the sintering temperature to 650 °C, the temperature is sufficiently high to ensure the generation of single phase CaCo_2O_4 . Nevertheless the continuous growth of nanoplates consumes nearby materials and ultimately produces spacing between the neighbouring plates, thus resulting in the novel hierarchical 1D nanostructures of CaCo_2O_4 . Similarly, above 750 °C, the growth of CaCo_2O_4 nanoplates are encouraged by the progressively increase in sintering temperature. Finally, the scaffold of the fiber is virtually damaged and eventually exhibit randomly distributed nanoplates. Therefore, the sintering temperature takes a great effect in controlling not only the morphology evolution but also the phase transition of CaCo_2O_4 1D nanostructures.

Figure 5.7 Schematic demonstration for the fabrication of 1D CaCo_2O_4 nanostructures sintered at different temperature.

5.2.3 Electrochemical studies

Figure 5.8 Electrochemical measurements of hierarchical CCO-NFs: (a) the initial four CV curves at scan rate 0.1 mV s^{-1} (b) charge/discharge curves at a current density of 100 mA g^{-1} .

Figure 5.9 The initial discharge-charge profile of the as-obtained three samples at the current density of 100 mA g^{-1} in the voltage range of $0.005\text{--}3.0 \text{ V}$.

To illustrate the effect of hierarchical CCO-NF (sintered at $650 \text{ }^{\circ}\text{C}$) in enhancing the electrochemical properties, the lithium storage properties of as-prepared samples as

electrode in LIBs are studied. Figure 5.8a presents the representative initial four CV curves of hierarchical CCO-NF evaluated at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.005–3.0 V. Evidently, the CV curves look similar with those of the Co_3O_4 nanostructures, implying that CaO molecules in CaCo_2O_4 can't take part in electrochemical reactions and play buffering matrix role to accommodate the volume variation during charge/dicharge process.^[157] Actually, during first cathodic scan, two reduction peaks can be clearly observed. The broad peak located at $\sim 1.36 \text{ V}$ may be attributed to a little amount of Li^+ built into the structure of CaCo_2O_4 before the collapse of the crystal structure. This is a commonly observed phenomenon in many other metal oxides.^[160, 165] Moreover, the prominent reduction peak centered at around 0.84 V corresponds to the reaction of lithium with CaCo_2O_4 to produce a mixture compound including CaO, Li_2O , and Co. While, in the following anodic scan, two broad oxidation peaks located at 1.92 V and 1.41 V can be related to the regeneration of Co_3O_4 and the formation of CoO, respectively. In the subsequent cycles, we found that the intensity of reduction peaks appears slightly increase, which is similar with previous reports.^[157, 160] From the third cycle onwards, the shape of CV curves maintain unchanged, suggesting that the electrochemical reactions possess excellent reversibility.

Subsequently, the discharge/charge properties of hierarchical CCO-NFs are further studied, as shown in Figure 5.8b. Consistent with the above CV results, the similar voltage plateau can be observed, that is the special feature of Co_3O_4 -based nanomaterial. Additionally, the discharge/charge behaviours of another two different samples were also investigated and almost identical electrochemical reaction mechanism can be identified, thus confirming that CaO can't take part in the electrochemical reaction and the redox reaction can't be influenced by the variation of morphologies (Figure 5.9). Specifically, hierarchical CCO-NF could deliver the first discharge/charge capacity of around $940 \text{ mAh g}^{-1}/637 \text{ mAh g}^{-1}$. The generation of the solid/electrolyte interface (SEI) film is the main reason for the first irreversible capacity loss. Surprisingly, Figure 5.8b shows that no obvious capacity fading can be observed, instead, it gradually gives rise to 744 mAh g^{-1} ($\sim 6.2 \text{ mol Li}$) even after 30 cycles. According to the conversion reaction, such value has exceeded its theoretical value (6 mol Li per formula unit). The reversible formation of electrochemical active polymeric gel-like film, which is caused by the electrolyte

degradation on the surface of active materials, might account for the excess capacities. Such phenomenon is also seen in many other transition metal oxides.^[166] Besides, a large deviation in potential can be clearly seen between charge and discharge profiles. This is because there is a large polarization related to ion transfer during cycling process, which is usually observed in many other metal oxide electrodes because of poor electrical conductivity.^[166, 167]

Figure 5.10 Cycling stability of 1D CaCo_2O_4 nanostructures (a) at current density of 100 mA g^{-1} (b) at different current density.

To deep insight into the superiority of such hierarchical nanostructures on the electrochemical properties of CCO-NF, comparative electrochemical measurements were performed to discover the cyclability of the as-prepared three different samples. Figure 5.10a exhibits the the Coulombic efficiency of hierarchical CCO-NFs and cyclability of the as-prepared three different samples between 0.005 – 3.0 V at a current density of 100 mA g^{-1} . Apparently, the hierarchical CCO-NF presents the best cycling stability and largest lithium storage capacity (650 mAh g^{-1} at 60 cycles) among the three samples. In contrast, only a relatively low capacity (463 mAh g^{-1} at 60 cycles) can be delivered by the sample sintered at $750 \text{ }^\circ\text{C}$, while the capacity loses severely (264 mAh g^{-1} at 60 cycles) for the sample sintered at $550 \text{ }^\circ\text{C}$. Although, the initial coulombic efficiency of hierarchical CCO-NF is relatively low, it rapidly increases in the following cycles and maintains at around 99.6% even up to 60 cycles. Significantly, Figure 5.10b shows that hierarchical CCO-NF presents much better rate capability compared to the two

counterparts. Specifically, a capacity as high as 382 mAh g^{-1} can be obtained by hierarchical CCO-NF even at high current density of 2 A g^{-1} , which is much larger compared to that of the sample sintered at 550°C (109 mAh g^{-1}) and the sample sintered at 750°C (206 mAh g^{-1}) at the same testing conditions. While, reducing the current density back to 150 mA g^{-1} , a high discharge capacity (564 mAh g^{-1}) still can be achieved. We need to pointing out that the discharge capacity of hierarchical CCO-NFs is still slight higher than that of commonly used graphite anode (372 mAh g^{-1}) even at the current as high as 2 A g^{-1} . Notably, Figure 5.11 shows that the hierarchical nanofibrous architecture of CCO-NF could be obviously found even after 60 cycles, illustrating the superior electrochemical performance of CCO-NFs.

Figure 5.11 FESEM images of (a) raw hierarchical CCO-NF electrode (b) electrode of hierarchical CCO-NF after 60 cycles. The inset shows the corresponding TEM image of hierarchical CCO-NF after 60 cycles. (It should be noted that the particles around the hierarchical nanofibers are conductive carbon black and PVDF binder).

In fact, the diffusion of lithium ion in active materials and interfacial charge transfer process has great impact on the cycling performance and rate capability. To achieve deep understanding on the electrochemical kinetic properties, EIS analysis for the as-obtained three samples are carried out on the cells after 20 cycles at room temperature (Figure 5.12a). Apparently, all the Nyquist plots compose of an inclined line in low frequency region and a depressed semicircle in the high and medium frequency zones. The impedance data are evaluated by fitting to an equivalent electrical circuit in Figure 5.12b and Figure 5.12c shows the fitting values which is calculated from the equivalent circuit. As observed, the semicircle corresponds to the combination of the charge transfer

impedance (R_{ct}) at the electrode surface and Li^+ migration impedance (R_{sf}) through the SEI film, while the inclined line can be assigned to the Warburg impedance relating to the solid-state diffusion of Li^+ into the bulk of active materials. In addition, hierarchical CCO-NF shows lower R_{sf+ct} value (28Ω) than that of the sample sintered at 550°C (92Ω) and the sample sintered at 750°C (70Ω), implying that the charge transfer impedance and SEI resistance remarkably decrease in hierarchical CCO-NF. Significantly, it is worth mentioned that the steeper tail of hierarchical CCO-NF in low frequency region suggests higher lithium ion conductivity in the electrode compared to that of the other two counterparts,^[168-170] ensuring much easier Li-intercalation kinetics. Hence, the novel hierarchical 1D configuration of CCO-NF is regarded as an important factor in enhancing the lithium storage properties of CCO-NF.

Figure 5.12 (a) Nyquist plots of the as-obtained samples at various temperatures as anodes, which are tested after 20 cycles (at delithiated state) at 100 mA g^{-1} ; (b) The equivalent electrical circuit applied to fit the experimental impedance data. The elements in the equivalent circuit consist of ohmic impedance of the cell components and electrolyte (R_e), charge transfer impedance and surface film resistance (R_{sf+ct}) at the interface of electrode and electrolyte, a constant phase element (CPE) used instead of pure capacitance because of the depressed semicircle, Warburg impedance (W); (c) Fitted impedance data acquired from Nyquist plots by using the circuit in Figure 5.12b.

Considering the superior cyclability and good rate capability, it is anticipated that the unique hierarchical CCO-NF is an excellent substitute as anode for advanced LIBs. We

believe that such novel hierarchical 1D configuration of hierarchical CCO-NF could account for its remarkable electrochemical performance. Specifically, the open space between the neighboring nanoplates definitely provides a pathway for fast penetration of electrolyte and helps to relieve the strain caused by huge volume variation during cycling process, thereby leading to the improved cycling stability. Moreover, the unique hierarchical architecture and well-organized 1D configuration are very crucial to eliminate the electrode pulverization issue and facilitate Li^+ diffusion, particularly benefiting to enhance the rate performance of hierarchical CCO-NF. Furthermore, the relatively large surface areas and the nanoplates subunits enable the reversible formation/dissolution of polymeric gel-like film on the surface of electrode, thus achieving high specific capacity. By virtue of all of these unique features, enhanced the battery's performance would be undoubtedly realized.

5.2.4 Summary

In summary, we have successfully fabricated hierarchical CCO-NF, which is built by thin nanoplates, through a facile and convenient electrospinning method followed by suitable thermal treatment. It is found that the morphology of 1D CaCo_2O_4 nanoarchitecture can be simply tuned by precisely controlling the sintering temperature. When served as anode for LIBs, hierarchical CCO-NF achieves superior cycling stability (650 mAh g^{-1} at 60 cycles at a current density of 100 mA g^{-1}) and excellent rate performance, demonstrating significantly enhancement over nanoplates-in-nanofibers and nanoplates structure. It is believed that the large specific surface area and the unique hierarchical 1D configuration could account for its intriguing electrochemical performance. These results presented here provide obvious evidence that the lithium storage properties of metal-oxide-based electrode could be optimized or enhanced by rationally designing the 1D nanoarchitecture with novel morphologies. Optimistically, it is expected that this versatile strategy shows huge potential to prepare innovative electrode materials with novel morphologies for energy related devices.

5.3 Porous NiCo_2O_4 Nanotubes (NCO-NT)[†]

Since electrospun CCO-NF (in section 5.2) and eggroll-like CSO-NT (in section 4.3) has shown promising electrochemical performance after combining inactive elements Ca with Co-based and Sn-based oxides, respectively. Although these results indicate that inactive matrix elements do have important effect on the electrochemical cyclability. Considering the gravimetric capacity, electrochemical active matrix elements like Ni has been regarded as superior host materials without sacrificing the overall capacity. This is because that they can react with Li by conversion reaction. With this in mind, NiCo_2O_4 1D nanostructures are constructed by using the same synthesis procedure to demonstrate the effect of A-site substitution in Co-based ternary oxides.

Remarkably, there is still no report about the preparation of 1D NiCo_2O_4 nanomaterials by electrospinning as well as their application as electrode for LIBs. Inspired by the high lithium storage properties of the 1 D electrospun nanostructures, in the present work, we illustrate a facile method of single-nozzle electrospinning followed by thermal treatment to prepare ternary 1D NiCo_2O_4 nanomaterials. The obtained porous NiCo_2O_4 nanotubes (denoted as NCO-NT) present 1D configuration with hollow interior and porous features. It is found that we can also obtain nanofibers and nanobelts by tuning the concentration of the precursor. Significantly, the as-obtained NCO-NT manifests large capacity, good cycling stability and superior rate performance. To the best of our knowledge, there is no report on the fabrication of electrospun NCO-NT as LIBs electrode. It is expected that our work demonstrate a facile and promising strategy for the preparation of structure-tunable metal oxides nanoarchitectures with improved battery performance, which can be potentially used in advanced energy storage devices.

5.3.1 Structure and morphology analysis

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Figure 5.13 (a) TGA curve of as-spun $\text{Ni}(\text{NO}_3)_2/\text{Co}(\text{NO}_3)_2/\text{PVP}$ composites nanofibers; (b) XRD pattern of NiCo_2O_4 after sintered at 550 °C for 2 h.

Figure 5.14 FTIR spectra of as-spun $\text{Ni}(\text{NO}_3)_2/\text{Co}(\text{NO}_3)_2/\text{PVP}$ nanofibers, porous NCO-NT.

Figure 5.13a shows the TGA analysis results, which was conducted to explore the suitable sintering temperature for as-spun precursor nanofibers. The initial 8.7% weight loss

before 200 °C could be assigned to the decomposition of crystal water in the metal nitrate, the removal of residual solvent and absorbed moisture. The sharp peak at around 262 °C is related to the decomposition of metal nitrate, while the obvious inclination at 390 °C can be attributed to the elimination of PVP. It should be mentioned that no more weight loss occurs at the temperature ranging from 410 to 500 °C, indicating the complete decomposition of metal precursor and thoroughly removal of PVP polymer. Further increasing the temperature, a peak at about 506 °C is detected, relating to the partial decomposition of NiCo_2O_4 and the generation of NiO .^[171] Moreover, the XRD results in Figure 5.13b suggests that NiO presents in the products after sintering at 550 °C. Hence, sintering temperature of 450 °C could be employed on the as-spun precursor nanofibers in order to form the pure phase of NiCo_2O_4 and thoroughly removal of PVP.

Figure 5.15 (a) crystal structure of NiCo_2O_4 ; (b) Rietveld refined XRD pattern of NiCo_2O_4 calcinated at 450 °C for 2 h.

FTIR spectroscopy was applied to prove the disappearance of PVP in NiCo_2O_4 after sintering at 450 °C by investigating the molecular structural changes (Figure 5.14). For the as-spun precursor nanofibers, the peaks centered at 3446 cm^{-1} and 1652 cm^{-1} could be interpreted as the vibrations of $-\text{OH}$ groups for the residual ethanol solvent or absorbed water. The bands located at 2963 cm^{-1} and 1384 cm^{-1} corresponds to C–H bending and stretching modes owing to the existence of PVP. The band centered at 1291 cm^{-1} can be

ascribed to the tertiary amine group of PVP. After sintering at 450 °C for 2 h, the bands, which belonged to PVP, disappeared, instead, two peaks located at 668 and 563 cm^{-1} present which might derive from the metal–oxygen M–O vibrations of NiCo_2O_4 .^[172, 173] Thus, this demonstrates sintering at 450 °C of as-spun precursor nanofibers leading to the simultaneously elimination of PVP and crystallization of NiCo_2O_4 nanocrystallites.

Figure 5.16 EDX spectrum of porous NCO-NT.

Figure 5.15a shows that NiCo_2O_4 possesses the spinel structure (space group $\text{Fd}\bar{3}\text{m}$) with Co atoms located at both tetrahedral and octahedral sites and Ni atoms centered at the octahedral sites. It is found that the edge-sharing octahedral establish a 3D network of tunnels for ions diffusion. The XRD pattern in Figure 5.15b, which presents the phase information and crystallinity of the product, also demonstrates the formation of the pure phase NiCo_2O_4 . All the peaks can be readily assigned to cubic NiCo_2O_4 with a spinel structure (JCPDS card no. 73-1702, $a = 8.114 \text{ \AA}$). No impurities could be observed. The lattice parameters of NiCo_2O_4 evaluated by Rietveld refinement are $a = 8.130 \text{ \AA}$, matching well with $8.114 \text{ \AA}$. Additionally, the EDX analysis is also in good agreement with the

XRD results (Figure 5.16). Moreover, the XRD result match well with TGA and FTIR studies, demonstrating the formation of single phase NiCo_2O_4 under such conditions.

Figure 5.17 (a) SEM images of as-spun $\text{Ni}(\text{NO}_3)_2/\text{Co}(\text{NO}_3)_2/\text{PVP}$ composites nanofibers with $\text{M} : \text{PVP} = 0.61 : 1$ at a low magnification and the inset shows high magnification; (b) SEM images at different magnification; (c) TEM images at different magnification; (d) corresponding HRTEM image; (e) SAED pattern; (f) EDX image of porous NCO-NT.

The detailed structural information and morphology was analyzed by SEM and TEM. Figure 5.17a shows the continuous as-spun precursor nanofibers with smooth surface and

uniform diameter of around 250 nm. After sintering in air at 450 °C for 2 h, the inset of Figure 5.17b clearly displays that the continuous 1D fibrous structure can be well inherited. Interestingly, a close observation in Figure 5.17b indicates that NiCo_2O_4 1D nanostructures, which is sintered at 450 °C for 2 h, present tube-like architecture with smaller diameters of around 100 nm and a variety of nanopores could be identified on the surface of the nanotubes. The obvious shrinkage in diameter is interpreted as the decomposition of metal precursors and the removal of PVP. To deep understanding the microstructure and morphology of the porous NCO-NT, we carried out TEM analysis. The obvious contrast between the light centre and dark edge clearly exhibits the well-defined tube-like structure, which is consistent with the SEM analysis (Figure 5.17c). Moreover, it can be seen that the wall thickness of porous NCO-NT is around 33 nm. Figure 5.17d exhibits that the wall of the nanotube is composed of numerous NiCo_2O_4 nanocrystals with size of around 10 nm and meanwhile a variety of pores can be observed with diameter of around 3 – 10 nm. The HRTEM image presents the lattice fringe with an interplanar distance of around 0.469 nm, in consistent with the spacing of the (111) plane of NiCo_2O_4 (Figure 5.17e). Figure 5.17f shows the SAED pattern with the well-defined rings, which corresponds to the (440), (224), (311), (111), (220) and (400) planes, suggesting that they are polycrystalline with the d-spacing in good agreement with the XRD analysis.

Figure 5.18 SEM images of as-spun $\text{Ni}(\text{NO}_3)_2/\text{Co}(\text{NO}_3)_2/\text{PVP}$ composites nanofibers with (a) $\text{M} : \text{PVP} = 0.44 : 1$, (b) $\text{M} : \text{PVP} = 0.87 : 1$.

Figure 5.19 (a) SEM images at different magnification, (c) TEM images and (e) HRTEM images of NCO-NF. (b) SEM images at different magnification, (d) TEM images and (f) HRTEM images of NCO-NB.

Electrospinning process is very intricate. This is because many factors, including electrospinning parameters (solution feed rate, working distance and applied voltage), the concentration of metal precursor (denoted as M concentration), the type of polymer, and viscosity of precursor solution, have an important impact on the diameters, size distributions and morphologies of NiCo_2O_4 1D nanoarchitectures. In the present work, to

gain deep insight into the morphology evolution of the 1D NiCo_2O_4 nanoarchitecture, a series of M concentration-dependent experiments were carried out and NiCo_2O_4 nanofibers (denoted as NCO-NF) and NiCo_2O_4 nanobelts (denoted as NCO-NB) can be prepared by precisely tuning the weight ratios of M concentrations over PVP from 0.87 : 1 (NCO-NB) to 0.44 : 1 (NCO-NF). Importantly, we propose a possible formation mechanism to demonstrate the evolution of the 1D NiCo_2O_4 nanoarchitectures.

Figure 5.20 XRD patterns of NCO-NF and NCO-NB. The results confirm the formation of NiCo_2O_4 in both cases.

Figure 5.18a and b reveal the fibrous structure of the as-spun precursor nanofibers with various weight ratios of M : PVP, in which continuous nanofibers with smooth surface and uniform diameter are presented in both cases. After sintering at 450 °C for 2 h, when the weight ratio of M : PVP is 0.44 : 1, the fibrous structure of NiCo_2O_4 can be retained, as shown in Figure 5.19a and its inset. Besides, it can be seen that the average diameter of NCO-NF is around 89 nm with the length up to several micrometers. Figure 5.19c shows

the TEM image of NCO-NF with clearly observed nanoparticulate interconnected fibrous morphology, which further confirms the SEM results. Moreover, NiCo_2O_4 phase (JCPDS: 73-1702) can be found in the corresponding HRTEM image in Figure 5.19e. And the SAED pattern indicates that NCO-NF is polycrystalline (inset in Figure 5.19e). When the weight ratio of M : PVP is increased to 0.87 : 1, resulting in the formation of NCO-NB owing to the completely rupture of the interior hollow structure (Figure 5.19b and its inset). Similarly, the formation of solid belt-like structures of NCO-NB is further confirmed by the TEM results in Figure 5.19d. Additionally, the nanoparticles around the nanobelts also indicate the collapse of hollow structures. Meanwhile, the corresponding HRTEM image and SAED pattern (Figure 5.19f and its inset) further confirm the formation of NiCo_2O_4 phase (JCPDS: 73-1702). Moreover, the XRD pattern of NCO-NF and NCO-NB in Figure 5.20 also demonstrates the existence of NiCo_2O_4 and no detectable impurity phase, indicating the variation of M concentration without influences on the formation of NiCo_2O_4 single phase.

Figure 5.21 (a) N_2 adsorption/desorption isotherms and (b) corresponding pore-size distribution of NCO-NF, NCO-NT and NCO-NB.

Notably, both NCO-NF and NCO-NB also clearly display the porous feature. Thus, in order to distinctly demonstrate their porous feature, the N_2 adsorption/desorption isotherm of the as-obtained samples is shown in Figure 5.21a to investigate the textural properties and porosity. All of the adsorption/desorption isotherms looks quite similar in appearance

and can be defined as type IV isotherms with H3 hysteresis loops, which demonstrate that the as-obtained sample possess typical mesoporous structure. Moreover, the inset in Figure 5.21b exhibits the Barrett-Joyner-Halenda (BJH) pore size distribution data, which further confirms the mesoporous structure of the as-obtained samples. The pore distribution is relatively narrow, and mainly located in the range of 5 – 25 nm. Furthermore, The porous NCO-NT possesses a much larger BET surface area and total pore volumes (around $36.9 \text{ m}^2 \text{ g}^{-1}$ and $0.22 \text{ cm}^3 \text{ g}^{-1}$), compared to those of NCO-NF ($\sim 16.1 \text{ m}^2 \text{ g}^{-1}$ and $0.06 \text{ cm}^3 \text{ g}^{-1}$) and NCO-NB ($\sim 12.7 \text{ m}^2 \text{ g}^{-1}$ and $0.05 \text{ cm}^3 \text{ g}^{-1}$). Therefore, the larger surface area of NCO-NT can be related to the higher total pore volume and novel hollow tubular nanoarchitecture. The unique porous nanotube configuration with high surface area can be regarded as a very suitable candidate for application in LIBs and possesses great potential to further enhance their electrochemical properties, because these novel structures play very critical part in facilitating the ions and electrons transportation.^[174, 175]

5.3.2 Formation mechanism

As we all know, by rationally adjusting the electrospun parameters, we can obtain 1D nanostructures with various morphologies, including ribbons, belts and tubes. Additionally, the decomposition of PVP polymer and the rapid evaporation of solvent during thermal treatment process also have significant effect on the morphology of the electrospun products. Herein, according to the experimental data, we propose a possible formation mechanism for the NCO-NT, which is depicted in Figure 5.22. Initially, a gel layer can be gained on the surface of the electrospun precursor nanofibers because of the solvent evaporation during the electrospinning procedure. Generally, a thinner gel layer would form because the amount of metal precursor is not enough, and if we increase the amount of metal precursor, leading to the formation of thicker gel layer.

This layer plays a crucial part in keeping the fibrous texture during thermal treatment.^[172] Besides, two opposite factors have important influence on the formation of NiCo_2O_4 nanotubes during thermal treatment process. One is the shrinkage of the composite nanofibers, leading to the generation of solid nanofibers, and the other is the diffusion of

the gas generated from the decomposition of PVP, which promote the expansion of the composite nanofibers to develop tube-like structure.^[141] Thus, in this case, whether the tube-like structure can be built or not, strongly depend on the composite of fibers. On the one hand, when the rate of gas diffusion across the surface of the fibers is smaller than that of gas evaporation inside the fibers, the pressure outside of the fibers is smaller than the inside of the fibers, leading to the generation of tube-like structure of NiCo_2O_4 . On the other hand, the decrease of the amount of metal precursor leads to the decrease in the thickness of surface gel layer, thus, the hollow structure could not be maintained, resulting in the generation of solid structure of NiCo_2O_4 . In contrast, a very thick gel layer would be built by increase the amount of metal precursors, consequently, leading to the generation of solid belt-like structure of NiCo_2O_4 . This may be due to the very thick layer could efficiently prohibit the diffusion of gas from the inside toward the outside of composite fibers. Thus, by precisely controlling the M concentration, fiber-like, tube-like and belt-like NiCo_2O_4 can be prepared.

Figure 5.22 Schematic demonstration for the fabrication of NCO-NF, NCO-NT and NCO-NB.

5.3.3 Electrochemical studies

In consideration of functional nanomaterials with unique porous hollow structures beneficial for the use as electrode in LIBs, the lithium storage properties of as-obtained 1D NiCo_2O_4 nanostructures was investigated as anode for LIBs. Figure 5.23a gives the initial three consecutive CV of the electrode prepared from porous NCO-NT at a scan rate of 0.1 mV s^{-1} in the voltage range of $0 - 3.0 \text{ V vs. Li/Li}^+$. Three cathodic peaks can be observed in the first cathodic scan. The broad peak located at $\sim 1.35 \text{ V}$ may be related to the crystal structure destruction or amorphization, which is notably distinguished from the other cycles. The prominent peak centered at $\sim 0.95 \text{ V}$ could be interpreted as the reduction of Ni^{2+} and Co^{3+} to metallic Ni and Co, respectively. Besides, the minor peak located at 0.73 V can be attributed to the generation of solid-electrolyte interface (SEI) film. In the following anodic scan, two oxidation peaks observed at around 1.4 V and 2.1 V correspond to the oxidation of metallic Co and Ni to Co oxides and Ni oxides, respectively.^[176, 177] The characteristic redox peaks of around 1.0 and around $1.4/2.1 \text{ V}$, which can be interpreted as the reduction/oxidation of Ni oxides and Co oxides, can be clearly observed in the second cycle.^[85] From the second cycle onwards, the CV profiles maintain unchanged, which suggests that the electrochemical reactions possess outstanding reversibility.

Figure 5.23 Electrochemical characterization of porous NCO-NT (a) first three CV curves and (b) discharge/charge profiles of the 1st, 2nd, and 3rd cycles.

Figure 5.23b shows the characteristic discharge/charge curves of the as-obtained porous NCO-NT electrode, which is measured at a current density of 100 mA g^{-1} . The initial discharge/charge capacity is 1722.5 ($\sim 15.5 \text{ mol of Li}$)/ $1442.6 \text{ mAh g}^{-1}$ ($\sim 12.9 \text{ mol of Li}$), respectively. Additionally, there is a large irreversible capacity loss in the first cycle, which can be ascribed to the generation of SEI film. Surprisingly, it is found that the first charge capacity overpasses the theoretically delivered 8 mol Li , which is on the basis of the conversion reaction. The reversible formation/dissolution of polymeric gel-like film, which originates from the electrolyte decomposition, might be the main reason.^[85, 166] Moreover, a large potential difference between charge and discharge profiles can be distinctly observed. Such phenomenon can be attributed to the electrode polarization, which can be related to ion transfer during electrochemical cycling and be commonly seen in other transition metal oxides.^[167]

Figure 5.24 Cycling performance of 1D NiCo_2O_4 nanostructures (a) at current density of 100 mA g^{-1} (b) at different current density.

In order to deep understanding the superiority of NCO-NT as electrode for LIBs, comparative electrochemical measurement were carried out to study their cycling performance and rate capability of NCO-NF, NCO-NT and NCO-NB under the same condition. Figure 5.24a presents the cycling behaviour of NCO-NF, NCO-NT and NCO-NB in the voltage range of $0.005 - 3.0 \text{ V}$ at current densities of 100 mA g^{-1} . As predicted, NCO-NT demonstrates superior cycling performance over NCO-NF and NCO-NB. Moreover, we can clearly see that the discharge capacities of NCO-NT delivered for the

first and second cycles are 1722 and 1456 mAh g^{-1} , respectively. After 100 cycles, the discharge capacity can be retained at 1245 mAh g^{-1} , which corresponds to $\sim 85\%$ of the second discharge capacity (1456 mAh g^{-1}). However, the capacity retention of NCO-NF and NCO-NB is only 51% and 42%, respectively. Thus, these demonstrate that a superior nanoarchitecture (including morphology and inner structure) is beneficial for enhancing battery performance. More significantly, it suggests that such porous hollow nanotube configuration is definitely helpful for the real use of NiCo_2O_4 anode in LIBs.

Figure 5.25 Nyquist plots of the as-obtained NCO-NF, NCO-NT and NCO-NB (all bare electrodes under OCV).

The high rate performance of electrode material is a critical factor for LIBs, owing to reduce lots of discharge/charge time in the actual application. Therefore, we investigate the rate capability of as-obtained NiCo_2O_4 1D nanostructures, as shown in Figure 5.24b. Benefiting from the novel configuration, the porous NCO-NT presents remarkable cycling stability at various current densities. Even at high current density as high as 2 A g^{-1} , a discharge capacity of around 700 mAh g^{-1} still can be achieved, that is almost 1.8 times of commercially used graphite (372 mAh g^{-1}). When the current density is set back to 400

mA g^{-1} , and an average discharge capacity of $\sim 883 \text{ mAh g}^{-1}$ can be recovered. Apparently, NCO-NF and NCO-NB exhibit poor rate capability compared with NCO-NT. Therefore, it indicates that the excellent rate performance illustrates that the porous NCO-NT have promising potential as advanced electrode for LIBs.

Actuary, it is well-accepted that the Li^+ diffusion and interfacial charge-transfer process play a critical role to determine the cycling performance and rate capability. To get deep understanding on the transport kinetics for the lithium storage procedure, the EIS of NCO-NF, NCO-NT and NCO-NB, which have been proved as a useful and important tool to study the kinetics of Li^+ inserted into the electrodes, were performed. The impedance spectra of all bare electrodes under OCV (Figure 5.25) compose of two partially overlapped semicircles in the high and medium frequency region and an inclined line in the low-frequency domain. Generally, the semicircles in the high frequency region can be related to the combination of the charge-transfer resistance ($R_{\text{sf+ct}}$) and the surface film impedance, while the linear zone can be interpreted as the Warburg impedance (W) reflecting the solid-state diffusion of Li^+ into the bulk of the active materials. Apparently, the porous NCO-NT possesses apparently lower interface impedance and surface charge transfer resistance compared to NCO-NF and NCO-NB, suggesting the faster Li intercalation kinetics. Besides, it is worth pointing out that the steeper tail of NCO-NT in the low-frequency region suggests higher lithium-ion conductivity in the electrode than that of the other two counterparts, ensuring much easier Li-intercalation kinetics. Hence, these results further confirm the better capacity retention and rate capability of NCO-NT, and also indicate the advantages of porous hollow tubular structure.

A high specific capacity with improved cycling performance and excellent rate capability can be obtained in our work by engineering the nanostructure of NiCo_2O_4 . We believe that the superior electrochemical properties of NCO-NT could be probably attributed to the novel porous tubular configuration and higher surface areas. Specifically, the 1D porous feature of NCO-NT is in favor of the rapid Li^+ and electrons transportation because of their efficient transport pathways, thereby improving the electrochemical kinetics. Remarkably, the hollow tubular configuration of NCO-NT not only serves as “ion-buffering reservoirs” of Li ions, minimizing the diffusion distance to the interior interface, but also buffers the volume variation deriving from the high rate of insertion and

extraction of Li ions. In addition, the relatively large specific surface areas enlarge the interface between the electrolyte and electrode, and thus providing more active sites for fast electrochemical reactions.

5.3.4 Summary

In summary, porous NCO-NT were fabricated successfully via a simple and versatile electrospinning method. The superiority of this strategy is that the morphologies of NiCo_2O_4 1D nanoarchitectures could be controlled by precisely tuning the precursor concentrations, which are crucial for the formation of porous NCO-NT. Such unique configuration of porous NCO-NT not only benefits fast Li^+ and electrons transportation but also buffers the volume variation during Li^+ insertion/extraction processes. It illustrates that the unique NCO-NT anode manifests a large specific capacity (1722 mAh g^{-1} at 100 mA g^{-1}), outstanding rate capability and remarkable cycling stability (85% loss after 100 cycles), which can be used as an advanced anode materials for LIBs. These results also demonstrate that metal oxides nanocomposites electrode materials with enhanced battery performances could be obtained by rationally controlling of 1D nanostructures with novel morphologies and advanced configuration. It is also worth mentioned that this versatile strategy could be extended to the preparation of other electroactive materials with properly designed morphologies.

5.4 Introduction Effect of A-site substitution in ACo_2O_4

In this section, we aim to understand the influence of A-site substitution on the battery performance in ACo_2O_4 . Herein, the comparison is based on the batteries results of electrospun hierarchical CCO-NF (in section 5.2) and porous NCO-NT (in section 5.3), and the data is summarized in Table 5.1.

Table 5.1 The comparison of electrochemical properties of hierarchical CCO-NF with porous NCO-NT.

Sample	BET surface area (m ² g ⁻¹)	Initial discharge/charge capacity (mAh g ⁻¹)	60 th discharge capacity (mAh g ⁻¹)
CCO-NF	35.7	940/637	650
NCO-NT	36.9	1722/1442	1264

Clearly, by simply using electrochemical active elements Ni to replace inactive element Ca, both the specific capacity and cycling stability of NiCo₂O₄ anode exhibit remarkable improvement compared to CaCo₂O₄ anode. As reversible capacity is an important factor to choose anode materials for LIBs, so active matrix element Ni is a more superior and attractive counter ion in ACo₂O₄ system than inactive matrix element Ca. The excellent electrochemical performance of NiCo₂O₄ anode can be related to the following reasons. Specifically, the significant feature of combining matrix elements in ACo₂O₄ anodes system is the improved cycling stability. This is because the uniformly dispersed matrix in the anode system could efficiently accommodate the huge volume changes of active materials and avoid aggregation of nanosized particles, thus resulting in good cycling performance.^[35, 158] However, if the matrix element is no electrochemical activity, this implies that the enhanced cycling stability is based on the sacrificing the specific capacities of anodes. While, in the NiCo₂O₄ system, Ni not only possesses high electrochemical activity but also guarantees good electric conductivity owing to the uniformly dispersed metallic Ni and Co particles during cycling process.^[32, 178] All of these would definitely lead to improved cycling stability and rate capability without sacrificing the specific capacity.

Chapter 6 Fundamental Studies of Ternary Metal Oxides (AB_xO_y)

6.1 Reaction Mechanism of as-prepared AB_xO_y

As ternary metal oxides (AB_xO_y) plays important role in LIBs applications. It is crucial to determine their interaction towards Li^+ during cycling process. In this section, *ex-situ* studies by using XRD, XPS, and EIS, were performed to investigate the detailed interaction between as-prepared electrospun products and lithium ions. Accordingly, the reaction mechanism was proposed.

6.1.1 Eggroll-like CSO-NT

Figure 6.1 *Ex-situ* XRD pattern of electrospun eggroll-like CSO-NT electrode on Cu foil (a) discharged and (b) charged to specific cutoff voltage during first cycle.

To understand the reaction mechanism of eggroll-like CSO-NT anode with Li^+ , the *ex-situ* XRD pattern and EIS of cycled electrodes were collected, as shown in Figure 6.1 and Figure 6.2. Any obvious reduction/oxidation peaks appeared in the CV curve indicates the involvement of active materials in taking/releasing lithium ions. Thus, according to the CV curve of eggroll-like CSO-NT (Figure 4.25), the electrodes were proposed discharge

to specific cut off voltage.

Figure 6.1a exhibits the *ex-situ* XRD pattern of eggroll-like CSO-NT electrodes at fresh, 0.7, 0.2 and 0.005 V during first discharge. Interestingly, characteristic peaks that belonged to CaSnO_3 appear no obvious structural variation at 0.7 V except to the decrease in the peak intensity, indicating that the crystal structure is starting to destruction under such condition. In addition, when discharging to 0.2 V, only small amount of peaks could be observed, implying that the alloying reaction is in the process. Further discharging to 0.005 V leads to the completely irreversible amorphization of CaSnO_3 nanostructures, thus no peak could be found. While, there are no presence of any crystalline products during charging process (Figure 6.1b).

Figure 6.2 Nyquist plots of electrospun eggroll-like CSO-NT electrode (a) discharged and (b) charged to different cutoff voltage during first cycle.

EIS as a powerful tool was usually applied to determine the electrode reaction kinetics. Herein, some significant results were provided by EIS to correlate the *ex-situ* XRD data. According to the impedance spectrum in Figure 6.2a, the impedance spectra of fresh electrode composed by a single semi-circle and inclined line. Both the charge transfer and surface film result in the total resistance. As the discharge reaction proceeds to 0.7 V, the spectra presents remarkable changes and two semi-circles can be observed. The first one corresponds to the combination of charge transfer and surface film impedance, while the second one can be ascribed to the bulk impedance, which is developed due to the crystal

structure destruction and generation of SEI film. As can be expected, the impedance exhibits declining trend and remains nearly constant at below 0.7 V, suggesting the generation of Li-Sn alloy and Sn-metal takes place in the range of 0.7 – 0.005 V. This is consistent with the CV and galvanostatic profile during first discharge (Figure 4.25). Figure 6.2b shows impedance spectrum during initial charging process. The remarkable decrease in the impedance, when charging voltage increases from 0.55 to 1.28 V, could be interpreted as the dealloying of Li-Sn alloy and formation of Sn particle. Based on all the above results, and meanwhile considering that CaO is an electrochemically inactive matrix during cycling process, the reaction mechanism of eggroll-like CSO-NT with Li can be proposed as follow:

6.1.2 Hierarchical CCO-NF

Figure 6.3 *Ex-situ* XRD pattern of electrospun hierarchical CCO-NF, which is scratched from Cu foil, (a) discharged and (b) charged to specific cutoff voltage during first cycle.

Up to data, there is still no available report to clearly elucidate the reaction mechanism of CaCo_2O_4 anode with lithium ions. To gain a deep understanding, *ex-situ* XRD, XPS, and EIS were conducted on the hierarchical CCO-NF electrodes, which were purposely

discharged or charged to various cut-off voltages.

Figure 6.4 *Ex-situ* XPS spectra of electrospun hierarchical CCO-NF, which is scratched from Cu foil, (a, b) discharge to 0.84 V; (c, d) discharge to 0.005 V.

Generally, the crystal structure of Co-based oxides is destroyed accompanied by the reduction of metal oxides to metallic particles during first discharge, which has been observed in CoO and Co₃O₄. To verify the above assumption in the case of CaCo₂O₄, further research was carried out, as shown in Figure 6.3 (XRD), Figure 6.4 and 6.5 (XPS), and Figure 6.6 (EIS). Figure 6.3a shows the XRD pattern of hierarchical CCO-NF electrodes at different discharged state. Nevertheless, the XRD pattern of electrode discharged to 1.36 V is almost identical with the fresh electrode, implying that there are no electrochemical reactions initiated till 1.36 V. However, any compound peaks are devoid when the electrode discharge to 0.84 V, demonstrating that the structure

destruction occurs at 1.36 – 0.84 V. This also match well with the galvanostatic profiles (Figure 5.8) where the prolonged voltage plateau centers at ~ 1.0 V, suggesting the two-phase region. In addition, any peak corresponding to metallic Co and CaO in the XRD pattern could not be observed when the electrode discharge to 0.84 and 0.005 V, which is mainly because of the nanoparticle nature of the electrochemically *in-situ* generated species. Similarly, any peaks could not be found from the XRD pattern of charged electrode (first charge to 3.0 V) in Figure 6.3b, thus confirming that the oxidized-electrode constituents also exist in the form of nano-size, and the original structure of CaCo_2O_4 , once destroyed during the initial discharge, could not be re-formed during charging process.

Figure 6.5 *Ex-situ* XPS spectra of electrospun hierarchical CCO-NF, which is scratched from Cu foil, (a, b) charge to 1.92 V; (c, d) charge to 3.0 V.

During the re-oxidation process of metallic Co nanoparticles, it can be oxidized to either Co^{2+} or Co^{3+} , which are determined by the reaction efficiency. However, it is out of scope of XRD to detect the valence state of Co. Thus, *ex-situ* XPS was employed to identify the phase transition during first cycle (Figure 6.4 and 6.5). The XPS spectra of cycled electrodes, which first discharged/charged to specific voltage reveals that both Co^{2+} and Co^{3+} co-exist in the mixture. The $\text{Co}^{2+}/\text{Co}^{3+}$ present in the discharged electrode at 0.005 V, mainly due to the inevitable oxidation of metallic Co nanoparticle during *ex-situ* testing procedures. More importantly, the XPS spectra of Ca remains unchanged during cycling process, further suggesting that it serves as inactive matrix elements and do not take part in electrochemical reactions.

Figure 6.6 Nyquist plots of electrospun hierarchical CCO-NF (a) discharged and (b) charged to different cutoff voltage during first cycle.

Impedance measurements on the discharged/charged electrode at different cut-off voltages could give information on the electrochemical reaction mechanism. Figure 6.6a shows the impedance spectra of hierarchical CCO-NF during first discharge. As seen at 1.36 V, the crystal structure destruction and the generation of insulated CaO and Li_2O lead to the increase in the impedance. While further discharge to 0.84 and 0.005 V, the diameter of semi-circle reduced enormously, suggesting remarkable decrease in the resistance values. The formation of more and more metallic Co nanoparticles during discharging process could account for it. As expected, the changes in the Nyquist plots during first charged to 1.41 and 1.92 V are barely discernible (Figure 6.6b). However, further charged to 3.0 V,

the conversion from Co nanoparticle to Co oxides causes the increase in the impedance. Based on the analysis above, lithium storage mechanism related to Li^+ insertion/extraction procedures are regarded as follows:

6.1.3 Porous NCO-NT

Figure 6.7 *Ex-situ* XRD pattern of electrospun porous NCO-NT, which is scratched from Cu foil, (a) discharged and (b) charged to specific cutoff voltage during first cycle.

Since Ca, as an inactive matrix element, rendered Co-based anode with good battery performance. A simple substitution of Ca by Ni, electrospun porous NCO-NT presents enhance cycling stability compared to hierarchical CCO-NF. Importantly, Ni, as an active matrix element, plays significantly different role with Ca in electrochemical cycling process. Therefore, gaining better insight into the reaction mechanism of porous NCO-NT is necessary and significant. So, *ex-situ* XRD, XPS, and EIS were conducted to discern the detail interaction between the NiCo_2O_4 with Li^+ .

Figure 6.7a shows the XRD pattern of porous NCO-NT at different discharge states. The representative peaks observed from fresh electrode still exist at 1.35 V and disappear at

0.95 V. This demonstrates that the amorphization of the lattice occurs below 1.35 V, also corroborating the CV and galvanostatic cycling results (Figure 5.23). Further discharge to 0.73 and 0.005 V, the low intensity peaks may be related to some Ni or Co oxides. Similar with CaCo_2O_4 , any peaks belonged to NiCo_2O_4 could not be found from the charged electrode at 3.0 V (Figure 6.7b), thus affirming that the original crystal structure of NiCo_2O_4 could not be re-formed upon charging.

Figure 6.8 *Ex-situ* XPS spectra of electrospun porous NCO-NT, which is scratched from Cu foil, (a, b) discharge to 1.35 V; (c, b) discharge to 0.73 V.

Similarly, XPS were also carried out on the cycled electrodes of porous NCO-NT to further corroborate the XRD results (Figure 6.7). Interestingly, the valence states of Ni and Co exhibit variation during discharge/charge process, implying that both Ni and Co could participate in the electrochemical reaction and they play “self-matrix” roles to buffer the volume variations and prohibit the aggregation of active materials, thereby

enhancing the cycling stability. Meanwhile, it can be found that Ni^{2+} and Co^{2+} coexist in the discharged electrodes (Figure 6.8), while Co^{3+} could also be found in the charged electrode at 3.0 V (Figure 6.9).

Figure 6.9 *Ex-situ* XPS spectra of electrospun porous NCO-NT, which is scratched from Cu foil, (a, b) charge to 1.4 V; (c, d) charge to 3.0 V.

Next, EIS was performed to complement the above studies. The impedance data, which is collected at selected voltage, is shown in Figure 6.10. The Nyquist plot of fresh electrode (Figure 6.10a) exhibits a semi-circle in the high frequency range, followed by an inclined line corresponding to Warburg region. While the spectrum at 1.35 V remains unchanged in the spread of semi-circle. This is because the crystal structure of porous NCO-NT could not be destroyed, which is consistent with *ex-situ* XRD results. Discharge to 0.95 and 0.73 V, the spectrum presents prominent change and the spread of the semi-circle increases, marking that the destruction of structure takes place and accompanied by the generation of

insulated metal oxides and Li_2O . Further discharge to 0.005 V, the impedance appears significant decrease. This is because more and more metallic Co and Ni nanoparticles are being generated, thereby bringing down the cell resistance. In addition, the impedance spectrum in the charging process shows continuous increase, mainly due to the oxidation of metallic Co and Ni to Co and Ni oxides, respectively.

Figure 6.10 Nyquist plots of electrospun porous NCO-NT (a) discharged and (b) charged to different cutoff voltage during first cycle.

Based on the analysis above and together with previous reports,^[85, 177] the involved electrochemical reactions for the as-prepared porous NCO-NT electrode can be believed to proceed as follows:

6.2 Lithium Diffusion Studies in as-prepared AB_xO_y

To gain deep insight into the electrochemical characteristics, lithium diffusion studies were performed on the as-prepared electrospun ASnO_3 and ACo_2O_4 . As an important tool, CV measurement at different scan rate was used to determine the lithium diffusion

coefficient, which could be calculated by Randles-Sevcik equation (equation 3.1). Herein, assuming that the Li intercalation reaction mainly occurs by the solid-state diffusion of lithium ions and meanwhile, for consistency, the peak current of the main oxidation peak in the CV are used and plotted against the square root of the scan rate for different materials.

6.2.1 Lithium diffusion studies in ASnO_3 ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$)

Figure 6.11 CV curves of electrospun (a) eggroll-like CSO-NT, (b) SrSnO_3 , (c) BaSnO_3 at various scan rate; (d) peak current vs. $v^{1/2}$.

Figure 6.11 a, b, and c give the CV curves of eggroll-like CSO-NT, SrSnO_3 , and BaSnO_3 at various scan rates, respectively. Overall, it can be clearly seen that eggroll-like CSO-NT possesses larger current density than that of two counterparts, confirming a relatively

higher specific capacities. Moreover, there are two pairs of redox peaks for all the electrodes. This means of a two-stage Li^+ intercalation\deintercalation reactions, which matches well with the two-plateau of charge\discharge profile. Furthermore, the two redox pair appears difficult to distinguish with the increase of scan rate, which is mainly caused by the prominent electrochemical polarization.

Besides, good linear relationship between I_p and $v^{1/2}$ can be observed for all the investigated ASnO_3 samples (Figure 6.11d), further confirming that Li diffusion is controlled by solid-state diffusion. The determined value of lithium diffusion coefficients for eggroll-like CSO-NT , SrSnO_3 , and BaSnO_3 are 3.5×10^{-8} , 1.1×10^{-8} , and $8.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, respectively. Obviously, eggroll-like CSO-NT possesses largest D_{Li} compares with SrSnO_3 and BaSnO_3 , which mainly comes from their different crystal structure, crystalline size, as well as morphologies. As a result, eggroll-like CSO-NT benefits of faster Li^+ intercalation kinetics.

6.2.2 Lithium diffusion studies in ACo_2O_4 ($\text{A} = \text{Ca}, \text{Ni}$)

Figure 6.12 CV curves of electrospun (a) porous NCO-NT and (b) hierarchical CCO-NF at various scan rate.

Similarly, CV analysis was used to understand the enhanced performance of porous NCO-NT and hierarchical CCO-NF. Figure 6.12 shows the comparative CV curves of both samples at various scan rates. Notably, at the same scan rates, the porous NCO-NT shows

significantly higher peak current density than that of hierarchical CCO-NF, indicating the largely improved reactivity.

In addition, a good linear relationship between I_p and $v^{1/2}$ for both porous NCO-NT and hierarchical CCO-NF could be observed from Figure 6.13. The diffusion coefficient (D_{Li}) in the porous NCO-NT is calculated to be $4.1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. In comparison, the D_{Li} value for hierarchical CCO-NF exhibits a relatively lower value of $1.8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$. Clearly, the transportation rate of Li^+ in porous NCO-NT is two orders higher than that in hierarchical CCO-NF. The unique crystal structure and novel morphology of porous NCO-NT could account for it.

Figure 6.13 Peak current of electrospun porous NCO-NT and hierarchical CCO-NF vs. $v^{1/2}$.

6.3 Importance of Ternary AB_xO_y

In this thesis, a series of ternary metal oxides, which based on Sn-based (ASnO_3) and Co-based ternary oxides (ACo_2O_4), have been prepared using a facile electrospinning techniques. As anode for LIBs, good battery results can be obtained. Considering their

excellent electrochemical performance, the advantages and importance of ternary metal

Figure 6.14 XRD pattern of electrospun 1D NiO.

Figure 6.15 XRD pattern of electrospun 1D Co_3O_4 .

oxides will be emphasized in this section. Since porous NCO-NT demonstrates large specific capacity and excellent cycling stability (Section 5.3.3). Herein, taking porous NCO-NT as an example, comparative electrochemical investigations were conducted on NiO, Co_3O_4 , porous NCO-NT, as well as stoichiometry mechanical mixed NiO and Co_3O_4 .

Figure 6.16 SEM images of electrospun 1D NiO at different magnification.

Figure 6.17 SEM images of electrospun 1D Co_3O_4 at different magnification.

For consistency, binary metal oxides with 1D nanostructures, such as NiO and Co_3O_4 , were also prepared using the same electrospinning synthesis procedures. Figure 6.14 and 6.15 display the XRD patterns of NiO and Co_3O_4 , respectively, verifying the formation of corresponding pure phase. The typical electrospun 1D nanostructures of NiO and Co_3O_4 are illustrated by the FESEM images in Figure 6.16 and 6.17. Both samples present

similar 1D fibrous morphologies with uniform diameter.

Figure 6.18 The comparative electrochemical characterization of NiO , Co_3O_4 , porous NCO-NT, and mechanical mixed NiO and Co_3O_4 (a) CV curves during first cycles at scan rate 0.1 mV s^{-1} ; (b) initial discharge/charge curves at current density of 100 mA g^{-1} .

Figure 6.19 The comparative cycling performance of NiO , Co_3O_4 , porous NCO-NT, and mechanical mixed NiO and Co_3O_4 at current density of 100 mA g^{-1} .

To identify the superiority of porous NCO-NT as anode for LIBs, the comparative

electrochemical measurements were performed on the four samples. Figure 6.18a gives the CV curves of the four samples at the same scan rate of 0.1 mV s^{-1} . Although the contents of metal oxides are almost identical for both porous NCO-NT and mechanical mixed samples, there is clearly difference on the cathodic scan. Porous NCO-NT demonstrate significantly higher peak current response and more symmetrical redox peaks compared to that of mechanical mixed samples and simply binary oxides, suggesting improved electrochemical reactivity. More importantly, porous NCO-NT present relatively higher cathodic peak potential (E_{pc}) and lower anodic peak potential (E_{pa}), which means a smaller separation between E_{pc} and E_{pa} than another three samples. Surprisingly, the galvanostatic observations are coincidence with the above CV results (Figure 6.18b). A relatively higher discharge plateau and lower charge plateau can be noticed for porous NCO-NT. The smaller voltage gap between the discharge and charge curves indicate lower polarization experienced by porous NCO-NT electrode, which is crucial for the enhancement of battery performance.

In terms of cycling behaviour, porous NCO-NT manifests the best cycling stability (Figure 6.19). Although all of another three samples experience rapidly capacity loss after 100 cycles, the simple binary oxides still displays slightly higher capacity retention than the mechanical mixed sample. This circumstance apparently implied that mechanical mixing is not a good way to optimize the electrochemical properties of electrode materials, which may be due to the inhomogeneous mixture and thereby causing some electrochemical inactive area. Figure 6.20 presents the EIS results of the four samples. All the Nyquist plots look similar, which compose of one semicircle at high-frequency zone followed by an inclined line at the low-frequency zone. Figure 6.20c displays the fitted impedance data derived from Nyquist plots using the circuit in Figure 6.20b. Obviously, porous NCO-NT electrode exhibits lower R_{ct} than another three samples due to the improved electron conductivity. As semiconductors, the band gap of Co_3O_4 , NiO , and NiCo_2O_4 electrode are significantly different. According to band theory, impurity bands could be introduced after in-situ mixing these binary oxides, thereby resulting in enhanced electron conductivity.^[179] At lower frequencies region, the inclined line represents the diffusion impedance (Warburg impedance) of the electrolyte ions in active materials. Benefiting from the porous hollow tubular 1D nanostructures, porous NCO-NT possess

lowest Warburg impedance. All the above results definitely confirm that the ternary NiCo_2O_4 exhibit remarkable advantages than its corresponding binary counter-parts.

Figure 6.20 (a) The comparative Nyquist plots of NiO , Co_3O_4 , porous NCO-NT, and mechanical mixed NiO and Co_3O_4 ; (b) The equivalent electrical circuit applied to fit the experimental impedance data. The elements in the equivalent circuit include ohmic resistance of the electrolyte and cell components (R_e), surface film resistance and charge transfer impedance (R_{sf+ct}) at the interface between the electrolyte and electrode, a constant phase element (CPE) to replace the pure capacitance due to the depressed semicircle, Warburg impedance (W); (c) Fitted impedance data obtained from Nyquist plots utilizing the circuit in Figure 6.20b.

The superiority of ternary metal oxides can be interpreted from the following aspects. Taking NiCo_2O_4 as an example, on the one hand, the electrochemical *in-situ* generated NiO and Co_3O_4 could uniformly mix together in the anode system during first discharge. This could effectively lower the electrode polarization, which is critical to enhance the battery performance especially at high current density. On the other hand, although the formed Li_2O can act as inactive buffering matrix during cycling process, when Co oxides reacts with lithium, Ni oxides could serve as a “active matrix” and in turn, Co oxides could also function as a “active matrix”. In other words, the resultant metal oxides could play a role as “active self-matrix” to alleviate the large volume variation and inhibit the aggregation of active materials during cycling process, thereby resulting in excellent cycling stability.^[178]

Chapter 7 Conclusions and Future Work

7.1 Conclusions

This thesis gives an in-depth studies on the controllable synthesis of various 1D nanostructured Sn-based (ASnO_3) and Co-based (ACo_2O_4) ternary oxides using a facile electrospinning technique as anode for LIBs. Precisely designed morphology and rationally tuned electrochemical properties could be purposely obtained. Significantly, the effect of morphology modification and counter ion substitution (especially A-site substitution) on the battery performance was systematically investigated. Meanwhile, the fundamental understanding for the electrochemical reaction mechanism of the as-prepared ternary oxides were also proposed.

As Sn-based oxides are always regarded as prospective anode for LIBs, so a series of Sn-based ternary oxides (ASnO_3) with distinctly different morphologies were firstly fabricated using electrospinning method. By introducing suitable inactive matrix element Ca, large capacities and good cycling performance could be achieved by 1D CaSnO_3 nanostructures. Specially, the morphologies of CaSnO_3 could be easily modified to produce nanofibers, nanotubes, and nanobelts structures through adjusting the sintering temperature. A possible formation mechanism of different CaSnO_3 configurations was proposed. Benefiting from the tube-like morphology, CSO-NT could achieve a higher reversible capacity of 565 mAh g^{-1} compared to CSO-NF and CSO-NR. With the aim to further explore the influence of electrospinning methodology on the surface morphology of CaSnO_3 , eggroll-like CSO-NT was prepared by utilizing different polymer. Meanwhile, it is found that the viscosity of precursor solution plays key role to determine the final structure of metal oxides. Basically, eggroll-like CSO-NT achieved large capacities of $\sim 648 \text{ mAh g}^{-1}$ at 50th cycle, much higher compared to its corresponding counter-part CSO-NR. The cycling stability of eggroll-like CSO-NT is also superior to CSO-NT. The unique channel-like surface structure, relatively large effective contact surface area, as well as low internal impedance of eggroll-like CSO-NT enable its outstanding battery performance as electrode for LIBs. In Consideration of the novel electrode configuration,

simple preparation procedure, and excellent battery results, this facile strategy may be readily extended for fabrication other nanostructured anode materials.

With this in mind, A-site substitution was carried out by electrospun SrSnO_3 and BaSnO_3 using similar procedures. The obtained results indicate that the electrochemical performance of ASnO_3 system could be optimized by incorporating appropriate inactive matrix elements. Ca, as inactive matrix, is better than Sr and Ba to enhance the battery performance of Sn-based anode. Generally, the variation in electrochemical properties can be related to the difference in the starting crystal structure, the oxygen co-ordination, the atomic weight, and ionic size. These observations provide important evidence for choosing appropriate inactive matrix element in TMOs systems, which is the original contribution from this thesis.

Considering the superiority of inactive matrix element Ca in boosting electrochemical properties, the investigation of B-site substitution was conducted by introducing of Ca into the Co-based oxides to prepare CaCo_2O_4 . The as-prepared CaCo_2O_4 architectures consist of well-organized ultrathin nanoplates which arrange themselves in an oriented manner to assemble into 1D hierarchical nanostructures. The controllable formation mechanism is also discussed. Moreover, as a demonstration for the impact of morphology modification of CaCo_2O_4 on batteries performance, comparative battery results suggest that hierarchical CCO-NF not only delivers a large reversible capacity of 650 mAh g^{-1} at a current of 100 mA g^{-1} , and with 99.6% capacity retention over 60 cycles, but they also show excellent rate performance compared to counterpart nanoplates-in-nanofibers and nanoplates structures. Since, Ca has been demonstrated as good inactive matrix elements to enhance the battery performance in Co-based and Sn-based oxides systems, respectively. Although these results are promising, considering the gravimetric capacity, electrochemical active matrix elements like Ni, may be another good choose. This is because active matrix elements could not only play “self-matrix” role to accommodate the volume variations of active materials during lithiation\delithiation process but also contribute to the overall specific capacity due to their high electrochemical activity. Based on the above analysis, NiCo_2O_4 1D nanostructures are constructed by using the same synthesis procedure. Similarly, the impact of precursor concentration on the morphologies of the as-prepared samples was systematical studied. Owing to their novel structure, the

as-obtained porous NCO-NT electrode displays a large specific capacity, remarkable rate performance, and outstanding cyclability (1264 mAh g^{-1} after 60 cycles at a current of 100 mA g^{-1}). By comparing the battery performance of hierarchical CCO-NF and porous NCO-NT, it is found that the influence of A-site substitution is pronounced in improving the specific capacities and cycling stability of ACo_2O_4 . Particularly, it implies that active matrix element Ni is a more desirable candidate than inactive matrix element Ca to enhance the battery performance of Co-based anodes.

To address the role of active/inactive matrix elements in optimizing electrochemical properties of Sn-based and Co-based anodes, as well as further understanding the lithium storage mechanism in the as-prepared samples, comprehensive *ex-situ* characterization was conducted on the cycled electrodes in this thesis. The reaction mechanisms of eggroll-like CSO-NT, hierarchical CCO-NF, and porous NCO-NT during cycling process were proposed. Importantly, the obtained results confirm the role of Ca and Ni as inactive and active matrix during charging/discharging process, respectively. Besides, the lithium diffusion studies also verify the excellent electrochemical properties of eggroll-like CSO-NT, hierarchical CCO-NF and porous NCO-NT, respectively, which corroborate the results on the impact of A-site substitution in Sn-based and Co-based ternary oxides, respectively. Moreover, electrochemical performance of porous NCO-NT surpassed their respective binary oxides with higher reversible capacity, lower electrode polarization, and better cycling stability. These results clearly certify the importance of ternary oxides, and also greatly expand our knowledge to prepare some other ternary or mixed oxides systems, which might be find broad application in a variety of field.

7.2 Novel Contributions

Based on the results obtained in this thesis, several scientific and technological contributions have been made and are summarized in the sections below.

7.2.1 Scientific contributions

1. Preparation a series of ASnO_3 ($\text{A} = \text{Ba}, \text{Sr}, \text{and Ca}$) and ACo_2O_4 ($\text{A} = \text{Ca and Ni}$)

1D nanoarchitectures with various morphologies (nanofibers, nanotubes, nanorods, and nanobelts) using electrospinning technique. By rationally adjusting the thermal treatment conditions or precursor concentration, the morphology of final products can be easily tuned. Hollow tube-like structures and hierarchical nanofibers demonstrate enhanced battery performance compared to their counter-parts, respectively, mainly because of the unique morphology, high surface area, and presence of 1D configuration to facilitate lithium diffusion.

2. Investigation on the influence of morphology modification and A-site substitution on the lithium storage behavior.
3. Comprehensive characterization on cycled electrode to study the reaction mechanism of as-prepared ternary oxides anodes with lithium.
4. Fundamental understanding the importance of ternary oxides, as well as the functionality of active/inactive matrix elements in ternary oxides systems.

7.2.2 Technological contributions

1. Electrospinning methodology was systematically explored to produce a variety of 1D nanostructures with desirable morphologies.
2. Provide a route to introduce appropriate active/inactive matrix elements in metal oxides anode materials in order to greatly boosting the battery performance.

7.3 Recommendation for Future Work

Based on the work done in this thesis, the following section recommends several possibilities for future work to further develop a better commercial anode for LIBs.

7.3.1 Fundamental understanding the influence of active/inactive matrix elements on the electrochemical performance

In the present work, some brief discussion and comparison have been made to demonstrate how the active/inactive matrix element enhances the batteries performance.

Nevertheless, more thorough and detailed evidence should be provided and would be necessary to reveal the influence of active/inactive matrix elements on the electrochemical properties. Both experimental and theoretical studies should be given to further understanding the role of the active/inactive matrix elements in different ternary metal oxide systems, such as how they accommodate the volume changes of Sn or Co oxides and when the structural destruction occurs. A better illustration from the standpoint of fundamental electrochemistry might offer some guidance for the design and development of promising anode materials.

7.3.2 In-deep understanding both the influence of various nanostructures on the batteries performance from more points of view and reaction mechanism using in-situ techniques

It is well accepted that nanostructures plays a critical role to determine the batteries performance. And, different nanostructures not only mean the difference of micromorphology but everything (except chemical component). Therefore, we should pay more attention on the potential difference of the various structures in the future. As different nanostructures will form different texture of electrodes, and the different textures will mean different mass transport network for ion diffusion, electron transfer, and solid-liquid interfaces. Hence, it will be more reasonable if we analyze the difference in electrochemical performance from more points of view.

Investigation of phase transition of ternary metal oxides during cycling process is critical to provide useful information to deep comprehend the lithium storage mechanism, improved battery performance and lithium diffusion route which takes place at electrode/electrolyte interfaces. Up to now, most of our observations are based on the *ex-situ* characterizations such as XRD, XPS and EIS, which is carried out on the electrode after charge/discharge to specific voltages. It is possible that the surface properties of the electrodes might have changed because of the inevitable exposing in the environment. In this regard, *in-situ* techniques, as power tools, could give direct real-time evidence about the electrochemical reactions occurred within the electrode. Therefore, it is suggested that efforts can be devoted to gaining a further insight into the lithium storage mechanism by

using *in-situ* XRD, XPS and TEM. Specifically, *in-situ* TEM could capture the real-time situation in transient states at atomic resolution, thereby providing information about structural transformation processes. Besides, *in-situ* XRD and XPS could accurately probe the crystallographic structure and valence state variation of active materials during cycling process, which would help to reinforce our previous assumptions about the electrochemical reaction mechanism of the ternary metal oxides with lithium ions.

7.3.3 Full cell investigation on NiCo_2O_4

Since porous NCO-NT presents quite very well electrochemical performance in half cells with Li as both reference and counter electrode. To validate the applicability in practical application of this novel anode material, it would be necessary to further research on the full cells using porous NCO-NT as anode. Moreover, to obtain an optimized electrochemical performance and long lifetime, many scientific and technical issues should be firstly addressed, including finding suitable cathodes materials to match with the porous NCO-NT anode. Furthermore, it is well known that the thermal stability of LIBs is vital for the real use in large scale. Thus, the investigation of the thermal stability of the full cell should be performed. The thermal safety of the as-assembled full cell could be evaluated by using electrochemical thermodynamic measurement studies (ETMS) and other thermodynamics studies.

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