Synthesis and electrochemical studies of iron oxide-based hybrids for lithium ion batteries

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NANYANG
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**SYNTHESIS AND ELECTROCHEMICAL STUDIES
OF IRON OXIDE-BASED HYBRIDS FOR LITHIUM
ION BATTERIES**

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2017

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ION BATTERIES**

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**A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
Doctor of Philosophy**

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

With increasing demand for enhanced lithium ion batteries applied in electronic vehicles, hybrid vehicles and mobile electronics, intensive research is being focused on exploring new generation anode materials with high storage capacity, low cost and great safety. Transition metal oxides, as a kind of promising candidates, have attracted much attention and shown much higher capacities, compared with carbon based anode materials (372 mAh g^{-1}), through conversion or insertion/extraction reaction. Among them, iron oxide is of great interest due to its high corrosion resistance, abundance, nontoxicity and low cost. However, there still exist several issues (e.g. low electronic conductivity and large volume change) needed to be addressed before the large-scale commercialization of iron oxide based anodes. Therefore, it's necessary to conduct scientific studies to further investigate and improve their electrochemical performance and behavior as anodes for lithium ion batteries.

Design of novel hybrid nanostructure has been proved to be an effective approach to the technical bottleneck of electrode materials. The hybrid materials present desirable properties by integrating various functions into a single system. In view of the iron oxide/carbon hybrids, Fe_3O_4 @porous carbon matrix and Fe_3O_4 @porous carbon matrix/graphene, are synthesized and the nanostructure's effect on their electrochemical performance is investigated in depth in this thesis. In the well-defined iron oxide/carbon hybrids, the conductivity and electrical contact of nanocomposites are improved with additive carbon materials. Moreover, hierarchical porous framework can offer large electrode/electrolyte contact area and shorten diffusion distance of lithium ions, which is crucial for the good rate capability. Meanwhile, the cushion to volume change can be provided from the reserved void and porosity during the charge/discharge process.

However, the hybridization between metal oxide and carbon species still exhibits a limited improvement, due to the restricted theoretical capacity of

carbon species. The mixture of metal oxides with well-fined micro/nanostructures can endow composites with much improved capacity and remarkable rate capability. Therefore, a series of $\text{Fe}_2\text{O}_3/\text{MnO}_2$ nanocomposites are prepared via controllable annealing conditions. As demonstrated in characterization and performance evaluation, the hollow-structured oxygen-vacancy-rich $\text{Fe}_2\text{O}_3/\text{MnO}_2$ provides superior electrochemical properties as anode materials for lithium ion batteries, ascribing to their increased contact area with electrolyte and enhanced electronic and ionic conductivity.

To further reveal the structure and morphology evolution of iron oxide based anodes during long-term electrochemical cycling, the investigation of hollow-porous Fe_2O_3 microspheres is conducted via ex-situ X-ray diffraction (XRD) and ex-situ transmission electron microscopy (TEM) techniques. As revealed in the test results, a crystal size induced phase transition ($\alpha \rightarrow \gamma \rightarrow \beta$) is found to be contributed to an abnormal performance fluctuation during cycling. These research results are expected to make insightful suggestions to other scientific studies.

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Table 5.1 Cycling performances of some reported hybrid nanomaterials

Table 5.2 Physical and electrochemical properties of the as-prepared samples

Table 7.1 Current state of investigations for Fe-based ternary metal oxide anode for LIBs

Abbreviations

LIB	Lithium ion Battery
EDS	Energy Dispersive X-ray Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
CB	Conduction Band
VB	Valence Band
SEI	Solid Electrolyte Interface
1D	One-Dimensional
PVDF	Polyvinylidene Fluoride
CMC	Sodium Carboxymethyl Cellulose
PAA	Poly (acrylic acid)
GG	Guar Gum
CNT	Carbon Nanotube
PVP	Polyvinylpyrrolidone
PANI	Polyaniline
PEDOT	Poly (3, 4-ethylenedioxythiophene)
PPY	Polypyrrole
PPP	Polyparaphenylene
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$
MOF	Metal-organic Framework
PCP	Porous Coordination Polymers
TPA	Terephthalic acid
DMF	N, N-Dimethylformamide
GO	Graphite Oxide
HMT	Hexamethylenetetramine

λ	Wavelength of Incident X-ray Beam
θ	Diffraction Angle
d	Distance Between Atomic Layers
FESEM	Field emission scanning electron microscopy
CCD	Charge Couple Device
STEM	Scanning Transmission Electron Microscopy
BET	Brunauer-Emmett-Teller
XPS	X-ray Photoelectron Spectroscopy
TGA	Thermogravimetric Analysis
IR	Infrared
NMP	N-methylpyrrolidone
EC	Ethylene Carbonate
DEC	Diethyl Carbonate
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
BJH	Barret-Joyner-Halenda
FFT	Fast Fourier Transform
DMC	Dimethyl Carbonate
XAS	X-ray Absorption Spectroscopy
TXM	Transmission X-ray Microscopy
FTIR	Fourier transform-infrared spectroscopy
MS	Mass Spectroscopy
NMR	Nuclear Magnetic Resonance

Chapter 1

Introduction

This chapter begins with disclaiming the importance of lithium ion batteries from the viewpoint of energy storage. Then, the issues confronted by the limited commercial anodes is elaborately discussed. Subsequently, the project's purpose, hypothesis and objective is discussed based on related researches. In this thesis, the studies will be focused on iron oxide-based hybrid anodes for lithium ion batteries.

1.1 Hypothesis/Problem Statement

Nowadays, the increasing energy consumption and call for a cleaner environment has lead scientists from many countries to focus on developing renewable and sustainable energy resources. In the design of renewable energy system, energy storage devices play a critical role in terms of electrical energy storage and conversion in the form of chemical energy. In comparison with traditional Pb acid, Ni-MH and Ni-Cd batteries, rechargeable lithium ion batteries (LIBs) have shown the most promising potential as energy storage devices with multiple advantages including high energy density, long cycle life, high specific capacity and memory free effect.^{1, 2} Therefore, LIBs have been treated as dominant power source for many portable devices, electric vehicles (EVs) and hybrid electric vehicles (HEVs).

It has been more than 30 years, since the first commercialized LIBs was successfully developed by SONY Corp. in 1991. The rocking-chair concept has been proposed as the working principle of LIBs. During charge/discharge, the migration of Li ions occurs between cathode and anode, facilitating the electric energy storage and chemical energy conversion. To date, in typical commercial LIBs, lithium metal oxide such as LiCoO_2 , LiMnO_2 and recently LiFePO_4 and graphite are employed as cathode (positive) and anode (negative) electrodes, respectively. According to the stoichiometry of full Li-intercalation graphite (LiC_6), the theoretical capacity is calculated to be 372 mAh g^{-1} , resulting in the limited power density and specific capacity of LIBs.³ As for the cathode, the theoretical capacity of LiCoO_2 is as low as 140 mAh g^{-1} .⁴

Recently, significantly improved LIBs, with respect of lifetime, power density, safety and cost, are urgently needed. However, the performance of rechargeable LIBs is dominantly affected by employed active materials. Thus, it is highly required to investigate and develop advanced alternative electrode materials with better electrochemical performance.

In order to meet the requirement of continuously revolutionized technologies, the anode candidates for next generation LIBs are required to possess excellent performance with respect to capacity, cycling life time and stability. During the past decades, lots of novel anode materials have been discovered and developed as alternatives to replace the commercial carbon and graphite anodes whose theoretical capacity is as low as 372 mAh g^{-1} .⁵⁻⁸ Among them, transition metal oxides such as ZnO, NiO, MnO₂ and Fe₂O₃ have appealed tremendous attention, due to their high theoretical capacity as a result of the conversional decomposition reaction behavior. The detailed conversion reaction process between lithium and transition metal oxides is shown in Equation (1).⁹

From Equation (1), one formula unit of metal oxide could be fully lithiated with $2y$ lithium ions through a conversion reaction, resulting in a structural modification and a large volume expansion. Finally, a composite of transition metal with lithium oxide would be approached in the lithiation process. During delithiation, the metallic component is conversely oxidized to form transition metal oxide.

In comparison with other conversion reaction-based transition metal oxides, Iron oxides not only deliver considerable theoretical capacities (more than 900 mAh g^{-1}) and also have attractive properties such as low cost, abundance, and environmental benignity.^{10, 11} However, the further optimization on iron oxides is still needed to address the existing unsatisfactory electrochemical properties during cycling. First of all, their huge volume change, along with lithium ion insertion/extraction, causes loss of structural integrity and consequently results in breakdown of electrical conductivity and rapid performance degradation.^{12, 13} In addition, the intrinsic low electrical conductivity hampers their application and commercialization for high rate and power charge/discharge.^{14, 15}

As reported, exploitation of nanostructured materials (such as porous, hollow, yolk-shell and modified with carbon species, hybridization) can effectively accommodate the yield strains and stresses during lithiation/delithiation. Besides, these 3-D structural designs could provide an increased electrode-electrolyte contact area and fasten ionic diffusion, which have been demonstrated to accommodate electrochemical cycling of anode materials.¹⁶⁻¹⁸ Moreover, preliminary results by research society illustrate that incorporation of one or more electrochemically active components, constructing nanostructured hybrids, will effectively facilitate the Li alloying process.^{7, 19, 20} On one hand, the volume changes, which are initiated at various potential stages during cycling, could alleviate the induced strains and stresses, leading to the minimized fading capacities. On the other hand, the incorporated active species are beneficial to stabilize the integrated electrode structure along with maintaining the hybrids' capacity. In this view, a large quantity of nanostructured iron oxide-based hybrids with different composites have been studied and developed over the years, showing different properties and functionality. Inspired by previous studies, more fundamental investigations are worth to conduct to fully understand this field. The basis hypothesis of this study is described as followed:

- The nanostructure and composition of transition metal oxide anodes play critical roles in determining the long-term Li cycling stability. The morphology control of the nanostructure could improve rate and cycling performance with higher electrode/electrolyte interface and reserved buffer area. The introduced conductive species (e.g. carbon) could bring about series of benefits: (1) the increased electronic conductivity, (2) stabilized integrity of electrode structure because of their ductile and elastic nature, (3) a wide range of stable window for electrochemical reaction with electrolyte.
- The rational designed hybrid nanostructure shows great enhancement in the

electrochemical performance of TMOs with different structures and composites as anode for LIBs. The use of nanostructured hybrid electrode materials will bring several advantages. First of all, the synergic effect from the integrated functional materials can promote each component's inherent properties, for instance their electrical/ionic conductivity, electrochemical reactivity, and mechanical. Secondly, ascribing to the core-shell structure, the surface electrochemical activity of the nanomaterials can be effectively decreased, giving rise to a low level of electrochemical irreversibility and avoiding particulate aggregation.

- Phase evolution of TMOs anodes is involved in a long-term electrochemical cycling. The morphology and structural evolution of the active materials in a battery is usually responsible for the gradual capacity fading. With advanced diagnostic tools, such as XRD and TEM, the irreversible phase transition process in LIBs can be probed as a function of cycling number.

1.2 Objective and Scope

The main research scope and objective of this thesis is to synthesis high performance iron oxide-based hybrids as anode materials for LIBs. Meanwhile, reveal their detailed structural evolution process during cycling. To achieve the above objectives, the detailed scope of this thesis is listed below:

1.2.1 Investigation of the impact of the nanoarchitecture on the electrochemical properties of Fe₃O₄/Carbon hybrid anodes

Nanoarchitecture offers a great approach to optimize the electrochemical properties of iron oxide based anodes for lithium ion batteries. According to previous studies, lithium storage performance of electrodes highly depends on

their intrinsic structure, composite and morphology.^{7, 21, 22} Among all the nanoarchitecture, the rational designed hierarchical hybrid nanostructure, due to the synergetic effect from composites, could not only suppress the induced strains and stresses from volume change, but also resulting in enlarged contact area between the active materials and electrolyte, rendering the material with excellent electrochemical property.²³⁻²⁵

From the point of view, iron oxide/carbon-based hybrids, Fe_3O_4 @prous carbon matrix and Fe_3O_4 @prous carbon matrix/graphene are fabricated with enhanced electrochemical performance as anode. From series of electrochemical characterization, the influence of the rational designed nanostructure on their electrochemical performance will be addressed. Moreover, the possible formation process of the nanostructure will be proposed with the aim of the controlled fabrication of the similar structured anodes.

1.2.2 Study the effect of morphology and structure on the electrochemical performance of $\text{Fe}_2\text{O}_3/\text{MnO}_2$ hybrid anodes

The restricted improvement of conductivity and performance on iron oxide based anodes is usually achieved through external modification by carbon species. However, the low theoretical capacities of carbon could cause the integral capacity loss of iron oxide-based hybrids. Assembly of different TMOs into a hybrid nanocomposite would cause synergic advantages into their electrochemical properties as anode materials for LIBs. Meanwhile, the sacrifice, in terms of intrinsic capacities, for conductivity improvement could be avoided via internal modification of TMOs components, such as doping and defects formation. Therefore, series of $\text{Fe}_2\text{O}_3/\text{MnO}_2$ nanocomposites with different structures and morphologies are fabricated under controlled annealing conditions. In addition, their origination of superior performance will be discussed and the most potential anode materials will be identified.

1.2.3 Fundamental studies the crystal structural evolution of Fe₂O₃ anodes during cycling process

The irreversible phase transition of anodes for LIBs is critical for understanding the electrochemical reaction mechanisms and capacity degradation. In the light of related reports, the ex-situ characterization, such as ex-situ TEM, ex-situ XRD and ex-situ XPS, have been utilized as powerful and indispensable tools to probe the morphology evolution and phase transformation process during lithiation/delithiation process. Thus, in this thesis, the phase transition process of the Fe₂O₃ electrode will be proposed and investigated during long-term cycling in LIBs. The research conclusion is hoped to shed light on the performance fluctuation mechanism.

1.3 Dissertation Overview

The organization of the thesis is presented as below.

Chapter 1 provides a rational introduction for the critical role of LIBs in the novel energy system and the problems and challenges they are facing based on current situations. The study hypothesis, objectives and scope in this thesis are clarified. This thesis is aimed to fabricate high performance iron oxide-based hybrids for LIBs and investigate its structural evolution during electrochemical cycling.

Chapter 2 reviews the literature concerning the working principle and historical developments of LIBs. Categorized by lithium storage mechanisms, advantages and disadvantages of various anode materials are reviewed.

Chapter 3 discusses the principles underlying the material synthesis, morphology and structure characterization, performance measurement. The detailed methodology for data analysis are also described.

Chapter 4 investigates the electrochemical properties of iron oxide/carbon hybrids as anode for LIBs. Hierarchical Fe_3O_4 @prous carbon matrix and Fe_3O_4 @prous carbon matrix/graphene anodes are successfully synthesized. The investigation on merits of the designed hybrid nanostructure is experimentally demonstrated.

Chapter 5 investigates the electrochemical properties of $\text{Fe}_2\text{O}_3/\text{MnO}_2$ anodes. A series of $\text{Fe}_2\text{O}_3/\text{MnO}_2$ hybrids with different morphologies and structure are successfully prepared. The impact of nanostructure on their electrochemical performance is experimentally discussed.

Chapter 6 carries out ex-situ characterizations to fundamentally study the phase transition process of Fe_2O_3 anode during long-term cycling.

Chapter 7 draws conclusion of the thesis work and gives some recommendations on the future works.

1.4 Findings and Outcomes

This research led to several outcomes:

1. The hierarchical three-dimensional Fe_3O_4 @prous carbon matrix and Fe_3O_4 @porous carbon matrix/graphene are synthesized using a facile thermal decomposition of Mil-53(Fe) templates. In the electrochemical evaluation, the introduction of graphene species delivers an improved cycling performance, due to its huge contribution to the nanostructure stabilization of the active materials. The Fe_3O_4 @ porous carbon matrix/graphene can maintain a reversible capacity of over 1000 mAh g^{-1} after 500 cycles at 1 C.

2. Hollow structured oxygen-vacancy-rich $\text{Fe}_2\text{O}_3/\text{MnO}_2$ nanorods are prepared via a method combining the PVP assisting coating and the subsequent annealing in the air. The oxygen vacancies are believed to be formed via nanoscale elemental intermixing and lead to the increasing intrinsic conductivity. As shown in the electrochemical characterization, the hollow-structured $\text{Fe}_2\text{O}_3/\text{MnO}_2$ shows excellent potential as superior anode materials for LIBs, corresponding to its unique nanostructure.

3. The fabrication of hollow-porous $\alpha\text{-Fe}_2\text{O}_3$ microspheres by a facile cation exchange process is proposed. The obtained Fe_2O_3 electrode exhibits great electrochemical performance, owing to its intrinsic nanostructure. Meanwhile, a phase transition process for Fe_2O_3 anodes ($\alpha \rightarrow \gamma \rightarrow \beta$) during long-term cycling is observed using ex-situ TEM and XRD techniques. The transformation process is believed to be activated by the change of crystal size, resulting in the enhanced ionic conductivity.

Chapter 2

Literature Review

The chapter demonstrates the background of anode materials' investigation by reviewing related reports. Various anode materials are discussed and compared in terms of electrochemical behaviors and performances. Established approaches to tuning negative electrodes' electrochemical properties in historical and contemporary studies are thoroughly evaluated. Based on the literature review, the rationale for our exploration and investigation is verified.

2.1 Overview of Lithium ion Batteries

It's been over 40 years since the first lithium battery cell with lithium metal and MnO_2 as the negative and positive electrodes, respectively, was developed in 1970s. The related research shows two of its attractive advantages: the highest working potential (around 3.0 V) and the impressive energy density.²⁶ Lithium, as the lightest of all metallic element, has the highest electrochemical potential (-3.04 V vs. standard hydrogen) and provides the largest specific energy per weight.²⁷ However, it was shown that the metallic lithium electrode would suffer the generation of dendrites during deposition process, which could cause short circuits, leading to an explosion hazard.²⁸ To avoid the serious safety problem during long-term cycle life, the prolonged charging time for Li metal-based electrode is require, which would take several hours in every cycle. In the meanwhile, the families of intercalation oxides (e.g. Mn, Ni and Co) that hold much higher capacities and voltages were proposed under efforts of Bell Labs and Goodenough.²⁹ To circumvent the safety issues derived from Li electrode, the pursued alternative approach was to substitute the metallic Li for a second intercalation anode material. Based on this concept, Murphy, Scrosati and et. al. proposed the so-called Li-ion or rocking-chair battery system, in the early of 1990s.³⁰ In lithium ion batteries, the ionic state of lithium rather than metallic was used, bring up an non-dendrite and inherently safer power system. In June 1991, the first commercialized C/LiCoO₂ lithium ion battery was successfully created by Sony Corporation. The type of cell possess a over 3.6 V of working potential (three times of alkaline batteries) and 120-150 Wh kg⁻¹ of gravimetric energy density (two to three times compare with Ni-Cd batteries), which make it perfect power source for future high-performance potable electric devices.³¹

Figure 2.1 Schematic presenting the working mechanism of a LIB.³²

In a typical commercialized LIB, graphite and LiCoO_2 are usually used as isolated and untouchable anode and cathode electrodes, respectively, which is further separated by an electrolyte-filled porous membrane separator to prevent short circuits and allow lithium ions transfer at the same time. The Li equivalent electrochemical potentials of positive and negative electrodes play a critical role to determine the LIBs' potential. The detailed charge/discharge process of LIBs is illustrated in Figure 2.1. During charge process, lithium ions are deintercalated from the cathode and flow to the anode through the separator via electrolyte. Meanwhile, electrons transfer from the cathode to the anode via the external circuit. When LIBs are discharging, the reverse process would take place with regards to the movement of lithium ions and electrons. During charge and discharge, the reversible shuttle of lithium ions between the

electrodes enables the energy conversion from electrical state to chemical state whilst stores the electrochemical energy within LIBs. The involved chemical reactions can be described as below:³³

Since LIB energy density is determined by electrochemical properties of active materials utilized for lithium storage, it is not surprising the urgent demand is coming to develop advanced anode and cathode materials for LIBs to satisfy the future needs of high capacity electrified transportation industry. Currently, the most widely used anode material is graphite, due to its possessed advantages, which includes high cycling stability, low cost and a flat and low working potential. However, as shown in the above equation, only one lithium ion can be accommodated by per graphene unit, leading to its low theoretical electrochemical capacity (372 mAh g^{-1}).³⁴ Moreover, the low lithium intercalation voltage of graphite ($\leq 0.25 \text{ V vs. Li/Li}^+$) brings up the safety concerns ascribing to the lithium dendrite formation during the overcharge process.³⁵ These drawbacks of graphite, as anodes, is becoming hinders for our convenience. Therefore, worldwide efforts are conducted to develop novel anode materials to replace the graphite in LIBs. For the extensive research over recent years, there are a wide variation of transition metal oxide based anodes with different electrochemical mechanisms, namely intercalation/deintercalation, alloying/dealloying and conversion reactions, showing potential of application for commercial LIBs.

2.2 Transition Metal Oxides Based Anode

The related research on anode materials for LIBs has revealed that the ideal next-generation anode materials should involve these following properties³⁶⁻³⁹: (1) element or compounds of materials should be low formula weights or density with fairly large amounts of Li accommodation capacity per formula unit. (2) The working potential curve of ideal anodes should be flat, stable and close to that of lithium metal electrode as possible, contributing to a large and applicable voltage gap in full LIBs. (3) The ideal anodes should be chemically and physically inert in electrolyte. (4) The ideal anodes should have good electronic and ionic conductivity. (5) The ideal anodes should be low cost and non-toxic. To develop novel anodes meeting all these requirements, different transition metal oxide based materials were developed and investigated as anode for LIBs in terms of their performance and electrochemical behavior. To our best knowledge, there exist three kinds of electrochemical reaction processes related during cycling, including intercalation/deintercalation, alloying/dealloying and conversion reactions.

2.2.1 Intercalation/deintercalation Reaction

The definition of intercalation/deintercalation reaction mechanism refers to the reversible intercalation lithium into the two-dimensional (2D) layer structured or 3D network structured transition metal oxide and other compounds. Similar to graphite, the electrochemical lithium ions insertion/extraction wouldn't destroy the host's crystal structural features. Titanium (Ti) -based oxide anodes (TiO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) exhibit the electrochemical property of lithium intercalation/deintercalation in LIBs, accompanied by little or no volume change or structural straining, leading to excellent cycle life.

For TiO_2 , several polymorphs such as anatase, rutile and $\text{TiO}_2\text{-B}$ with different morphologies and structures have been studied and investigated as anode for LIBs.⁴⁰⁻⁴² The general intercalation/de-intercalation electrochemical reaction of TiO_2 with Li ions can be described as following.

As seen in the equation, the value of X is responsible for the theoretical capacity of TiO_2 . However, with limitation of the maximum $X=0.5$, its highest theoretical capacity is just 167.5 mAh g^{-1} .^{43, 44} Its insertion/extraction electrochemical reaction typically take place at a high voltage (more than 1.5 V vs. Li), guaranteeing safe and stable operation with the fewer formation of SEI (solid electrolyte interface) through the electrolyte decomposition.⁴⁵ However, the drawback of the poor lithium and electronic conductivity which is quite common in transition metal oxide anodes limits the practical use of TiO_2 . To address this issue, the nanostructure engineering of one dimensional (1D) and three dimensional (3D) has been intensively explored and investigated to improve the rate capability.^{46, 47}

The spinel lithium titanate oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) has been considered the most promising candidates to place graphite anode for large-scale backup energy systems due to great stability and its excellent safety characteristics.⁴⁸ Three molar of Li ions associated with the intercalation-deintercalation electrochemical reaction of per LTO formula allows a theoretical capacity of 175 mAh g^{-1} , leading to a negligible volume change during cycling.⁴⁹ The LTO electrode shows a horizontal and extend voltage plateau at about 1.55 V, corresponding to a phase transition between a Li-rich phase (rock-salt-LTO) and a Li-poor phase (spinel-LTO).⁵⁰ However, its poor electrical conductivity leads to a low lithium accommodation and poor rate capability. Many effective strategies such as nanostructure design, doping and conductive materials coating, have been explored to overcome this problem.^{51, 52}

2.2.2 Alloying/Dealloying Reaction

Some metallic and semi-metallic elements (e. g. Sn, Al, Mg, Si and Zn) have

been discovered to have the ability to conduct an electrochemical reaction with Li ions forming lithium-metal alloys at a low voltage (less than 1 V vs. Li).⁵³ The alloying reaction usually delivers 2-10 times of capacities, compared to that of graphite.⁵⁴ Representatively, the theoretical capacity of Sn is evaluated as around 994 mAh g⁻¹, ascribing to the full lithiation stoichiometry of Li_{4.4}Sn. Another advantage of alloy materials is their reasonable working potential versus Li/Li⁺, such as Sn, whose working potential is 0.3-0.4 vs. Li.⁵⁵ The merit averts the safety issue caused by lithium deposition, during charging. The main challenge for alloy anodes is the induced huge volume change during cycling, leading to the electrode disintegration and the rapid performance fading. At the same time, the coulombic efficiency of alloy electrodes of the first cycle is too low, corresponding to the high irreversible energy loss.⁵⁶ In these decades, extensive research, focusing on the nanostructure engineering and fundamental mechanism, has been performed to solve these issues.

Sn-based oxide anode materials, such as SnO₂ and SnO, have attracted much attention to be investigated and explored as high capacity anode materials. The alloying/dealloying reaction is involved in their electrochemical cycling process, which is shown as below.

With regards to bulk SnO₂, the first reaction is irreversible, thus the maximum of 4.4 Li⁺ per Sn could be accommodated during alloying/dealloying reaction.⁵⁷ Therefore, the theoretical capacity is calculated to be 780 mAh g⁻¹.⁵⁸ But the first reaction of the nano-sized SnO₂ turns to be reversible/ part reversible, leading to an increased theoretical capacity of 1494 mAh g⁻¹.⁵⁹ Fig. 2.2 shows the comparison of the micrometer-sized and nano-sized SnO₂ in terms of electrochemical reaction as anodes for LIBs. As shown in Fig. 2.2c, there exists an extend peak at 1.24 V in the anodic sweep of the nano-sized SnO₂,

corresponding to the phase transition from Sn to SnO₂. While, the broad peak is not observed in the micrometer-sized SnO₂, suggesting the reversible/ part reversible of the first reaction in the nano-sized SnO₂.⁶⁰

Nowadays, in order to improve reversible capacity and coulombic efficiency and lengthen cycle life of Sn-based oxides anodes, various strategies have been proposed and explored. The first one is to synthesize Sn-based oxides with different nanostructure to buffer the volume change and shorten the diffusion length.⁶¹ The second one is to build hollow and porous structure to alleviate the electrode disintegration during cycling.⁶² The third one is to construct hybrid nanostructure with conductive species to improve its conductivity.

Figure 2.2 The first and second galvanostatic charge/discharge cycling curves and the corresponding derivative capacity plots of 10 μm SnO₂ (a, b) and the first three CV (c) and galvanostatic charge/discharge cycles (d) of the SnO₂ NC@N-RGO electrode.⁶³

2.2.3 Conversion Reaction

Recently, numerous research has discovered that some transition metal oxides such as Co_3O_4 , MnO_2 and Fe_2O_3 , show potential application in LIBs as anode materials. These transition metal oxides anodes exploit conversion reaction wherein high energy conversion is expected to attain. In a typical conversion reaction, an active compound material, MX_y , reacts with Li and is reduced to metallic element and corresponding lithiated compound. The relevant equation is shown as following:

For example, the transition metal oxide, Co_3O_4 , undergoes the below conversion reaction with lithium in LIBs.

From the equation, the maximum of 8 Li is stored in per Co_3O_4 molar through a conversion reaction. A large volume expansions of about 100% could be induced through the reaction, resulting in the destruction of the electrode integrity and the agglomeration of active materials.⁶⁴ The voltage plateaus of the Co_3O_4 electrode are located at 1.3 and 0.8, for the initial discharge, and 2.2 V, for the charge.⁶⁵ Many attempts have been made to reveal the detailed reaction process via different characterization techniques. According to the research of Luo et al., in the early stage of lithiation, lithium inserted $\text{Li}_x\text{Co}_3\text{O}_4$ is formed through Li ions diffusion leading to an about 20% volume expansion.⁶⁶ Then, the phase transition from amorphization of Co_3O_4 to small Co-Li-O clusters occurs along with the lattice fringe disappearance, attributed to insertion of more Li ions. Finally, the composite of Co metal crystals embedded in Li_2O matrix grows as a result of Li further reduction.

Most conversion reaction-based transition metal oxides could offer the advantage of attractive capacity compared to graphite (372 mAh g^{-1}). Despite their improved theoretical capacity, the further optimization is necessary to address some intrinsic unsatisfactory electrochemical properties, such as voltage hysteresis, large volume change and low conductivity. The difference voltage plateaus during lithiation and delithiation processes could cause high energy loss and decreased efficiency.^{67, 68} Large volume expansion and extraction during cycling would induce a huge strains and stresses leading to the deterioration of the electrode structure and cycle fading. Low conductivity brings about poor capability and low specific capacity under high rate, hindering their commercial application in LIBs. To solve these problems, different transition metal oxide materials with different nanostructures, such as porous, hollow and hybrid with different components have been synthesized and evaluated as anodes for LIBs.^{7, 69, 70}

2.3 Iron Oxides Based Anode

Iron oxides such as FeO, Fe₂O₃ and Fe₃O₄ have attracted much attention in the application for LIBs as anode materials because of their economy, non-toxicity and high theoretical capacity (for example, 1007 mAh g^{-1} for Fe₂O₃ and 924 mAh g^{-1} for Fe₃O₄). In the 1980s, the first observation of the conversion reactions in iron oxide electrodes was using molten salt electrolytes.⁷¹ Following this initial investigation, it took lots of scientists' effort to employ iron oxides as anodes for LIBs. However, the irreversibility of the macro-sized iron oxides based electrodes caused their rapid capacity fading during cycling. Until the 2000s, a breakthrough in the nanotechnology was achieved, leading to an improvement of the electrochemical reversibility when nanosized iron oxide was introduced.⁷²

Recently, two kinds of iron oxides, namely α -Fe₂O₃ (hematite) and Fe₃O₄ (magnetite) have been intensively studied and explored for LIBs anodes. For its

most stable property among iron oxides and n-type electronic conductivity, hematite phase $\alpha\text{-Fe}_2\text{O}_3$ is widely used in catalysts, pigments and gas sensors. As an n-type semiconductor, hematite possesses a band gap of 2.3 eV, where the conduction band (CB) is occupied by empty d-orbitals of Fe^{3+} and the valence band (VB) is consisting of mixture of Fe^{3+} 3d crystal field orbitals of and O 2p non-bonding orbitals.⁷³ As shown in Figure 2.3a, the confined Fe atoms occupying 2 kinds of octahedral site by the hexagonal close packing of O atoms forms the rhombohedral crystal structure of $\alpha\text{-Fe}_2\text{O}_3$ with an $R\bar{3}C$ space group.^{74, 75}

Figure 2.3 Illustration of crystal structures of the α phase Fe_2O_3 (hematite) and Fe_3O_4 (magnetite, the black, green and red balls are marked as Fe^{2+} , Fe^{3+} and O^{2-} , respectively).⁷⁶

In the respect of Magnetite phase Fe_3O_4 , the spinel crystal of face centered cubic structure consisting of 32 O^{2-} ions and close-packed along the [111] direction is shown in Figure 2.3b. The most obvious difference between Fe_3O_4 and Fe_2O_3 is its incorporation of both iron atoms (3+ and 2+). In a cubic inverse spinel structure of Fe_3O_4 , half of the octahedral sites are taken up by all the Fe^{2+} ions and the remained octahedral site and the tetrahedral sites are taken by even split of the Fe^{3+} ions.⁷⁶ The lowest resistivity of Fe_3O_4 , as a result of small

bandgap (0.1 eV), among iron oxide brings it the potential possibility of tuning electronic property (n-type and p-type) by partly or fully replacing the divalent irons by other ions with similar valence (Co^{2+} , Mn^{2+} , Zn^{2+} , etc).⁷⁷

As a promising candidate of anode materials, the reversible electrochemical insertion/extraction of Li ions occurs in the $\alpha\text{-Fe}_2\text{O}_3$ electrodes in an extended voltage window of about 1.5-4.0 V vs Li/Li^+ . Furthermore, as the potential was cathodically polarized to 0.9 V, two molars of Li ions can be irreversibly inserted into the corresponding oxides composite matrix without further crystal structure modification.^{78, 79} As the discharging potential drops to 0.005 V, the total 8.5 molars of Li ions can participate in the insertion reaction. Accordingly, the detailed multistep reaction of interaction between Li ions and $\alpha\text{-Fe}_2\text{O}_3$ anodes during cycling can be demonstrated as following.⁸⁰

In the light of related studies, regardless of the phases of Fe_2O_3 anodes, a similar conversion reaction of $\text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6e^- \leftrightarrow 2\text{Fe} + 3\text{Li}_2\text{O}$ dominates the electrochemical process of Fe_2O_3 electrodes.^{36, 81} As shown in the equation above, the maximum uptake of Li ions for $\alpha\text{-Fe}_2\text{O}_3$ is 6, account into the complete reduction from Fe_2O_3 to Fe. Based on the Li uptake amount, the calculated theoretical specific capacity is expected to be as much as 1006 mAh g^{-1} . Moreover, in the related research, the first cycle for the Fe_2O_3 anodes usually shows a different profile and extra discharge capacity, due to activation processes and an irreversible textural modification.

Li ions insertion and extraction processes of Fe_3O_4 electrodes also show a typical conversion reaction $\text{Fe}_3\text{O}_4 + 8\text{Li}^+ + 8e^- \leftrightarrow 3\text{Fe} + 4\text{Li}_2\text{O}$ similar to that of Fe_2O_3 .⁸² According to previous studies, its electrochemical behavior in the discharge process indicates a multistep lithiation reaction consisting of two

segments, such as a short line from about 3.0 V to 0.75 V and a long plateau at about 0.75 V.⁸³ In the former potential window, the partial lithiation process of $\text{Fe}_3\text{O}_4 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Fe}_3\text{O}_4$ carries out. The latter one is assigned to the complete reduction to Fe^0 , $\text{Li}_x\text{Fe}_3\text{O}_4 + (8-x)\text{Li}^+ + (8-x)e^- \rightarrow 3\text{Fe} + 4\text{Li}_2\text{O}$. As we know from above, Fe_3O_4 anodes have a high theoretical capacity of 924 mAh g^{-1} , corresponding to 8 Li ions accommodation per Fe_3O_4 when discharging to 0 V.

Figure 2.4 Schematic illustration of the in situ experimental setup (a), and the TEM images of Fe_2O_3 /graphene electrode before (b) and after (c) fully lithiation. In-situ observation of Fe_2O_3 nanoparticles during lithiation (d-f).⁸⁴

2.3.1 Issues of Iron Oxides as Anodes for LIBs

Although the much higher theoretical capacity of iron oxides anodes compared with traditional graphite, some unpleasant problems still exist and hinder the

implementation of iron oxide in commercial LIBs.

(a) Loss of active materials

Large volume (around 100%) expansion/contraction of iron oxide materials occurs during Li ions insertion and extraction, which could result in cracking and pulverization of active materials and the deterioration of the surrounding matrix structure.⁸⁵ The destruction of electrode integrity often leads to the iron oxide particles disconnecting from the conductive matrix and peeling off from current collector. Su et al. thoroughly investigated the conversion mechanism of Fe_2O_3 /graphene through in situ transmission electron microscope.⁸⁴ Upon lithiation, the obvious volume expansion and morphological changes of the Fe_2O_3 nanoparticles was observed. Meanwhile, the complete lithiated product shows a core-shell nanostructure covered by a nanocrystalline Li_2O layer. With respect to single-crystalline Fe_2O_3 , it was found that the nanocomposite of Fe nanograins embedded in Li_2O matrix was formed. The volume expansion process was confirmed in Figure 2.4.

Figure 2.5 Schematic of SEI formation on active materials during cycling.⁸⁶

(b) Formation of solid-electrolyte interface (SEI) film

In lithium-ion batteries with either liquid or gelled polymer electrolytes, the solid electrolyte interphase (SEI), a typical passivating layer is usually formed

in the cycling discharge/charge process for anodes/cathodes through decomposition of electrolyte.^{54, 87} The formation of SEI film on the active materials' surface can suppress the additional consuming of electrolyte, due to its negligible electric resistance and high Li ions conductivity.⁸⁸ The issue of SEI stability at the interface between the iron oxides and the electrolyte could be triggered by the repetitive volume expansion and contraction.⁸⁶ As is schematically shown in Figure 2.5, the breakage of SEI film which is formed during lithiation process can be initiated by the shrinkage of active materials' volume. The repeated exposure of fresh active materials' surface induces the progressive formation of thicker and thicker SEI film along with cycling. The phenomenon usually causes the degradation of active materials' performance of LIBs during cycling, due to (1) the abnormal consumption of electrolyte and Li ions for the continuous formation of SEI film; (2) the increased electronic and ionic resistance ascribing to the thickened SEI film; (3) structure deterioration of the electrode induced by mechanical strains and stresses from the thick SEI film. In order to enhance the long-term cycling performance of iron oxides anodes, numerous efforts have been made to realize a stable and thin SEI film.

(c) Irreversible capacity

Although the conversion Li ions insertion/extraction reaction of iron oxides anodes is general reversible, the poor Li ions release kinetics and formation of the thermodynamically highly stable Li_2O phase and inactive Fe domains through could cause the permanent trapping of Li ions.^{89, 90} In the micrometer-sized Fe_2O_3 electrode, the initial transition from a hexagonal packing ($\alpha\text{-Li}_x\text{Fe}_2\text{O}_3$) to cubic phase ($\text{Li}_2\text{Fe}_2\text{O}_3$) is usually irreversible as soon as 0.3 Li per Fe_2O_3 is uptaken, leading to severe capacity loss.⁷⁸ Based on Jain et al.'s study, nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$ anodes possesses an alternative structural change compared with the microcrystalline ones during lithiation/delithiation.⁷⁴ A much higher single-phase lithiation capacity of 0.47 Li per Fe_2O_3 was observed in the

nanocrystalline electrode showing a much better electrochemical reversibility. Until now, various nano-sized iron oxides with different morphology have been successfully synthesized, exhibiting an enhanced electrochemical performance as anodes for LIBs to different extent.

2.3.2 Approaches of electrochemical performance improvement

In an attempt to maximally eliminate the irreversible capacity and retain long-term cycling performance, various strategies have been applied to accommodate the large volume changes and moderate the electrolyte decomposition during cycling. The common approaches are listed in the following context.

(a) Particle size control

It has been confirmed that micrometer-sized iron oxides possess high irreversible capacity as anode for LIBs during cycling, making it quite difficult for commercialization. The drawback can be overcome by reducing their particle size to nanometer range forming nanocrystals, verified by many previous studies.^{91, 92} Until now, considerable efforts have been made to synthesize iron oxides with different properties, by controlling their size and shape, such as nanocrystals, nanoparticles, nanorods, nanotube, nanowire and nanospindles.^{75, 93, 94} The improved cycling performance can be credited to the structure and morphological stability of nanoparticles under large stresses and strains.^{34, 95} Decreasing materials' grain size usually causes their strength increasing, as known in the Hall-Petch relation (1, 2). Along with reducing crystal sizes, the lattice dislocation motion could be constrained by the grain boundaries and defects.⁹⁶ In addition, the complete lithiation process of nanocrystalline Fe_2O_3 electrodes forms metallic Fe nanoparticle coated by Li_2O unlike the Fe/ Li_2O composite product of micrometer-sized Fe_2O_3 , implying the high reversible solid reaction of nanosized iron.⁸⁴ Moreover, the electronic

transport and Li ions diffusion distance could be shortened by the decreased particle size.⁹⁴

However, the reduction of particle size could also give rise up to some unexpected properties such as large surface area, high cost and aggregation during cycling, leading to an increased side-reaction with electrolyte, poor cycling performance and short cycle life. The effective approach to address these issues is to prepare different iron oxide composites with controllable nanostructure. For example, Zhu et al. prepared reduced graphene oxide/Fe₂O₃ through homogeneous precipitation and microwave assisted reduction processes, which exhibited an improvement of electrochemical performance.²² It has been reported that the novel Fe₃O₄ (around 3.5 nm)/MoS₂ nanosheets composite provide a superior cyclic and rate performance, owing to the introduced MoS₂ nanosheets.⁹⁷

(b) Nanostructure and morphology control

Recent progresses in electrochemistry have verified the merits introduced by nanotechnology in the application of controlling nanostructure and morphology to materials' electrochemical properties. The construction of morphologies, such as hollow, porous and yolk-shell, in 1D (one-dimensional), 2D and 3D nanostructure could improve the cycling performance of iron oxides anodes for LIBs.⁹⁸⁻¹⁰⁰ Several expected advantages have been reported to be provided by these reserved void nanostructures.¹⁰¹ First of all, the large volume change which causes severe pulverization and agglomeration of active materials and subsequent structural disintegration could be accommodated with these reserved void nanostructures. Secondly, the shortened effective Li ions diffusion pathways and enhanced electronic conductivity can be ensured, due to the increased solid-electrolyte contact area.

Based these theories, lots of nanotechnologies have been utilized to prepare high performance iron oxides materials with different designed morphologies,

in the implement of LIBs. Zhang et. al. reported a yolk-shell structured iron oxide@carbon ($\text{FeO}_x\text{@C}$) with controllable void sizes.¹⁰² With an optimal void size, the yolk-shell structured $\text{FeO}_x\text{@C}$ exhibits a high reversible capacity of around 790 mAh g^{-1} at 0.2 C after 100 cycles. Through a facile solvothermal method, porous hollow structured Fe_3O_4 microspheres were prepared, showing a reversible capacity of 500 mAh g^{-1} at 0.1 C after 50 cycles. After treatment of carbon coating, the reversible capacity can be increased to 700 mAh g^{-1} .¹²

(c) Operating voltage control

Compared with a limited voltage range, anodes cycled within the full voltage range are more vulnerable to cracking, crumbling and pulverization, due to the large volume expansion/contraction, leading to a severe capacity fading.^{53, 103, 104} Therefore, cycling stability can be improved by employing the floor and cap condition in terms of characterization voltage, restricting the degree of volume change. For example, in the research of Reddy et al., in the upper cut-off voltage of 1.0 V , micron size- $(\text{V}_{1/2}\text{Sb}_{1/2}\text{Sn})\text{O}_4$ delivers a reversible capacity of around 535 mAh g^{-1} after 50 cycles.¹⁰⁵ In contrast, if the cut-off voltage was added to 1.3 V , the reversible capacity was reduced to 455 mAh g^{-1} after 50 cycles. Nano- SnO_2 electrode exhibited a much better electrochemical reversibility showing a much higher capacity retention in the restricted operating potential range of $0.005\text{--}1.0 \text{ V}$ vs. Li^+/Li .¹⁰⁶

(d) Binder and electrolyte

Though lots of binder-free iron oxides anode have been synthesized, showing several advantages of enhanced stability, high specific mass capacity, improved conductivity. from the viewpoint of commercialization, it is impossible to form a continuous and stable negative composite adhered on a current collector without the incorporation of binder. Therefore, the properties of binders such as

strength, conductivities, elasticity and et al. are critical for the overall performance of anode electrodes. Some polymer binders such as the thermoplastic material PVDF (polyvinylidene fluoride) have been widely used in LIBs' electrodes.^{107, 108} However, its poor elastomeric properties make it incapable to accommodate the large volume change of iron oxides leading to a fragile electrode structure during cycling. Thus, it's reasonable to improve the anode's cycling performance by developing alternative binders with some desirable and expected structures such as cross-linking polymers and elastomer binding systems.^{109, 110}

Li et al. investigated the electrochemical performance of Si negative electrode using CMC (sodium carboxymethyl cellulose) binder which indicated an increased cycling capacity of 1100 mAh g⁻¹ for 70 cycles, compared to the conventional PVDF.¹¹¹ High-molecular weight PAA (poly (acrylic acid)) as an improved binder was used to prepared the Fe₃O₄ nanoparticles electrode. The electrode exhibited a better capacity retention and electrode stability, in contrast with the one using PVDF.¹¹² In the recent Liu et al.'s research, the biopolymer guar gum (GG) was characterized as a binder for the Si anodes of LIBs. The unique properties of GG guaranteed the robust stability and improved electronic conductivity of the electrode, demonstrating its potential as a candidate binder for Si anodes.¹¹³

2.4 Hybridization

Nanostructured materials, as results of their attractive advantages over their bulk counterparts, have been looked upon as the most promising alternatives for high performance LIBs. Though downsizing transition metal oxides into nanoscale and/or engineering porous and hollow nanostructure can effectively eliminate the pronounced volume expansion and contraction and facilitate Li ions diffusion during cycling, the SEI thickening, at the same time, can't be avoided, causing the increasing electrical resistance.^{38, 70, 114, 115} Meanwhile, the increased additional side reaction between electrolyte and active particles would

be brought about by the high specific surface area.^{7, 116-118} In order to satisfactorily address these issues and design high performance LIBs, nanostructured hybrid materials with different structural complexity have been prepared and exploited, as shown in Figure 2.6.¹¹⁹

Figure 2.6 Categories of heterogeneous nanostructured materials with different morphologies.¹¹⁹

Based on related studies, the construction of hybrid nanostructure could effectively boost the electrochemical performance of the transition metal oxide electrode for LIBs.^{19, 120, 121} In contrast with single-phase active materials, the synergic effect of hybrid materials consisting of different materials can cause the enhancement of different components' electrochemical performance.^{51, 61} In addition, the typical hybridization of core-shell nanostructure could effectively decrease the electrochemical activity of materials' surface, forming a stable SEI film and showing a great cyclability.^{33, 119, 122} Finally, the ordered electrode architected on conductive substrates, such as nickel foam, carbon paper and titanium film can be used to develop binder-free electrodes revealing excellent

electrochemical performance for the high and fast energy storage.¹²³⁻¹²⁵ In a summary of recent progress, there mainly exist three systems of metal oxide/metal oxide, metal oxide/carbon, metal oxide/conductive polymer which have been explored and developed as LIBs' anodes with high cycling performance and rate capability.

(a) Metal oxide/carbon composite nanostructure

One of the most economic and promising solutions to enhance metal oxides' electrochemical performance is to synthesize its composite via introducing conductive second phase forming a homogeneous nanostructure.^{126, 127} One of the most preferred conductive second phases is carbon material, such as carbon nanotubes (CNTs), graphene and carbon paper, whose utilization could provide multiple advantages: (1) the improved ionic and electronic conductivity of the active materials, (2) the suppression of nanoparticles' agglomeration during cycling, (3) acting as buffer layer for the volume change induced strains and stresses, (4) the inhabitation of the undesired side reaction between electrolyte and metal oxide particles.^{126, 128-131} Therefore, researchers around the world show great interests into designing various nanostructures of the metal oxide/carbon composite as anodes for the next generation LIBs. One simple and common method to reasonably design the hybrids is to form a core-shell nanostructure by carbon coating. For example, Wang et al. prepared Mn_3O_4 homogeneously wrapped by 5 nm carbon via a facile one-step solvothermal reaction using PVP (polyvinylpyrrolidone) as carbon precursors.¹³² The $\text{Mn}_3\text{O}_4@\text{C}$ indicated an enhanced capacity retention during cycling (473 mA h g^{-1} after 50 cycles). Zhang et al. propose a facile method to fabricate Gr- SnO_2 -C (carbon-coated SnO_2 /graphene nanosheets) which exhibited an excellent electrochemical performance in terms of great cycling stability and improved capacity (757 mA h g^{-1} after 150 cycles).¹³³ The superior cycling performance can be ascribed to the synergic effects between the effects of carbon coating, the

nanosize of SnO₂ particles and the high conductivity of graphene. Another performance enhancement approach is to establish coaxial carbon core-oxide shell nanostructures, usually as binder-free anode for application in LIBs. Taking CNTs@SnO₂@C (carbon nanotubes@SnO₂@carbon) as an example, SnO₂ and carbon layer were homogeneously deposited on CNTs templates and the corresponding product was applied as anode materials for LIBs.¹³⁴ In comparison with the pure CNTs and CNTs@SnO₂ anodes, the CNTs@SnO₂@C could provide a higher specific capacity and better cycling performance (462.5 mAh g⁻¹ after 65 cycles), due to its unique nanostructure, integrating the high electronic and ionic conductivity and buffering matrix.

(b) Metal oxide/conductive polymer composite nanostructure

Another promising candidate as a category of supplementary second phase for nanostructured composites is conductive polymer (for example, PANI (polyaniline), PEDOT (poly (3, 4-ethylenedioxythiophene)), PPY (polypyrrole) and et al.).¹³⁵⁻¹³⁷ Compared with other materials, conductive polymer possesses several advantages, namely ease of synthesis, forming of elastic and flexible matrix and high ionic and electronic conductivity.¹³⁶ For example, Chen et al. synthesized nano-Si/PPP (polyparaphenylene) composite via embedding nano-Si particles into a Li⁺-conductive polymer, PPP. The experimental results showed that the composite held a high initial capacity (3184 mAh g⁻¹) and an excellent capacity retention rate (60%, after 400 cycles).¹³⁸ The improved electrochemical properties can be attributed to the role of conductive polymer in the accommodation of volume expansion/contraction and the prevention of the direct contact between Si surface and electrolyte. Jeong et al. prepared hierarchical hollow spheres of Fe₂O₃@polyaniline by a template-free method combining with a polymer coating.¹³⁹ The as-prepared anode demonstrates an excellent electrochemical performance (893 mAh g⁻¹, after 100 cycles, at 0.1 C), compared to the urchin-like Fe₂O₃ electrode, due to the unique hierarchical and

conductive polymer coating nanostructure.

Recently, some researchers have found the functionality of the conductive polymer coating shell as A-SEI (artificial SEI) for the application as anode in LIBs.^{140, 141} The moderate reaction condition, environmentally friend solvent and flexibility of tailoring its functionality make conductive polymers much more favorable, compared to other materials, such as carbon and metal oxide.¹⁴² For example, Li et al. achieve favorable electrode/A-SEI/electrolyte interfacial properties by rationally designing multifunctional polymer coating. In the investigation, the polymeric coating containing two polymers, poly (ally amine) and polyethylene glycol tert-octylphenyl ether, leads to an expected improvement in the cycling performance and rate capability of the studies anode.¹⁴² Incorporation of Si nanoparticles into a conducting polymer, polyaniline, matrix is formed via in-situ polymerization, in Wu et al.'s study.¹⁴³ Beneficial from the hierarchical hydrogel framework combining the continuous conductivity framework, high theoretical capacity of Si and porous space and crosslinker hydrogen bonding, the anode indicated a high cycling retention of over 90% after 5000 cycles at 6.0 A g^{-1} .

(c) Metal oxide/metal oxide composite nanostructure

Although some favorable properties, such as low cost, non-toxicity and high flexibility, can be achieved by introduction of carbon and conducting polymer based second phases into nanostructured composite, the limited total capacity of the composite could be initiated by their low theoretical capacities.^{144, 145} In the light of previous studies, some structure merits and synergic effects from the metal oxide/metal oxide composites could offer a desirable electrochemical performance as anodes for LIBs, meanwhile, maintaining their high specific capacities. For example, the multilayer CuO@NiO hollow spheres deliver a large reversible theoretical capacity of 1061 mAh g^{-1} , after 200 cycles.¹⁴⁶ the core-shell $\alpha\text{-Fe}_2\text{O}_3\text{@Li}_4\text{Ti}_5\text{O}_{12}$ composite synthesized through a facile

hydrothermal method showed an improved electrochemical performance with high surface stability and excellent security, ascribing to the LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) coating.¹⁴⁷ Hollow graphene foams encapsulated hollow $\text{SnO}_2@\text{Co}_3\text{O}_4$ spheres illustrates a remarkable electrochemical reversibility (815.2 mAh g⁻¹, after 100 cycles, at 200 mA g⁻¹), showing its potential as a promising anode for LIBs.¹⁴⁸ Hybridization have attracted lots of attention, as an outstanding flexible and versatile approach to fabricate high-performance anodes for LIBs. Up to date, lots of techniques, such as hydrothermal, template, annealing and microwave assisting, have been employed to construct nanostructured composites consisting of various components.¹⁴⁹⁻¹⁵¹ However, there still exist many challenges to overcome to realize the effective control of the final products' size, shape and composition in large scale.^{152, 153} Moreover, further investigations are needed to reveal the correlation of the composition and nanostructure with the material's electrochemical properties in LIBs.^{154, 155} We hope the researches in this thesis could enlighten others' scientific studies in terms of lithium ion batteries' anodes.

2.5 Summary

In a through literature review, iron oxides, a category of prospective candidates as anode for LIBs, show many virtues of low cost, high theoretical capacities and environmental benignity. However, some common issues of transition metal oxide anodes, such as severe volume change during cycling and low conductivity, are inevitable for iron oxide electrode. These issues are expected to be overcome from the aspects of particle size control, morphology engineering, operating voltage control and binder. By the virtue of the synergic effect and flexibility of tailoring functionality, heterogeneous nanostructure could effectively improve anodes' electrochemical performance, meanwhile, inhibiting the side-reaction between active particles and electrolyte derived from the downsizing into nanoscale. Nevertheless, it is still difficult to realize

the precise control of the nanostructured composites' particle size and morphology. Moreover, the detailed electrochemical reaction process and structure transition of iron oxides anodes during cycling is not yet fully understood. Then, further investigations on nanostructured iron oxides anodes are needed to resolve these puzzles.

Chapter 3

Experimental Methodology

In this chapter, the methods and chemical reaction mechanism of iron oxide-based anodes' preparation are demonstrated. The working principles of utilized characterization techniques are explained and all the related measurement conditions are exhibited. After all, the performance evolution procedures of the as-prepared electrodes for LIBs are illustrated.

3.1 Materials Preparation

3.1.1 Synthesis of Nanostructured Fe₃O₄/Carbon Composite

Recently, In-situ synthesis of nanostructured metal oxide/carbon hybrids via thermal decomposition of metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) has appealed lots of attention and been intensively investigated. As an alternative category of hybrid microporous materials, MOFs is formed in an appropriate solution via the coordination between metal ions or clusters and organic ligands to form various nanostructures. Due to the special crystalline structures of MOFs, some advantages, such as high specific surface area, tunable chemical property and tailored porosity, are expected to be accomplished. Therefore, MOFs have demonstrated a great potential for various applications of drug delivery, sensing, gas storage and catalysis. Inspired by the desirable frameworks of MOFs consisting of the nodes of transition metal ions or clusters and the struts of organic ligands, MOFs have been taken into account as effective precursor or precursors to prepare different nanostructured metal oxide/carbon based hybrids. In comparison with other methods, MOFs-derived carbon frameworks usually show high porosity and uniform nanostructure, giving rise to excellent electrochemical performance.

For example, ZnO nanoparticles and ZnO@C hybrid composites were synthesized using thermal annealing of Zn-MOF under different atmosphere conditions.¹⁵⁶ The obtained ZnO@C composites showed the nanostructure of faceted ZnO crystals embedded in the porous conductive matrix. Due to the organic pollutants, the nanostructured composite possessed an enhanced adsorption capacities and photocatalytic decomposition activity. A Fe₃O₄/carbon composite of high porosity was synthesized by pyrolysis of Fe-MOF in the nitrogen. The unique properties of the corresponding products, in terms of the hydrophobic behavior and surface area, can be achieved at different

pyrolysis temperature.¹⁵⁷ They have been considered to be promising recyclable superadsorbent for removal and recovery of pollutants. Additionally, the reduction intermediates of MOFs such as metallic nanoparticles can be used to catalysts for the growth of CNTs or graphene during the thermal process. Based on this theory, the Co@CNTs/porous carbon hybrids is synthesized by in situ thermal decomposition of MOF-encapsulated Co_3O_4 .¹⁵⁸ The as-prepared composite indicated an excellent electrocatalytic activity with high efficiency for the ORR and OER. Meanwhile, due to their unique nanostructure, the promising performance and long-term stability can be achieved in the application of Zn-air cells as active materials.

(a) Synthesis of Fe_3O_4 @porous carbon matrix

All the purchased chemicals were from Sigma Aldrich and utilized in analytical grades with no further purification. First of all, the synthesis of MIL-53 (Fe) was performed following the research described elsewhere¹⁵⁹. 0.2 mmol iron(III) nitrate hexahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 0.2 mmol TPA (Terephthalic acid) were dissolved in 10 ml DMF (N, N-Dimethylformamide). Subsequently, the mixture was sealed in a Teflon-lined stainless-steel autoclave with capacity of 20 ml, which was kept at 120 °C for 12 h. Then the MIL-53 (Fe) product of yellow color was collected with centrifugation and rinsed with methanol for at least 5 times, at the centrifugation speed and time of 5000 rpm and 5 mins. The product was then totally dried at 60 °C in an oven for overnight. Finally, the Fe_3O_4 @porous carbon matrix was obtained via the pyrolysis of MIL-53 (Fe) at 600 °C for 5 h in nitrogen at the heating rate of 2 °C min⁻¹.

(b) Synthesis of Fe_3O_4 @porous carbon matrix/graphene

All the purchased chemicals were purchased from Sigma Aldrich and used in analytical grades without purification. The synthesis of GO (graphite oxide)

sheets was performed using KMnO_4 (Potassium permanganate) in concentrated H_2SO_4 (Sulfuric acid) via modified Hummers method.¹⁶⁰ 2 g of graphite powder with the average size of less than 20 μm and 2 g of sodium nitrate (NaNO_3) were stirred into the solution of 100 ml concentrated H_2SO_4 . The mixture above was mixed and strongly stirred in a 1L reaction flask for 15 mins, which had been cooled to 0 $^\circ\text{C}$ in an ice-bath in case of safety issue. Then 12 g powder of KMnO_4 was slowly added into the suspension to prevent the temperature from exceeding 20 $^\circ\text{C}$, while vigorous agitation was maintained. The reaction was held for 48 h, keeping the suspension continuously stirred after the ice bath was removed. At the end of the reaction, 560 ml of DI water was stirred into the solution, causing the temperature climbing up to 98 $^\circ\text{C}$ and violent effervescence. Finally, 40 ml of H_2O_2 was added to reduce the residual KMnO_4 to soluble manganese salt. The resultant mixture was collected by centrifugation and washed with a mixture of 6 wt% H_2SO_4 /1 wt% H_2O_2 aqueous solution. Afterward, the product was further washed with DI water and dried at 60 $^\circ\text{C}$ for 36 h under vacuum.

Then, the approach of chemical deposition was utilized in the growth of MIL-53 on the GO substrate. MIL-53/GO was prepared by the method as following. 0.2 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added into 10 ml GO of DMF suspension (0.1 mg ml^{-1}) under ultrasound for 8 h. After that, 0.2 mmol Terephthalic acid was added into the above mixture and was treated under ultrasound for 2 h. Then, the mixed solution was transferred into a Teflon-lined stainless-steel autoclave with capacity. After solvothermal reaction at 120 $^\circ\text{C}$ for 12 h, the product of MIL-53/GO was washed with methanol and collected by centrifugation at speed and duration of 5000 rpm and 5 min. Then, the as-prepared MIL-53/GO hybrids were dried at 60 $^\circ\text{C}$ in an oven for overnight. Finally, the Fe_3O_4 @porous carbon matrix/graphene were obtained through the approach of thermal decomposition of MIL-53/GO at 600 $^\circ\text{C}$ for 5 h in nitrogen (2 $^\circ\text{C min}^{-1}$).

3.1.2 Synthesis of Nanostructured Fe₂O₃/MnO₂ Composite

To date, various nanostructured hybrids have been widely studied in the area of electrochemistry. The structural integrity of both the core and shell active materials could contribute to the enhanced electrochemical energy storage. There still many challenges in the fabrication of core-shell nanowires, nanorods and nanotubes with different nanostructures. The recent progress has been achieved in exploring and developing economic and facile approaches for controllable synthesis of core-shell and complicated heterostructure arrays. However, there is still no simple and high-efficiency method to prepare core-shell metal oxide/metal oxide hybrids with superior electrochemical performance. Herein, a facile method of chemical bath deposition would be applied to synthesize the Fe₂O₃/MnO₂ composite.

(a) Fabrication of FeOOH nanorods

All the purchased chemicals were from Sigma-Aldrich and employed in analytical grades without purification. First of all, the β -FeOOH nanorods were synthesized with the modified method.¹⁶¹ 1.08 g iron (III) chloride hexahydrate (FeCl₃·6H₂O) and 0.5 g PVP (Polyvinylpyrrolidone, 5,5000 MW) were dissolved in 40 ml DI water. The whole solution was kept gently stirring at 85 °C with water bath for a duration of 12 h. The as-obtained product of β -FeOOH nanorods was collected by centrifugation with the rotation speed and duration of 8000 rpm and 10 min and then washed with 50 ml water. The rinse procedure was conducted for 8 times. Afterwards, the β -FeOOH nanorods was dispersed into 40 ml DI water, forming a suspension.

(b) Fabrication of FeOOH/MnO₂ nanorods

All the purchased chemicals were from Sigma Aldrich and exploited in analytical grades with no requirement to purify. To obtain the FeOOH/MnO₂ core-shell nanorods, 0.5 ml of Manganese(II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O) solution (0.03g ml⁻¹, DI water) was added into the 4 ml of the as-prepared β-FeOOH suspension. Then, 0.5 ml of KMnO₄ aqueous solution (0.019 g ml⁻¹) was slowly dropped into the above slution under continuous stirring. The reaction was maintained for 24 h, keeping the condition of stirring at room temperature. To purify the product, the brown precipitate was collected by centrifugation (8000rpm, 5 min) and then rinsed with DI water for at least 3 times. Finally, the as-obtained FeOOH/MnO₂ composite was dried at 60 °C in an oven for overnight.

(c) Fabrication of Fe₃O₄@porous carbon matrix/graphene

The Fe₂O₃/MnO₂ hybrids with different nanostructure and composites were prepared under different anealing conditions. The hierarchical structured porous Fe₂O₃/MnO₂ nanorods was obtained via anealing of FeOOH/MnO₂ composite at 300 and 400 °C. As the annealing temperature of FeOOH/MnO₂ composite changed to 500 °C in the air (2 h, 1 °C min⁻¹), the hollow structured Fe₂O₃/MnO₂ nanorods could be prepared. The as-prepared product annealed at 600 °C for 2 h in the air with heating rate of 1 °C min⁻¹ was Fe₂O₃/(Fe_{0.42}Mn_{0.58})₂O₃/MnO₂ composite.

3.1.3 Synthesis of Hollow and Porous Fe₂O₃ Microspheres

Size and morphology control of nanomaterials synthesis attracts much attention of scientists around the world, in terms of scientific and technological interests. Compared to other morphologies, well-defined hollow and porous nanostructure have been extensively studied due to their extreme potential of application in my fields such as sensing, energy storage, drug delivery and

catalysis, ascribing to its high specific surface area and enhanced activity. To date, lots of researches have been made to explore and develop an effective and facile method for the fabrication of nanomaterials with hollow and porous nanostructure. Compared to other approaches, the ion exchange of sacrificing templates shows the superiorities of flexibility, ease of operation and controllability, and lots of inorganic materials with different interior nanostructures have been fabricated through cation or anion exchange. The complexity of interior nanostructure can be generated under the effect of nanoscale Kirkendall effect.

For example, the reaction of ionic exchange was exploited for forming multishelled structured Cu_2S microspheres.¹⁶² Through controlling a number of important process parameters such as reactant concentrations, amount of capping agents and reaction temperatures in the chemical conversion of Cu_2O to Cu_2S , the formation of single, double, triple or even quadruple shells can be achieved. Yu et al. reported a vapor-solid deposition approach for the evolution of hollow TiO_2 nanostructures.¹⁶³ The cation exchange reaction between TiCl_4 vapor and ZnO solid contributed to the phenomena of hollow nanostructures formation, which were in a good agreement with the Kirkendall effect. The as-prepared 3D TiO_2 nanoforests showed excellent photoelectrochemical performance, due to the unique hollow nanostructure and trace of Zn element left in the TiO_2 crystals.

(a) Fabrication of zinc citrate microspheres template

All the purchased chemicals were purchased from Sigma Aldrich and used in analytical grades without purification. The template of zinc citrates microspheres were prepared through a modified method reported previously¹⁶⁴. First of all, 0.392 g of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 0.110 g of sodium citrate tribasic dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) and 0.105 g of hexamethylenetetramine (HMT) were dispersed into 50 ml DI water to form a

solution. Then, after severe mixture for more than 20 min, all the reactants were thoroughly dissolved. Thereafter, the suspension was kept reacting at 90 °C with water bath for 20 min. The obtained zinc citrate templates were subsequently separated by centrifugation (rotation speed of 500 rpm and duration of 5 min) and washed with the DI water/ethanol mixture (volume ratio of 1:1) for at least 5 times. Finally, the zinc citrate product of white color was dried in an oven at 80 °C for 12 h.

(b) Fabrication of hollow and porous α -Fe₂O₃ microspheres

All the purchased chemicals were from Sigma Aldrich and utilized in analytical grades with no further purification. To synthesize hollow and porous α -Fe₂O₃ microspheres, 0.02g of zinc citrate templates was firstly dispersed into 10 ml of DI water via ultrasonication for 5 min. Then, 10 ml of 0.1 M iron(II) sulfate heptahydrate (FeSO₄·7H₂O) aqueous solution was quickly added into the as-prepared zinc citrate suspension and the reaction was maintained for 24hrs under gently stirring at room temperature. Afterwards, the yellow product was collected by centrifugation, with the limited rotation speed and duration of 4000 rpm and 5 min, and washed with a mixture of DI water and ethanol (volume ratio of 1:1) for 3 times. Finally, the as-obtained product was transferred to a box furnace and heated to 600 °C for 5h (2 °C min⁻¹) in the air, after the drying process in an oven at 80 °C for 12 h.

3.2 Materials Characterization

3.2.1 Power X-ray Diffraction

In 1912, the functionality of the crystal lattice spacing in the crystalline substances as 3D diffraction gratings for X-ray wavelengths was discovered by Max von Laue. Since then, X-ray diffraction (XRD) has turned to be a common

technique to identify the materials' atomic spatial arrangement and crystal structure. The interference between monochromatic X-rays and a crystalline sample could construct the X-ray diffraction. Though being filtered and collimated, the generated X-rays by a cathode ray tube can be tuned to be monochromatic and concentrated and directed towards the sample. According to Braggs' studies, the constructive interference between the X-rays and the samples should satisfy Bragg's Law which reveals the relationship between the wavelength of the incident X-ray beam (λ), the diffraction angle (θ) and the distance between atomic layers (d) in a crystal, as shown below.¹⁶⁵

$$n\lambda = 2d \sin \theta$$

Along with scanning of X-ray beam at different diffraction angles of 2θ , all the achievable diffraction directions of the lattice could be obtained owing to the the powder materials' random orientation, through detecting, processing and counting the diffraction X-rays. Due to the unique d-spacings of each crystal phase, the conversion of the diffraction peaks can be applied to identify the mineral. The identification is usually achieved as compared to the standard reference patterns in terms of the measurement result.

X-ray diffractometer is composed of three fundamental components, namely, an X-ray detector, a sample holder and an X-ray tube. In the X-ray tube, the cathode would produce electrons by heating a filament. Then the electron will be accelerated to bombard the target materials under the applied voltage. With electrons' enough kinetic energy to extricate inner shell electrons of the target materials, the characteristic X-ray can be obtained. After filtering by crystal monochrometers, the monochromatic X-rays required for diffraction would be obtained. In this thesis, the Bruker AXS D8 advance X-ray diffractometer was employed to perform the powder X-ray diffraction (XRD) to identify the chemical composition of materials. In the measurement, the Cu K_α radiation ($\lambda = 0.15406$ nm) was utilized as monochromatic X-ray beam using the maximum 2θ range from 10° to 80° .

Figure 3.1 Schematic illustration of working mechanism of XRD.¹⁶⁶

3.2.2 Field Emission Scanning Electron Microscopy

Field emission scanning electron microscopy (FESEM) could provide surface and elemental information at a high magnification. Compared with typical scanning electron microscopy, FESEM possesses multiple advantages including the clearer and less electrostatically distorted images, negligible electrical charging of samples and reduced penetration of electron probes.

Figure 3.2 Schematic diagram of the SEM working principle.¹⁶⁷

In FESEM, the field-emission cathode of the electron gun could provide a narrow probing beam with a high electron energy, leading to an enhancement of spatial resolution and eliminated charging and damage of materials. In a vacuum environment, electrons emitted by the Field Emission Source are further accelerated under an applied field gradient. Through the tuning of Electromagnetic Lenses, the electron beam focuses onto the observed materials surface. The bombardment of electron causes the emission of different electrons from materials. The generated secondary electrons are caught by a detector and the surface structure could be revealed by the contrast of the secondary electrons' intensity. Finally, the constructed SEM image is shown on a monitor. A FESEM (JEOL, Model JSM-7600F) was used to characterize the morphology of materials under 5KV and working distance of 6 cm. In order to reduce the materials' overcharge, the deposition of a platinum layer on the

sample was conducted using a sputtering coater (JEOL JFC-1600). The attached energy dispersive X-ray (EDS) system was employed to analyze the composite elements.

3.2.3 Transmission Electron Microscopy

As a powerful tool, transmission electron microscopy (TEM) has been widely utilized to analyze materials' nanostructure. The basic principle of TEM operation is similar to that of the light microscope instead of the usage of electrons. Corresponding to the much smaller wavelength of electrons compared with that of light, TEM can bring about many orders of magnitude, in terms of resolution, higher than a light microscope. As result of the advantages, the finest details of materials' crystal structure and features in the structure such as grain boundaries and dislocations.

In TEM, the electron gun generates the high-energy electron beam which is then focused, under the effect of the condenser lens, and turns into a small, thin and coherent beam. With the restriction of the condenser aperture, high angle electrons could be excluded. After being shone through very thin samples, the transmitted electron beam could be obtained, depending upon the thickness and electron transparency of the specimen. Through the further focus of the objective lens, the transmitted portion would be projected into an image on phosphor screen or charge couple device (CCD) camera. The contrast of images can be improved by the employment of optional objective apertures. In the TEM image, the darker area represents the area of the sample where only a few electrons could get transmitted through. In the high resolution TEM (HRTEM) characterization, the electron beam is scattered by the element atomic electrostatic potential of the sample. After passing through the electromagnetic objective lens, all the electrons scattered from one crystal atom can be reflected as one point in the image plane. Then, the HRTEM image can be taken,

meanwhile, the diffraction pattern is formed at the back focal plane of the objective lens.

In our work, the TEM images were taken by a TEM system (JEOL, Model JEM-2100) operating at 200 kV. The EDS elemental mapping characterization was performed using the scanning transmission electron microscopy (STEM) mode.

Figure 3.3 The schematic outline of a TEM.¹⁶⁸

3.2.4 Brunauer-Emmett-Teller (BET)

In this Thesis, Brunauer-Emmett-Teller (BET) was applied for the calculation of the specific surface area. By BET analysis, the porous structure, including the pore size distribution, of samples can be measured. In BET theory, the probing of the physical adsorption of a gas is utilized to quantify specific surface area of systems of multilayer adsorption. The BET adsorption isotherm equation for the data treatment is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption. The detailed BET equation is indicated as following.

$$\frac{1}{V_a \left(\frac{P_0}{P} - 1 \right)} = \frac{C - 1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

In the equation, the linear relationship can be maintained in the range of $0.05 < p/p_0 < 0.35$. The most commonly adsorbate applied for BET analysis of the surface area is Nitrogen. Meanwhile, the characterization process is often conducted at the boiling temperature. In order to allow the measurement of surface area at different temperature and measurement scales, some alternative adsorbates including argon, carbon dioxide and water are also utilized. During our research, the BET characterization was conducted by accelerated surface area and porosimetry system (ASAP 2020) using nitrogen at -196 °C. Before the sample's specific surface area was determined, the outgassing process was performed at 120 °C for at least 8 h under vacuum condition.

3.2.5 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive spectroscopic technique which can be used to analyze the electronic state, chemical state and elemental composition within the materials to a depth of 2 to 5 nm. In principle, the bombardment of an X-ray with a sample can generate the emission of electrons from atoms. In order to effectively eliminate the effects of ambient atmosphere, XPS is needed to be conducted in ultrahigh vacuum conditions (around 10^{-9} mbar). During XPS analysis, the sample is irradiated with x-rays of

sufficient energy which results in the excitation of electrons in specific bound states. Depending on the incident X-ray and binding energy of the atomic orbital, the photoelectron can be broken away from the nuclear with a specific kinetic energy. Except the inelastically scattered electrons, the photo-ejected electrons undergo no energy loss in escaping into the ambient environment. And then, these electron beams are captured by an electron analyzer creating XPS spectra (energy intensity versus binding energy) relying on the measurement of their kinetic energy.

Figure 3.4 Basic components of XPS system.¹⁶⁹

In a typical XPS spectrum, two kinds of features are expected to be obtained. The first one is that the shift of photo-ejected electrons energy correlates to the outer valence configuration of the element. The second one is that the binding energy of an element core level state relates to the identification of the element. Besides revealing the element's identification and chemical environment in the specimen, the intensity of the peaks can also tell the elemental composition. Due to the proportional relationship between the peak area and the number of atoms, the chemical composition can be confirmed by calculating the respective contribution of each peak area. Herein, the chemical states of the materials'

elements are characterized using an Omicron analyzer EA 125. Survey scans were performed from 0 to 1200 KV, which was calibrated by the C1s line at 284.2 eV.

3.2.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a kind of technique to measure the amount of weight change of a material, in various atmospheres, such as helium, nitrogen and air or in vacuum, either as the heating temperature increases under a constant climbing rate or along with different durations at constant temperature. Through TGA measurement, the information of physical properties, such as vaporization, sublimation, absorption and desorption, can be provided. Moreover, the thermal chemical reaction under various temperatures such as chemisorption, desolvation, decomposition and solid-gas reaction can also be revealed.

Some characteristics of materials can be determined using TGA technique via the mass change of materials as a result of decomposition, oxidation and loss of volatiles: (1) materials identification via the comparison of the thermal weight-loss patterns, (2) materials' thermal decomposition kinetics and reaction decomposition, (3) the composition of carbon and organic species in materials, (4) the thermal stability of materials. The temperature range for TGA is routinely from 25° to 900°. The weight of samples required for analysis is the range of 1 mg-150 mg. And it would be preferred that the sample weights of more than 10 mg. Herein, the TGA measurement system (TA instrument Q500 apparatus) is used to study the thermal decomposition process of samples, which were heated to the target temperature at the heating rate of 10 °C min⁻¹ under air flow.

Figure 3.5 The schematic outline of thermogravimetric analysis system.¹⁷⁰

3.2.7 Raman Spectroscopy

As a form of vibrational spectroscopy, Raman spectroscopy has been extensively employed to observe the vibrational, rotational and other low-frequency modes in a molecular. Through the characterization of Raman spectroscopy, the identification of molecular can be confirmed by the as-obtained fingerprints. Different from the infrared (IR) bands corresponding to a change in the dipole moment of a molecule due to an interaction between light and materials, Raman bands is due to the polarization change of molecular because of the same interaction. The observed certain bands can be observed in Raman spectroscopy and are forbidden in IR, and some bands may be allowed in both spectroscopies although with different intensities, which means that these techniques can be thought of as complementary.

The typical Raman measurement is operated via Raman scattering or inelastic scattering of monochromatic light. It is well known that Raman scattering (Raman Effect) is defined that in the incident laser light interaction with

molecular, due to the existence of vibration and rotation, the resulting energy of scattered radiation would shift up or down (Figure 3.6). The spontaneous formation of inelastic light scattering is originated from the difference of the materials' rotational or vibrational state after interaction with the photon. In this dissertation, Raman spectra were recorded with a Witec alpha300 SR confocal Raman system with the 532 nm excitation of a Nd:YAG laser.

Figure 3.6 Energy level involved in Raman measurement.¹⁷¹

3.3 Electrochemical Studies

3.3.1 Coin Cell Fabrication

Figure 3.7 The structure of the assembled CR 2016 lithium ion coin cells.

In order to fabricate the electrode for the electrochemical measurement, the homogeneous and viscous slurry was prepared by mixing 70% active materials, 20% super p-carbon (metals basis, Alfa) and 10% polyvinylidene fluoride (PVDF, Sigma Aldrich) in N-methylpyrrolidone (NMP, Sigma Aldrich). The copper foil was covered by an approximately 20 μm thickness of slurry was covered using a doctor blade and afterwards was left overnight to dry up at 60 $^{\circ}\text{C}$. The as-obtained sample was pressed in a twin roller under 10 MPa to improve the electric contact between active materials and current collector. After that, the 16 mm diameter of working electrode discs were collected by a punching machine and were further dehydrated under vacuum condition at 60 $^{\circ}\text{C}$ for at least 12 h. The CR 2016 coin cells were assembled in a glovebox filled with argon ($\text{H}_2\text{O} < 0.1\text{ppm}$, $\text{O}_2 < 0.1\text{ppm}$, Mbraun, Germany), before the electrochemical evaluation of materials as anode electrodes for LIBs. In the assembled coin cells (Figure 3.7), 1M LiPF_6 of ethylene carbonate (EC) and Diethyl carbonate (DEC) (1:1 by volume) solution was utilized as the electrolyte and pure lithium foils and Celgard 2400 membrane were used as counter electrodes and the separator, respectively.

3.3.2 Electrochemical Characterization

After the cell was aged for more than 8 h at ambient temperature, the galvanostatic charge-discharge cycling test was conducted at 25 °C with the Neware battery test system (Neware, BTS-5V10mA, China) in the voltage range of 0.01 V to 3.0 V (vs. Li/Li⁺). The Cyclic voltammetry (CV) test was performed by using an electrochemical workstation (autolab, PGSTAT302N) with a scan rate of 0.5 mVs⁻¹ over 0.1 V to 3.0 V (vs. Li/Li⁺) applied to the test cells. The electrochemical impedance spectroscopy (EIS) was used to characterize the electronic and ionic conductivity of the working electrode in the frequency range from 0.1 MHz to 0.01 Hz.

With regard to ex-situ TEM and XRD characterization, the cells were charged to 3.0 V after specific cycling number in the galvanostatic charge-discharge test. For the purpose of TEM characterization, the as-obtained fully charged cells were dismantled in the glovebox and the active materials were scraped off from the working electrode. After the dispersion of active materials into hexane, the solution was dropped onto the carbon coated copper grids. In terms of ex-situ XRD characterization, the working electrode was placed in the XRD holder for environmentally sensitive materials in the glovebox.

In ex-situ TEM measurements, several steps were used to eliminate the effect of surface SEI layer. First of all, the fully charged half-cell was disassembled in a glovebox filled with argon (H₂O < 0.1 ppm, O₂ < 0.1 ppm, Mbraun, Germany). Then, the active material was casted off from the copper substrate and dispersed in hexane under ultrasonication for at least 30 mins, after the fully delithiated material was recovered and washed with DEC three times. Finally, the as-obtained suspension was dropped on a copper grid in a glovebox and rapidly transferred to the TEM through a self-designed mobile airlock. Therefore, the degradation of SEI film and active material can be prevented by avoiding any exposure to air.

Chapter 4

Hierarchical Three-dimensional Fe₃O₄@porous Carbon Matrix/graphene Anodes

In this chapter, the hierarchical three-dimensional Fe₃O₄@porous carbon matrix and Fe₃O₄@porous carbon matrix/graphene are synthesized by a facile annealing of Mil-53(Fe) templates. Their electrochemical performances are evaluated as anode materials for lithium ion batteries. In comparison with Fe₃O₄@porous carbon matrix, the Fe₃O₄@porous carbon matrix/graphene electrode exhibits a much better cycling performance with the reversible capacity high up to 1000 mAhg⁻¹ after 500 cycles at 1 C. The improved performance can be ascribed to the high conductivity and structure stability provided by the unique graphene based hierarchical three-dimensional nanostructure.

4.1 Introduction

Recently, tremendous efforts have been laid on the development for the novel anode materials of lithium ion batteries (LIBs). In the lights of previous studies, transition metal oxide materials such Fe₃O₄¹⁷²⁻¹⁷⁴, Co₃O₄¹⁷⁵⁻¹⁷⁷, SnO₂¹⁷⁸⁻¹⁸⁰, ZnO¹⁸¹⁻¹⁸³ and MnO₂¹⁸⁴⁻¹⁸⁶ have attracted lots of interests for their high capacities compared with the traditional graphite (372 mAhg⁻¹) as the next generation anode materials. In comparison with other transition metal oxide materials, Fe₃O₄ is a great anode material candidate with extremely excellent properties such as storage abundance, high capacity and low cost^{187, 188}. However, transition metal oxide based anode materials usually suffer a severely huge volume expansion/shrinkage during lithiation/delithiation processes which would trigger their drastic nanostructure damages and rapid capacity fading^{189, 190}.

According to previous studies, tuning intrinsic nanostructures effectively addresses these issues caused by the volume change during cycling¹⁹¹⁻¹⁹³. The nanostructures such as porosity, hollow, core-shell and et. al., could provide a great strain accommodation, high electrode-electrolyte contact area and reduced Li-ion diffusion pathway. Graphene, the two-dimensional carbon material, has been considered as an advanced anode material for LIBs, ascribing to its superior electrical conductivity, large specific surface area, ultrathin thickness, chemical stability, and structural flexibility^{194, 195}. It's also been demonstrated that graphene can be used in the composites with transition metal oxide to

improve their electrochemical performance, because that graphene nanosheets could provide not only the highly conductive matrix for the reduced reaction resistance but also the buffer layer to address the high volume change induced strain/stress without aggregation of active particles during cycling^{196, 197}.

In the last few decades, Metal organic frameworks (MOFs), the class of crystalline materials comprising of organic ligands and coordinated metal ions or clusters, drew a continuous growing attention as the perfect template for the synthesis of the transition metal oxide materials, due to their tunable cavities, large internal surface area, chemical tenability and et. al¹⁹⁸⁻²⁰⁰. Until now, quite few of the transition metal oxide materials such as Co₃O₄, MnO₂, Fe₂O₃ and et. al. with porous and hollow structure have been successfully prepared with facile combustion method²⁰¹⁻²⁰⁸.

Herein, we report a facile strategy to prepare the hierarchical three-dimensional Fe₃O₄@porous carbon matrix/graphene as an advanced anode material for high-performance LIBs. The unique hierarchical three-dimensional nanostructure is designed by in-situ decomposition of the MIL-53(Fe) in nitrogen. In the evaluation as anode materials for LIBs, the composite displays a superior electrochemical performance of high reversible capacity, enhanced coulombic efficiency, excellent cyclic performance, and great rate capability.

4.2 Results and discussion

Both MIL-53(Fe) and MIL-53(Fe)/GO composites were viewed in SEM with their SEM images shown in Figure 4.1. Figure 4.1a and b are images of MIL-

MIL-53(Fe) particles, taken at different magnifications which appear octahedral shape with the average size of around 1 μm . However, when GO is introduced during the MIL-53(Fe) synthesis, GO will act as the template in the synthesis by providing functional groups such as hydroxyl for the nucleation of MIL particles. Meanwhile, the premixture and ultrasound treatment guarantee the sufficient interaction between Fe ions and GO, allowing the homogeneous nucleation of MIL on the GO surface²⁰⁹. As a result, dense and ordered amorphous nanoparticles of MIL-53(Fe) grow on the surface of GO as shown in Figure 4.1c, which can be seen more clearly in the image with higher magnification (Figure 4.1d). The average size of the MIL-53 particle drops down to around 200 nm.

Figure 4.1 SEM images of the MIL-53(Fe) (a, b) and the MIL-53(Fe)/GO (c,d).

XRD studies were conducted to identify the crystal structure of the samples. Figure 4.2a is an experimental XRD pattern collected from the successfully synthesized MIL-53(Fe) which is consistent with the simulated pattern. It is worth to note that the XRD pattern of the as-obtained sample doesn't exactly

match the simulated one, ascribing to the breathing effect of the framework of different guest molars inside ²¹⁰. The XRD pattern of MIL-53(Fe)/GO composite (Figure 4.2b) also shows the almost same phase structure as the sample MIL-53(Fe) does, which indicates the preserved crystalline MIL-53(Fe) on the surface of graphene oxide. At high temperature in N₂, MIL-53(Fe) and MIL-53(Fe)/GO are decomposed and transformed into the Fe₃O₄ as determined from the XRD patterns of the as-obtained products from MIL-53(Fe) and MIL-53(Fe)/GO composite by the indexing of the cubic magnetite phase of Fe₃O₄ (JCPDS file 19-0629), where five peaks located at the 2 θ values of 30.2, 35.6, 43.3, 57.3 and 63.0° are attributed to the reflections of (220), (311), (200), (511) and (440) lattice planes (Figure 4.2c and d). In addition, the broaden peaks located at around 28° in Figure 4.2c and d are generated from the (002) planes of carbon and graphene.²¹¹⁻²¹³

Figure 4.2 XRD patterns of MIL-53(Fe) (a), MIL-53(Fe)/GO (b), Fe₃O₄@porous carbon matrix (c) and Fe₃O₄@porous carbon matrix/graphene (d).

The morphological changes of MIL-53(Fe) and MIL-53(Fe)/GO composite during the process of high temperature treatment in N₂ were further investigated using SEM. Figure 4.3a shows the overall morphology of the as-obtained product from MIL-53(Fe) imaged in SEM at a low magnification. It is revealed to be the Fe₃O₄ nanoparticles with random sizes ranging from 100 nm to 500 nm and embed in porous carbon matrix from the high-magnified SEM image (Figure 4.3b). The porous carbon matrix is formed by the assembly of carbon nanowires with diameters of around 40 nm. In terms of the as-obtained product from MIL-53(Fe)/GO composite (Figure 4.3c and d), Fe₃O₄ nanoparticles are demonstrated to have a relatively uniform particle size distribution with a reduced diameter of around 150 nm. Meanwhile, the in-situ thermal decomposition of MIL-53(Fe)/GO constructs a hierarchical three-dimensional nanostructure, comprising of graphene nanosheets-supported Fe₃O₄@porous carbon matrix (Fe₃O₄@PCM).

Figure 4.3 SEM images of the as-obtained Fe₃O₄@PCM (a, b) and Fe₃O₄@PCM/graphene (c, d).

Figure 4.4a is a TEM image of Fe₃O₄@PCM, which shows an octahedral shape of Fe₃O₄ nanoparticles attached over the porous carbon matrix. The porous carbon matrix is comprised of around 40 nm sized carbon nanowires. The zoomed-in image of Fe₃O₄@PCM (Figure 4.4b) clearly shows a thin carbon layer that is coated on the surface of Fe₃O₄ nanoparticles with the thickness of 2.5 nm. The perfection of single crystal of the cubic magnetite phase Fe₃O₄ is demonstrated in the high resolution TEM image (Figure 4.4c) taken at a zone axis of [111]. With regards to Fe₃O₄@PCM/graphene, the Fe₃O₄ nanoparticles encapsulated by porous carbon matrix (Figure 4.5) are seen to be attached to graphene nanosheets. Figure 4.4e is a bright-field TEM image showing the projection of two equilateral triangles in the octahedron. It is a perfect cubic magnetite phase Fe₃O₄ crystal, as indicated from Figure 4.4f, an atomic lattice TEM image taken at the zone axis of [102]. Moreover, the elemental distribution of C, Fe and O elements was performed using STEM-EDX as shown in Figure 4.6, which proves the heterostructures of Fe₃O₄@PCM and Fe₃O₄@PCM/graphene.

Figure 4.4 TEM and high resolution TEM images of Fe₃O₄@PCM (a-c) and Fe₃O₄@PCM/graphene (d-f), respectively.

To further analyze the presence of the carbon component in the samples, the Raman measurement was carried out. As shown in Figure 4.7, the two peaks at 1100 and 600 cm⁻¹, in the low-frequency region, are attributed to the Raman characteristic bands of Fe₃O₄. the other two peaks located at 1350 and 1600 cm⁻¹ correspond to the D and G bands of the carbon matrix and graphene components, respectively. The intensity ratios of the D to G band of Fe₃O₄@PCM and Fe₃O₄@PCM/graphene are calculated to be 0.97 and 0.46, respectively, demonstrating the existence of the graphene nanosheets. Meanwhile, as compared with the Fe₃O₄@PCM, the intensity of the Fe₃O₄@PCM/graphene's 2D band at around 2700 cm⁻¹ is increased, ascribing to the introduced graphene component. As shown in the TGA spectra, the proportions of Fe₃O₄ in Fe₃O₄@PCM and Fe₃O₄@PCM/graphene are 59.6 wt. % and 70.0 wt. %, respectively, calculated based on the conversion of Fe₂O₃ (Figure 4.8).

Figure 4.5 TEM image of Fe₃O₄@PCM/graphene.

The specific surface area and porosity of the samples of Fe₃O₄@PCM and Fe₃O₄@PCM/graphene were investigated using N₂ adsorption-desorption isotherms. As seen in Figure 4.9, isotherms of the two samples show the obvious hysteresis loops, which are attributed to the large porosity and high surface area in their intrinsic morphologies. According to theoretical calculation, Fe₃O₄@PCM and Fe₃O₄@PCM/graphene display high BET surface areas of 67.7 m²g⁻¹ and 50.5 m²g⁻¹, respectively. The smaller surface area of Fe₃O₄@PCM/graphene is speculated to be caused by the reduction of MIL-53 crystal size which leads to the diminished porous carbon matrix. Unlike Fe₃O₄@PCM, Fe₃O₄@PCM/graphene presents a multimodal porosity. The mesoporous structure (20 nm) is believed to be derived from the porous carbon matrix. However, the macropore (60 nm) is attributed to the stacking of graphene nanosheets.

Figure 4.6 Elemental mapping of Fe₃O₄@PCM (a) and Fe₃O₄@PCM/graphene (b).

Figure 4.7 Raman spectra of the as-obtained Fe₃O₄@PCM and Fe₃O₄@PCM/graphene.

Figure 4.8 TGA curves of Fe₃O₄@PCM and Fe₃O₄@PCM/graphene.

Figure 4.9 Nitrogen adsorption-desorption isotherms and BJH pore size distribution (Inset) of the as-obtained Fe₃O₄@PCM (a) and Fe₃O₄@PCM/graphene (b).

The electrochemical performances of the as-obtained Fe₃O₄@PCM and Fe₃O₄@PCM/graphene as anode materials for LIBs were evaluated using the coin cells. To identify all the electrochemical progress during charge-discharge, CV was conducted on the cell with Fe₃O₄@PCM/graphene in the 0.01~3.0 V range at a scan rate of 0.5 mV s⁻¹. As shown in Figure 4.10a, the three cathodic peaks located at around 1.4 V, 0.45 V and 0.02 V in the first cycle are ascribed to the decomposition of electrolyte, the lithiation of Fe₃O₄ and graphene, respectively²¹⁴. Meanwhile, the oxidation of Fe⁰ to Fe₃O₄ is related to the anodic peak at around 1.7 V, which is quite consistent with the previous studies²¹⁵. Moreover, in the subsequent cycles, it's worth to note that both cathodic and anodic peaks shift positively, indicating the existence of the structural modification during the first cycle²¹⁶.

Figure 4.10 CV curves of the Fe₃O₄@PCM/graphene electrode at a scan rate of 0.5 mV·s⁻¹ (a) and discharge and charge profiles of the as-obtained Fe₃O₄@PCM/graphene (b).

The discharge-charge cycling of the Fe₃O₄@PCM and Fe₃O₄@PCM/graphene electrodes was conducted in the potential window of 0.01~3.0 V at a rate of 0.2 C (200 mA g⁻¹) for 100 times. The 1st, 2nd, 10th and 50th charge-discharge profiles of the Fe₃O₄@PCM/graphene are shown in Figure 4.10b. The initial discharge and charge capacity of the Fe₃O₄@PCM/graphene electrode are measured to be 1295 and 874 mAh g⁻¹. The high initial capacity loss is corresponding to the irreversible decomposition of electrolyte. The high active surface area from graphene may also cause the high energy consumption for the formation of SEI film as reported in the literature¹⁸⁷. Two discharge plateaus at 1.4 V and 0.75 V in the first cycle are observed, which can be attributed to the formation of SEI film and the reduction of Fe component, respectively. In the charge curve, the potential slop from 1.5 V to 2.3 V is due to the reverse electrochemical reaction of the active material. With continuous cycling, a long potential slop instead of the plateaus appears in the discharge profile, contributed by the textural modification²¹⁶, consistent with the result of CV test. There are no obvious changes visible in the charge-discharge curves of the subsequent cycles, demonstrating the excellent cycling stability of the Fe₃O₄@PCM/graphene electrode.

Figure 4.11 The cycling performance (a) and rate capability (b) of the Fe₃O₄@PCM and Fe₃O₄@PCM/graphene electrodes.

The superior cycling performances of Fe₃O₄@PCM and Fe₃O₄@PCM/graphene electrodes under low current density (0.2 C) for 100 cycles are presented in Figure 4.11a. The sample of Fe₃O₄@PCM/graphene delivers an excellent cycling performance with the initial reversible capacity of 874 mAh g⁻¹. After 100 cycles, the discharge capacity rises to 1077 mAh g⁻¹. Fe₃O₄@PCM produces the charge capacity of 837 mAh g⁻¹ in the first cycle, much like the charge capacity offered by Fe₃O₄@PCM/graphene. After 100 cycles, however, the cycling capacity of Fe₃O₄@PCM gradually drops to 600 mAh g⁻¹. The calculated capacity from carbon and graphene in Fe₃O₄@PCM and Fe₃O₄@PCM/graphene are around 46.92 and 427.4 mAh g⁻¹, respectively.

Figure 4.12 The cycling performance of the Fe₃O₄@PCM/graphene (a) and Fe₃O₄@PCM (b) at 1 C

Figure 4.11b proves the excellent rate performance of Fe₃O₄@PCM/graphene. In the multiple-step galvanostatic charge-discharge test, as the current density increases to 1 C, 2 C, 5 C and 10 C, the specific capacities are remained to be 760 mAh g⁻¹, 665 mAh g⁻¹, 510 mAh g⁻¹ and 407 mAh g⁻¹. The capacity of more than 1000 mAh g⁻¹ is recovered when the current rate returns to the initial value of 0.1 C. To further probe the high rate property of Fe₃O₄@PCM/graphene, the sample was investigated in the cycling test under 1 C rate for 500 cycles. As shown in Figure 4.12a, the retention of the specific cycling capacity is up to more than 1000 mAh g⁻¹. However, the capacity of Fe₃O₄@PCM/graphene fades rapidly to around 700 mAh g⁻¹ when it is subjected to the initial several cycles and then gradually rises to more than 1000 mAh g⁻¹. It is believed that the occurrence of this phenomenon relates to the reversible formation of the polymer-like film by the electrochemical degradation of electrolyte and the electrochemical activation process to facilitate lithium ions pathway between electrode and electrolyte during cycling^{217, 218}. In comparison, Fe₃O₄@PCM was also found to present great cycling performance under 1 C rate (Figure 4.12b). After 500 cycles, the cycling performance of Fe₃O₄@PCM is still maintained to be more than 800 mAhg⁻¹.

Figure 4.13 The Nyquist plots (b) of the Fe₃O₄@PCM and Fe₃O₄@PCM/graphene electrodes before cycling and after 500 cycles (1 C).

Apparently, such distinguished electrochemical performances provided by Fe₃O₄@PCM and Fe₃O₄@PCM/graphene are attributed to the intentionally designed three-dimensional hierarchical nanostructure on graphene nanosheets.²¹⁹⁻²²¹ On one hand, the synergic effects between Fe₃O₄ nanoparticles and graphene and porous carbon matrix not only suppress the aggregation, cracking or crumbling of active materials but also provides an elastic buffer layer to accommodate the dramatic volume change during discharge-charge process. The graphene and carbon matrix, on the other hand, serve a high ionic and electronic conductivity for intercalation/deintercalation of lithium ions. In addition, the interlayer space of graphene nanosheets enables to increase the effective contact area with electrolyte and shorten the diffusion pathway for lithium ions. As summarized in Table 4.1, the superiority of the designed nanostructure can be demonstrated in comparison with most of the state-of-art electrodes.

Figure 4.13 shows electrochemical impedance spectra (EIS) of Fe₃O₄@PCM and Fe₃O₄@PCM/graphene before and after 500 cycles. The semicircles located at high and medium frequencies are attributed to the contact and charge transfer impedance, respectively. The inclined straight line is associated with the lithium-diffusion process which is responsible for Warburg impedance. For fresh electrodes at the high and medium frequency, Fe₃O₄@PCM/graphene generates much smaller diameters of the semicircles than the Fe₃O₄@PCM, indicating that the introduction of graphene improves the electric and ionic conductivity of the electrode. Interestingly, after 500 cycles under 1 C rate, the diameters of the semicircles of samples in both high and medium frequency areas become noticeably smaller (inset Figure 4.13). This extraordinary phenomenon suggests the happening of the textual modification during the cycling process, which activates the electrochemical reaction progress of Li-ion insertion and extraction.

In order to verify the benefits from the designed hierarchical three-dimensional nanostructure, the morphologies of the Fe₃O₄@PCM and

Fe₃O₄@PCM/graphene after 500 cycles (1 C) were examined in TEM. The intrinsic morphology of the porous carbon matrix is seen to be maintained after a long cycle-life that is covered by a thick SEI film (Figure 4.14a). Meanwhile, the pristine Fe₃O₄ nanoparticles transform into the nanocrystals with the size of 10 nm which then attach to the carbon nanowires due to the lithium driven structural or textual modification (Figure 4.14b). These results suggest that the porous carbon forms a very stable framework which can accommodate the continuous volume change and rapid electron/ion transportation leading to the enhanced cycling performance. However, some Fe₃O₄ nanoparticles are found to be detached from carbon matrix (Figure 4.14b). After 500 cycles, the similar structural reconstruction is observed in the Fe₃O₄@PCM/graphene electrode (Figure 4.14c and d). Fe₃O₄ particles are found to turn into 5 nm sized ultrafine nanoparticles anchored on graphene nanosheets, affording a high specific active area and a short ion diffusion pathway. Benefiting from the graphene based hierarchical three-dimensional nanostructure, the effective utilization of the active Fe₃O₄ nanoparticles can be achieved, in addition, the electrical detachment of nanoparticles is eliminated (as seen in Figure 4.14d). Herein, we can emphasize that the existence of graphene could effectively suppress the mechanical disintegration of active material during cycling.

Table 4.1 Cycling performance comparison with some reported Fe₃O₄ anode

Fe ₃ O ₄ Anodes	Current Density (mA g ⁻¹)	Cycling Number	Capacity (mAh g ⁻¹)	Ref
Mesoporous Fe ₃ O ₄	90.5	50	825	222
Porous Hollow Fe ₃ O ₄ /C beads	500	50	537	12
Porous Fe ₃ O ₄ /C Microbelts	100	50	710	223
Flexible Free-standing Hollow Fe ₃ O ₄ /graphene	500	50	660	224
Graphene-wrapped Fe ₃ O ₄ -graphene Nanoribbons	400	300	708	225
Fe ₃ O ₄ @PCM	1000	500	800	Our work
Fe ₃ O ₄ @PCM/graphene	1000	500	1000	Our work

Figure 4.14 TEM images of Fe₃O₄@PCM (a, b) and Fe₃O₄@PCM/graphene (c, d) after 500 cycles at 1 C.

4.3 Conclusion

In summary, the Fe₃O₄@PCM was obtained by the in-situ decomposition of MIL-53 (Fe). Furthermore, the hierarchical three-dimensional nanostructure was built by the introduction of graphene to synthesize the Fe₃O₄@PCM/graphene. Compared with the Fe₃O₄@PCM, the Fe₃O₄@PCM/graphene delivers a much better cycling performance, whose reversible capacity can maintain over 1000 mAh g⁻¹ (500 cycles at 1 C). The

graphene based hierarchical three-dimensional nanostructure is believed to bring a huge contribution to stabilizing the intrinsic morphology of the active material during cycling.

Chapter 5

Investigation on Nanoscale Ion Intermixing Induced Activation of Fe₂O₃/MnO₂ Composites

In this chapter, we demonstrate a facile method to prepare hollow-structured oxygen-vacancy-rich Fe₂O₃/MnO₂ nanorods. Our results have shown that the oxygen vacancies are induced by nanoscale ion intermixing between Fe and Mn ions, during annealing process. In the performance evaluation, owing to the unique core-shell hollow nanostructure and the presence of oxygen vacancies, Fe₂O₃/MnO₂ nanorods show excellent electrochemical performances as anodes for lithium ion batteries, whose reversible capacity maintains more than 700 mAhg⁻¹ after 2000 cycles.

5.1 Introduction

Currently, transition metal oxide based materials have appelaed much attention for their promising potential of applications as elemental components of LIBs catalysis, chemical sensor and electronic deviecs.²²⁶⁻²²⁸ Due to their superior performance and applicability, lots of efforts have been laid on the rational development and synthesis of advanced core-shell heterostructured transition metal oxide materials such as metal oxide/metal oxide^{229, 230}, metal oxide/semiconductor^{231, 232}, metal oxide/conductive polymer^{233, 234} and metal oxide/metal²³⁵⁻²³⁷. The various hybrid architectures could effectively combine advantages of components and provide excellent synergetic properties and multifunctionalities through reinforcement or modification of composites.²³⁸⁻²⁴⁰ In this context, intensive studies have been devoted to developing different strategies for preparing various transition metal oxides based heterostructured nanomaterials.

However, to a great extent, the intrinsic electrochemical properties of heterostructured materials rely on their interior structure and components' properties.²⁴¹⁻²⁴³ From this perspective, different metal oxides based core-shell nanomaterials with hollow, porous and yolk-shell interior structures have been studied.^{102, 244-248} For example, Wang et. al.²⁴⁹ reported the synthesis of hierarchical core-shell tubular CuO/other metal oxides arrays with a controllable two-step fabrication technique, which presented higher lithium storage capacity and improved cycling performance, compared with CuO nanorods and CoO nanoneedles on Ni foam. Moreover, hollow and porous core-shell CoO/TiO₂ nanorods were prepared with the assistance of atomic layer deposition.²⁵⁰ In the aspect of lithium ion batteries (LIBs), the fabricated hollow interior with high surface area and short diffusion paths usually leads to an exceptionally improved electrochemcial performance. The large surface area endows

active materials with extra active sites and increased diffusion rate for Li ions and electrons. Meanwhile, the hollow structure could provide extra space to facilitate the large volume expansion/contraction and alleviate the structural strain and stress associated with Li ions insertion/extraction process.²⁵¹⁻²⁵³

Among all these candidates, Fe₂O₃ and MnO₂ have always been considered as two kinds of promising alternatives for next generation anode materials of lithium ion batteries (LIBs). They possess several superior properties such as high theoretical capacities (1007 mAh g⁻¹ and 1232 mAh g⁻¹, respectively), environmental friendliness and low cost.²⁵⁴⁻²⁵⁶ However, the poor electrical conductivity (10⁻⁵-10⁻⁶) of MnO₂ severely restricts its practical application as high-performance anode materials for LIBs.²⁵⁷⁻²⁵⁹ According to previous studies, the major strategy developed to improve its conductivity is to construct MnO₂ based nanocomposite with conductive materials such as carbon nanotubes, graphene and conductive polymer. An expected improvement on their electrochemical performance is usually brought about through the desirable nanostructure, but the limitation of the MnO₂/conductor interfaces would cause the restricted conductivity reinforcement from external components.^{26, 260-262}

Recent reports have shown that the introduction of oxygen vacancies into MnO₂ could effectively boost the intrinsic conductivity of MnO₂.^{263, 264} So far, numerous approaches such as doping and hydrogenation have been developed to fabricate oxygen-deficient MnO₂, yet there are lack of reliable and effective methods to intrinsically improve the conductivity of MnO₂ via the formation of oxygen vacancies.²⁶⁵⁻²⁶⁷ Herein, hollow-structured oxygen-deficient Fe₂O₃/MnO₂ nanorods were synthesized via a surfactant-assisted coating of MnO₂ on FeOOH nanorods, followed by thermal annealing in the air. The oxygen-vacancy-rich MnO₂ shell was observed to be formed as a result of ion intermixing during heating process. It is expected that the unique hollow structure with oxygen-

deficient MnO₂ shell could offer high specific surface area, enhanced ionic and electronic conductivity and great structural stability against volume change leading to a long-term cycling life, excellent rate capability and improved reversible capacity as anode materials for LIBs.

5.2 Results and discussion

Figure 5.1 FESEM images of FeOOH nanorods.

The hollow-structured Fe₂O₃/MnO₂ nanorods were prepared through a two-step process. First of all, PVP decorated FeOOH nanorods were fabricated through a typical hydrolysis reaction of ferric chloride in a PVP-containing aqueous solution. Rod-like products with an average diameter of 50 nm and an average length of 150 nm can be observed in Figure 5.1, a SEM image showing the surface morphology of FeOOH nanorods. Subsequently, the hierarchical MnO₂ shell uniformly grows on the surface of FeOOH nanorods using the typical symproportionation precipitation reaction whose formula could be described as followed [Eq. (1)]²⁶⁸:

Finally, the hollow-structured Fe₂O₃/MnO₂ composite is formed under the annealing condition of 500 °C in the air for 2 h.

Figure 5.2 XRD patterns and SEM images of the FeOOH/MnO₂ core-shell nanorods (a, c) and the hollow-structured Fe₂O₃/MnO₂ nanorods (b, d).

The crystal structure and phase purity of FeOOH/MnO₂ nanorods (Figure 5.2a) and the as-obtained product annealed at 500 °C (Figure 5.2b) were performed by the means of XRD measurement. All the XRD diffraction peaks of the pattern in Figure 5.2a are assigned to pure tetragonal β-FeOOH (JCPDS 34-1266), indicating the highly crystalline nature of β-FeOOH nanorods and the amorphous structure of the MnO₂ component in FeOOH/MnO₂ nanorods. The complete decomposition of FeOOH and the crystallization of MnO₂, after 500 °C calcination, can be verified in the XRD pattern of the final product, as shown in Figure 5.2b. All the reflections can be indexed to α-MnO₂ (JCPDS 44-0141) phase except the

weak peaks belonging to α -Fe₂O₃ (JCPDS 33-0664), suggesting the high purity of the as-obtained product.

Figure 5.3 TEM (a, b) and high resolution TEM (c, d) images of the FeOOH/MnO₂ nanorods.

Figure 5.4 TEM (a) and high resolution TEM (b-d) images of the hollow-structured Fe₂O₃/MnO₂ nanorods.

SEM and TEM were used to investigate the nanostructure formed during annealing process. Figure 5.2c and d show SEM images of both FeOOH/MnO₂ nanorods and the hollow-structured Fe₂O₃/MnO₂ composite. After precipitation reaction, the hierarchical structured MnO₂ homogeneously grows on the surface of FeOOH nanorods (Figure 5.2c). The TEM images of FeOOH/MnO₂ in Figure 5.3 confirm that the crystallized FeOOH nanorods were coated with around 10 nm-thick amorphous MnO₂ layer. In the case of the Fe₂O₃/MnO₂ composite, TEM images (Figure 5.4a and b) reveal that the Fe₂O₃/MnO₂ composite

possesses a core-shell hollow nanostructure, meanwhile, after annealing treatment, the hierarchical structured MnO₂ layer is converted to a relatively smooth and compact shell, in accordance with the SEM image (Figure 5.2d), which can be assumed to be originated from the inward movement of MnO₂, under heating conditions, according to the reduced nanorods diameter. The phase structure of the hollow-structured Fe₂O₃/MnO₂ nanorods is demonstrated in HRTEM images (Figure 5.4b-d). As shown in the selected-area electron diffraction (SAED) pattern (Figure 5.5), the entire Fe₂O₃/MnO₂ nanorod displays the property of single crystallization. The interior Fe₂O₃ core is covered by the MnO₂ layer of 5 nm thickness (Figure 5.4b). To reveal the relationship between Fe₂O₃ and MnO₂ crystal structure, the enlargements of the white line square parts are demonstrated in Figure 5.4c and d. As shown in Figure 5.4c, the interplanar distance of 0.26 nm measured corresponds to the spacing between (222) planes of α -Fe₂O₃ crystals which is imaged at a zone axis of [001]. Meanwhile, the outer shell of α -MnO₂ (Figure 5.4d) is nanocrystalized based on the indexing of FFT (the inset) and the interplanar spacing of (031) is measured to be 0.25 nm, indicating the epitaxial relationship between the MnO₂ shell and Fe₂O₃ core along the direction of (220) α -Fe₂O₃. The elemental distribution on Fe₂O₃/MnO₂ nanorods was performed using EDX in scanning TEM mode. The signals of Fe, Mn and O are indicated in Figure 5.6, which distribute in the whole nanorod region with a dark ring in the middle, revealing the occurrence of mutual ionic diffusion during annealing process. The SEM-EDX analysis was employed to determine the ratio of Fe to Mn, showing the molar ratio of around 1:1 in the Fe₂O₃/MnO₂ composite (Figure 5.7).

Figure 5.5 TEM image (a) and SAED pattern (b) of the hollow-structured Fe₂O₃/MnO₂ nanorod.

To analyze the chemical states of the Fe₂O₃/MnO₂ composite, XPS measurement was performed (Figure 5.8). As shown in C1s XPS data (Figure 5.8a), three refined peaks at binding energies of 284.6, 286.0 and 288.5 eV can be resolved from a broad peak, corresponding to various bonds related to C-C, C-O, and C=O, respectively, which could come from a result of the decomposition from PVP.²⁶⁹⁻²⁷² In the high resolution XPS spectrum of Mn2p (Figure 5.8b), the bonding energies of Mn2p_{3/2} and Mn2p_{1/2} centered at 641.8 and 653.3 eV, respectively, present a spin energy separation of 11.5 eV, which is in good agreement with the previous reported MnO₂.²⁷³ It also can be seen that the deconvoluted Mn2p_{3/2} and Mn2p_{1/2} spectra display doublet peaks with separated binding energies of 642.7 and 654.2 eV and 641.5 and 652.8 eV, attributed to Mn³⁺ and Mn⁴⁺, respectively.²⁷⁴⁻²⁷⁷ The surface oxidation state for the hollow-structured Fe₂O₃/MnO₂ is calculated to be 3.47, verifying the existence of oxygen nonstoichiometry in the MnO₂ layer. The introduction of oxygen vacancies can result in the conductivity enhancement of the MnO₂, leading to an improved electrochemical performance for LIBs anodes. Figure 5.8c shows the Fe2p XPS spectrum,

in which the $\text{Fe}2p_{3/2}$ and $\text{Fe}2p_{1/2}$ peaks appear at 710.2 and 724 eV, respectively, with a shake-up satellite peaks at 719 eV, indicating the formation of Fe_2O_3 , which is consistent with the XRD result.²⁷⁸ As for the $\text{O}1s$ spectrum (Figure 5.8d), the main portion of the response at 529.2 eV is originated from oxygen species in the oxide lattice and the peaks at 531 and 533.1 eV may come from the OH- radical and absorbed H_2O outside, respectively.²⁷⁹⁻²⁸¹

Figure 5.6 Elemental mapping of the hollow-structured $\text{Fe}_2\text{O}_3/\text{MnO}_2$ nanorods

Figure 5.7 EDX quantitative analysis of the hollow-structured Fe₂O₃/MnO₂ composite on the selected region.

Figure 5.8 C1s (a), Mn2p (b), Fe2p (c) and O1s (d) XPS spectra for the hollow-structured Fe₂O₃/MnO₂ nanorods

To further investigate the formation process of the unique oxygen-deficient nanostructure, FeOOH/MnO₂ nanorods were annealed at different temperature of 300, 400 and 600 °C for the same duration in the air. The as-obtained products were designated as Fe-Mn-300, Fe-Mn-400

and Fe-Mn-600, respectively, and characterized by XRD, SEM, TEM and XPS techniques. A morphological evolution from hierarchical core-shell porous nanorods to core-shell hollow and triple-layer core-shell nanorods is revealed in the sequential TEM and SEM images (Figure 5.9-5.12). The nanostructure transformation has indicated that there happens a slow thermal shrinkage of the MnO₂ layer, confirming the inward movement of MnO₂ initiated by the annealing treatment. Additionally, the solid reaction between Fe₂O₃ core and MnO₂ layer occurs to form the cubic (Fe_{0.42}Mn_{0.58})₂O₃ bixbyite intermediate layer, as the annealing temperature rises to 600 °C, verifying the presence of element diffusion across the interface (Figure 5.12). The migration of MnO₂ during annealing process is further studied by the EDX line-scanning technique. Figure 5.13 shows the EDX line-scanning profiles of Fe-Mn-300, Fe-Mn-400, hollow-structured Fe₂O₃/MnO₂ and Fe-Mn-600. As shown in Figure 5.13, the portion of Mn element tends to increase in the inner part of the nanorod with increasing temperature, which is in good agreement with the TEM results. As displayed in the high resolution XPS spectra of Mn2p (Figure 5.14), the mean valence states of Mn is 4.00, 3.90 and 3.40 in Fe-Mn-300, Fe-Mn-400 and Fe-Mn-600, respectively, showing the reduction of the Mn oxidation state with increasing temperature. And the low valence of Mn in Fe-Mn-600 is believe to be derived from the solid-state reaction at the Fe₂O₃/MnO₂ interface, forming the (Fe_{0.42}Mn_{0.58})₂O₃ phase. Our observation on these temperature-dependent final products reveals the process of MnO₂ inner migration accompanied by the formation of oxygen vacancies. We thus propose an ion-intermixing growth mechanism to understand the formation of oxygen vacancies based on our analysis.

Figure 5.9 SEM images and XRD patterns (d) of the as-obtained products from the subsequent annealing treatment of 300 (a), 400 (b) and 600 (c) °C.

Figure 5.10 TEM (a), high resolution TEM (b) images and elemental mapping (c) of the as-obtained products at 300 °C.

Figure 5.11 TEM (a) and high resolution TEM (b) images and elemental mapping (c) of the as-obtained products at 400 °C.

Figure 5.12 TEM (a), high resolution TEM (b-e) images and elemental mapping (f) of the as-obtained product at 600 °C.

Figure 5.13 Bright-field scanning TEM images (top) and corresponding EDX line-scanning profiles (bottom) of the products annealed at 300, 400, 500 and 600 °C.

As indicated in Figure 5.15a, the MnO₂ layer experiences a morphological transformation and thermal contraction under heating conditions, which turns the loosely hierarchical layer into the smooth and compact shell. In this process, the MnO₂ layer continuously migrates inward, at the same time, the mutual ionic intermixing takes place at the Fe₂O₃/MnO₂ interface, supported by the results of TEM and line-scanning EDX.^{282, 283} Owing to the Kirkendall effect, the rates of individual ionic diffusion are different at the composite interface, leading to the formation of the hollow interior during annealing treatment.²⁸⁴ In the Meanwhile, the oxygen deficiencies are gradually introduced into the MnO₂, which can be confirmed in the XPS data (Figure 5.14). Along with rising annealing temperature from 300 °C to 600 °C, the increase of Mn:O ratio is clearly observed, ascribing to the mutual ionic interdiffusion, in which sites of Mn⁴⁺ can be easily occupied by implanted Fe³⁺ ions, and thus, the charge neutrality gets lost, originated from the composite stoichiometry. Therefore, in order to preserve the charge neutrality, oxygen vacancies is formed.²⁸⁵⁻²⁸⁷ The formed vacancies further facilitate the inward movement of MnO₂. Finally, the smooth and compact MnO₂ shell is formed through the thermal-driven interdiffusion.²⁸⁸ It is worth to note

that the ternary oxide of cubic (Fe_{0.42}Mn_{0.58})₂O₃ phase is formed at a high temperature of 600 °C, which shows a similar phenomenon in the solid-state reaction of the Fe-implanted TiO₂ and the core-shell SnO₂/TiO₂ nanomaterials.^{289, 290} The detailed reaction process is demonstrated by the TGA measurement of the FeOOH/MnO₂ nanorods in the air with a heating rate of 10 °C min⁻¹. The weight loss and derivative weight loss of the sample are plotted in Figure 5.15b as function of the sample temperature. Figure 5.15b shows a slow weight loss related to the transformation from FeOOH to Fe₂O₃ and the decomposition of PVP between 200 and 400 °C after a rapid loss of physical and chemical adsorption of ethanol, water and organic species below 200 °C. With further increasing temperature from 400 to 600 °C, there obviously exists a moderate reaction leading to around 2% weight loss corresponding to the ion-intermixing process and the formation of oxygen vacancies, well consistent with the above discussion.

Figure 5.14 High resolution Mn2p XPS spectrum for the products annealed at 300 (a), 400 (b), 500 (c) and 600 (d) °C.

Figure 5.15 Illustration of the formation process for the oxygen-deficient MnO₂ layer (a) and TGA (blue solid) and the corresponding derivative curve (black solid) curves for the FeOOH/MnO₂ core-shell nanorods in flowing air (b).

The BET specific surface area and porosity of Fe-Mn-300, Fe-Mn-400, hollow-structured Fe₂O₃/MnO₂ and Fe-Mn-600 were investigated by nitrogen adsorption-desorption analysis (Figure 5.16). The BET specific surface area of the as-obtained products decreases from 131.75 to 17.84 m² g⁻¹ as annealing temperature increases from 300 to 600 °C. As compared in the BJH (Barret-Joyner-Halenda) pore size distribution calculated from adsorption branches, the morphological evolution from internal porous to hollow and solid nanostructure is demonstrated. These results are in a good agreement with the observation of TEM results. The inner cavity such as porous and hollow structure could increase the contact area between electrolyte and active materials, leading to a faster diffusion rate for Li⁺ ions. Moreover, the reserved internal space could improve the stability of the nanostructure via alleviating volume variation during Li⁺ insertion/extraction.^{8, 291}

Figure 5.16 BET isotherm plots and corresponding BJH pore size distributions (insets) of the as-obtained products at 300 °C (a), 400 °C (b), 500 °C (c) and 600 °C (d).

Figure 5.17 The first five cyclic voltammogram (CV) curves at a scan rate of $0.5 \text{ mV} \cdot \text{s}^{-1}$ (a) and discharge-charge curves (b) of the hollow-structured Fe₂O₃/MnO₂ nanorods.

The electrochemical properties of the core-shell hollow Fe₂O₃/MnO₂ nanorods, as anode materials for LIBs, were performed by the measurement of cyclic voltammograms, using a Li foil as the counter and reference electrode. There are two cathodic peaks at around 1.0 and 0.45 V in the first cycle, in Figure 5.17a, which are assigned to the valence change of Mn element from 4+ to 2+ and from 2+ to 0, respectively.²⁹² The peaks at 1.32 V, 1.0 V and 0.45 V are attributed to the Li insertion in the Fe₂O₃, the reduction of Fe³⁺ to Fe²⁺ and Fe²⁺ to Fe⁰ and the formation of SEI film from the irreversible decomposition of electrolyte, respectively.²⁹³ In the following cycles these intense peaks are moved to 0.25 V and 0.4 V, due to the structure reconstruction triggered by the formation of Li₂O and metals. The anodic scanning shows two broaden peaks at 1.3 V and 1.75 V, corresponding to the oxidative reactions of Fe⁰ to Fe²⁺ and Mn⁰ to Mn²⁺ and Fe²⁺ to Fe³⁺ and Mn²⁺ to Mn⁴⁺, respectively. The CV measurement was also conducted on the Fe-Mn-300, Fe-Mn-400 and Fe-Mn-600. As shown in Figure 5.18, in comparison, the CV curves of the hollow-structured Fe₂O₃/MnO₂ electrodes almost completely overlap from the second cycle onwards, revealing a much better chemical reversibility, indicating that the presence of oxygen vacancies could

effectively promote the electrode's electrochemical performance. Through inducing oxygen vacancies, not only could the electronic conductivity of MnO_2 be enhanced, but the Li-ions diffusion process would also be accelerated.^{294, 295}

Figure 5.18 The first five cyclic voltammogram (CV) curves of the Fe-Mn-300 (a), Fe-Mn-400 (b) and Fe-Mn-600 (c) anodes

Figure 5.19 Cycling performance of the electrodes made of the hollow-structured Fe₂O₃/MnO₂ (a) and Fe-Mn-600 nanorods (b) at a current of 0.2 C.

The electrochemical performance of the core-shell hollow Fe₂O₃/MnO₂ nanorods was further evaluated by the galvanostatic discharge-charge measurement. Figure 5.17b shows the 1st, 10th and 30th discharge-charge profiles of the Fe₂O₃/MnO₂ electrode performed under the current density of 0.2C (200 mA g⁻¹) in the voltage window ranging from 0.01 V to 3.0 V. In the first cycle, there are four plateaus, located at around 1.9 V, 1.5 V, 1.2 V and 0.7 V in the discharging process, which are associated with the cathodic peaks of the CV measurement. The initial discharge and charge capacities are measured to be 1658 and 1187 mAh g⁻¹, respectively. The formation of solid electrolyte interphase (SEI) and the incomplete restoration of metallic Fe and Mn into the original oxide is responsible for the irreversible capacity loss of the first cycle (27.48%). After 10 and 30 cycles, the respective discharge capacities are 1194 and 1252 mAh g⁻¹, which is greater compared to the theoretical capacity. The extra capacity is resulted from the pseudo-capacitive interfacial adsorption, the reversible reactions related to LiOH formation and the reversible formation of the polymeric/gel-like films on the active materials from the kinetical decomposition of the electrolyte.²⁹⁶⁻²⁹⁹

Figure 5.20 Cycling performance of the Fe-Mn-300 (a) and Fe-Mn-400 (b) electrodes at a current of 0.2C.

Figure 5.21 Cycling performance of the electrodes made of the hollow-structured Fe₂O₃/MnO₂ (a) and Fe-Mn-600 (b) nanorods at a current of 1 C.

Figure 5.19 shows the hollow-structured Fe₂O₃/MnO₂ and Fe-Mn-600 electrodes' cycling performance as anodes for LIBs at 0.2 C rate. Both electrodes of the Fe₂O₃/MnO₂ and Fe-Mn-600 show exceptional cyclability and provide high initial charge capacities of 1187 and 1042 mAh g⁻¹, respectively. In the subsequent cycles, their capacities undergo a slow continuous increase. After 50 cycles, the reversible capacities are increased to as high as 1310 and 1096 mAh g⁻¹. For the electrodes of the as-obtained porous nanorods at 300 and 400 °C (Fe-Mn-300 and Fe-Mn-400, Figure 5.20a and b, respectively), a continuous performance drop is

clearly observed and their discharge capacities are as low as 200 and 236 mAh g⁻¹, respectively, at the 50th cycle. To evaluate the electrochemical properties of the samples at a high rate, the cycling measurement was also conducted at 1 C (Figure 5.21). In the duration of 500 cycles, it is interesting to find that the capacities of the electrodes of the as-prepared products at 500 and 600 °C (hollow-structured Fe₂O₃/MnO₂ and Fe-Mn-600) suffer a rapid decline initially, followed by an increase at a slow rate until the maximum. With the additional cycle number, their capacities drop slightly and then continue to increase. According to previous studies, the abnormal capacity trend can be ascribed to the following two parts. On one hand, the in-situ formation of highly reactive pristine metallic nanograins during electrochemical conversion reaction promotes the growth of a conducting-type polymeric film, leading to an enhanced specific capacity.⁸² On the other hand, the high-rate lithiation induces a refinement of active materials into a mesoporous structure, resulting in a reactivation and enlarged active area.³⁰⁰ As cycling continues, the conductive polymeric and stable SEI film would be gradually formed on the freshly exposed surface area, which causes an improved electrochemical performance.³⁰¹ After 500 cycles, the reversible capacities are still remained to be 1167 and 888 mAh g⁻¹ for the hollow-structured Fe₂O₃/MnO₂ and Fe-Mn-600 electrodes, respectively.

Figure 5.22 Cycling performance of the Fe₂O₃/MnO₂ (a) and Fe-Mn-600 nanorods (b) at various current densities and cycling performance (c) of the hollow-structured Fe₂O₃/MnO₂ nanorods at a current of 5 C.

The rate capabilities of the hollow-structured Fe₂O₃/MnO₂ and Fe-Mn-600 electrodes were evaluated by the multiple-step galvanostatic charge-discharge measurement. The hollow-structured Fe₂O₃/MnO₂ anode presents the reversible capacities of around 1200, 1000, 750, 600, 470, 320 mAh g⁻¹ at current rates of 0.2, 0.5, 1, 2, 5 and 10 C, respectively, as shown in Figure 5.22a. It is noted that the electrode still shows a much higher value than 300 mAh g⁻¹ in the event of the lowest capacity of the high rate (10 C). As the current density is set back to 0.1 C, the reversible capacity is restored and goes up to 1250 mAh g⁻¹, indicating the excellent structural stability of the Fe₂O₃/MnO₂ composite. In comparison, the Fe-Mn-600 anode shows a slightly worse rate capability (Figure 5.22b). The measured specific capacities are 1050, 830, 575, 320, 120, 50 mAh g⁻¹, respectively, at the above six rates.

The long-term high rate performance of the hollow-structured Fe₂O₃/MnO₂ nanorods is shown in Figure 5.22c. The final reversible capacity at 5 C is measured to be as high as 706 mAh g⁻¹, after 2000 cycles. Like the phenomenon happened at 1 C, the capacity drops down to around 400 mAh g⁻¹ in the beginning and then slowly climbs up to more than 700 mAh g⁻¹. The increasing capacity is attributed to the reversible formation of polymer-like film during cycling.^{217, 299} As summerized in Table 5.1, the superior long-term high rate performance of the hollow-structured oxygen-vacancy-rich Fe₂O₃/MnO₂ is demonstrated in comparison to the previous reported. For instance, the electrode of MnO₂/3D-ordered hollow carbon sphere only displays a reversible capacity of 420 mAh g⁻¹ after 500 cycles.³⁰² With regards to ordered mesoporous carbon nanowire/Fe₂O₃ anode, the reversible capacity can be improved to 774 mAh g⁻¹ after 1200 cycles, however the current density has to be reduced to 500 mA g⁻¹.³⁰³ As compared with branched Fe₂O₃/ MnO₂ nanorods³⁰⁴, the remained capacity of the as-prepared oxygen-vacancy-rich Fe₂O₃/MnO₂ electrode exhibits a much higher value, even after 500 cycles, under the same current density. The superior electrochemical performance is attributed to the intentionally designed nanostructure. Firstly, the interior cavity could increase the stability of the material's structure and decrease the diffusion length for Li ions.³⁰⁵ Secondly, the core-shell structure brings out synergistic effect between hollow Fe₂O₃ core (less volume change and structural destruction) and MnO₂ shell (high theoretical capacity and preservation of structural integrity upon the consecutive Li ion insertion/extraction cycling).^{306, 307} Above all, the formation of oxygen vacancies in MnO₂ shell gives rise to a recognized boost to their intrinsic conductivity, providing a fast electronic and ion transport pathway for electrochemical reaction.^{308, 309}

Table 5.1 Cycling performances of some reported hybrid nanomaterials

Hybrid Nanomaterials	Current Density (mA g ⁻¹)	Cycle Number	Capacity (mAh g ⁻¹)	Ref.
Graphene-Wrapped MnO ₂ -Graphene Nanoribbons	400	250	612	292
α -Fe ₂ O ₃ Hollow Nanobarrels-Reduced Graphene Oxide	5000	1000	418	310
Ordered Mesoporous Carbon Nanowire/Fe ₂ O ₃	500	1200	774	303
Hierarchical Hollow TiO ₂ @Fe ₂ O ₃	200	200	516	311
MnO ₂ /3D-Ordered Hollow Carbon Sphere	1000	500	420	302
Hollow Core-Shell MnO ₂ /C Hybrid Spheres	1000	300	927	312
Porous Branched Fe ₂ O ₃ / MnO ₂ Nanorods	1000	200	1028	304
Hollow-structured Oxygen-Vacancy-Rich Fe ₂ O ₃ /MnO ₂	5000	2000	700	Our work
Hollow-Structured Oxygen-Vacancy-Rich Fe ₂ O ₃ /MnO ₂	1000	500	1167	Our work

The effect of oxygen vacancies in terms of conductivity is verified by the measurement of EIS. Figure 5.23a shows the EIS data of the fresh electrodes. In Figure 5.23a, the Nyquist spectrum is comprising of a depressed semicircle at high frequency corresponding to the charge transfer process and a straight line in the low frequency region ascribed to the Li ions diffusion.²⁰⁶ As compared, the smallest diameter of the semicircle and the most vertical straight line can be observed in the

hollow-structured Fe₂O₃/MnO₂ composite, showing its high electronic and ionic conductivity, which is attributed to their internal hollow structure and introduced oxygen vacancies. After 2000 cycles, the cells of the hollow-structured Fe₂O₃/MnO₂ composite were charged to 3V and disassembled to perform the morphological observation via TEM. As seen in Figure 5.23b, the Fe₂O₃/MnO₂ composite could still maintain the hollow rod-like nanostructure assembled by nanoclusters, after a long-term cycling, indicating its excellent structural stability. Meanwhile, the retained Mn and Fe elements can be confirmed by the elemental distribution profile (Figure 5.23c). For convenient comparison, all the information of the as-prepared samples' morphology and performance is concluded in Table 5.2.

Figure 5.23 Nyquist plots (a) of the uncycled cells for the products fabricated at 300 °C, 400 °C, 500 °C and 600 °C, respectively; TEM image (b) and elemental mapping (c) of the hollow-structured Fe₂O₃/MnO₂ nanorods after 2000 cycles at 5 C.

Table 5.2 Physical and electrochemical properties of the as-prepared samples

Samples	Morphology	composite	Surface area (m ² g ⁻¹)	Current Density (mA g ⁻¹)	Capacity at n cycles (mAh g ⁻¹)
Fe-Mn-300	Hierarchical porous core- shell	α -Fe ₂ O ₃ / α -MnO ₂	131.75	200	200/50
				1000	138/300
Fe-Mn-400	Hierarchical porous core- shell	α -Fe ₂ O ₃ / α -MnO ₂	109.39	200	237/50
				1000	472/300
Hollow- structured Fe ₂ O ₃ /MnO ₂	Hollow core- shell	α -Fe ₂ O ₃ / α -MnO ₂	34.56	200	1310/50
				1000	1520/500
Fe-Mn-600	Trilayer core- shell	α - Fe ₂ O ₃ /(Fe _{0.42} Mn _{0.5}) ₂ O ₃ / α -MnO ₂	17.84	200	1096/50
				1000	989/500

5.3 Conclusion

In summary, we have proposed a facile strategy to construct the hollow-structured oxygen-vacancy-rich Fe₂O₃/MnO₂ nanorods. The method combines the PVP assisted MnO₂ coating and the subsequent thermal treatment in the air. Under heating condition, the nanoscale ion intermixing, attributed to the inward flow of the MnO₂, raises the formation of oxygen vacancies. It is demonstrated that the hollow-structured Fe₂O₃/MnO₂ composite displays superior performance as anode materials for LIBs, ascribed to the unique core-shell hollow nanostructure and the presence of oxygen vacancies.

Chapter 6

Investigation on Phase Transition of Hollow-porous α - Fe_2O_3 Anodes

In this chapter, the hollow-porous α - Fe_2O_3 microspheres are prepared via cation etching of zinc citrate microspheres and subsequent thermal treatment. The superior performance of the as-obtained α - Fe_2O_3 microspheres is evaluated as anode materials for lithium ion batteries. After 1000 cycles, the capacity still remains more than 1100 mAhg^{-1} at current rate of 1 Ag^{-1} . Meanwhile, the crystal size induced phase transition of Fe_2O_3 microspheres ($\alpha \rightarrow \gamma \rightarrow \beta$) is observed during cycling by the measurements of ex-situ XRD and TEM, which is responsible for their abnormal performance fluctuation.

6.1 Introduction

Currently, numerous efforts have been devoted to the investigation of iron oxide (Fe_2O_3) based nanomaterials due to their promising application as anode materials for lithium ion batteries (LIBs).³¹³⁻³¹⁵ Compared with other anode materials, Fe_2O_3 exhibits much better compatibility and applicability, such as low cost, high theoretical capacity (1005 mAhg^{-1}) and environmental friendliness.¹⁶⁴ However, The Fe_2O_3 electrodes in LIBs generally are subject to the electrochemical process of conversion reactions (i.e. the reduction and oxidation between lithium and iron oxide (with 6 Li^+ per Fe_2O_3 molar)), which causes extremely large volume expansion and electrode destruction during cycling.^{316, 317} In order to address a series of triggered problems such as the loss of electrical contacts and active materials pulverization, the best strategy is to design and synthesize Fe_2O_3 based anode materials with porous and hollow nanostructures. In the light of some related studies, the perfection of the porous and hollow nanostructures could bring some obvious merits to the performance improvement of the Fe_2O_3 electrode. First, the interval of Fe_2O_3 primary particles acts as buffer layer for the volume change during cycling.³¹⁸ Second, the intrinsic porosity increases the specific active area for the lithiation/delithiation reaction.^{319, 320} Moreover, the channels built by the unique porous and hollow structures could offer a high rate of Li^+ ions diffusion process.^{321, 322} Based on these considerations above, recently, a large quantity of porous and hollow Fe_2O_3 nanomaterials with superior performance have been successfully prepared.

In spite of the high performance of Fe_2O_3 anode materials achieved by various techniques, the detailed electrochemical reaction process during cycling still needs to be investigated. The electrochemical reaction process has been widely accepted following the equation of $\text{Fe}_2\text{O}_3 + 6 \text{Li}^+ \longleftrightarrow 2 \text{Fe} + 6 \text{Li}_2\text{O}$.³²³⁻³²⁵ However, it is well known that the anode

materials usually undergo abnormal performance fluctuation, in which the initial capacities progressively decrease and then ramp up during cycling. The phenomenon is normally attributed to the formation of solid electrolyte interface (SEI) film and the reversible formation of the polymer-like film on the active materials' surface.³²⁶⁻³²⁸ In fact, the detailed mechanism on the performance fluctuation still remains unclear. The investigation on the phenomenon will bring a further perspective on their performance fading and nanostructure designation.

In the present work, we synthesized the hollow-porous α -Fe₂O₃ microspheres by a facile strategy. The method involves cation etching of zinc citrate microspheres template and annealing treatment. The as-obtained Fe₂O₃ electrode provides the capacity of more than 1100 mAhg⁻¹ at current rate of 1 Ag⁻¹ after 1000 cycles in the electrochemical test. The phase transition process of Fe₂O₃ nanoparticles initiated by the crystal size reduction, during high rate and long-term cycling, has been demonstrated to contribute this excellent performance revealed using ex-situ high-resolution TEM (transmission electron microscope) technique along with XRD (X-ray diffraction).

6.2 Results and discussion

Figure 6.1 SEM images of the zinc citrate microspheres template.

Figure 6.2 SEM image of the precursor (a) and SEM images (b, c) and XRD pattern (d) of the as-obtained α - Fe_2O_3 microspheres.

The chemical reaction of Fe^{2+} ions with zinc citrate templates (Figure 6.1) was employed to prepare the precursor of the hollow-porous α - Fe_2O_3 microspheres. In this process, the color of the suspension changes from green to red, indicating the formation of ferrous hydroxide and the subsequent conversion to ferric hydroxide. As shown in Figure 6.2a, the precursor appears the hollow microsphere structure with an average diameter of 1 μm . In addition, its amorphous phase structure is revealed from the XRD pattern (as shown in Figure 6.3). The formation mechanism of the hollow structure could be described as following: when zinc citrate templates are immersed in an aqueous solution of ferrous sulfate, the hydrolysis reaction of Fe^{2+} is spontaneously carried on around the surface of the zinc citrate with generation of ferrous hydroxide. Simultaneously, the hollow structures are built while zinc citrate templates are being etched by H^+ . As the reaction goes on,

ferrous hydroxide progressively turns to be ferric hydroxide due to the oxidation reaction of air. The detailed reaction process is summarized as:

and

After annealing in the air, the porous and hollow $\alpha\text{-Fe}_2\text{O}_3$ microspheres (as shown in Figure 6.2b and c) were obtained. Such hollow microsphere structure of the as-obtained $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles is apparently derived from the precursor. In addition, the porous surface of the obtained nanoparticles is clearly observed from their high-resolution SEM (scanning electron microscope) image (Figure 6.2c). Figure 6.2d shows the X-ray diffraction (XRD) pattern collected from the $\alpha\text{-Fe}_2\text{O}_3$ microspheres. All diffraction peaks are indexed (ICSD 40142) and generated from the $\alpha\text{-Fe}_2\text{O}_3$ particles demonstrating their high purity of $\alpha\text{-Fe}_2\text{O}_3$ phase as attributed to the complete chemical etching reactions.

Figure 6.3 XRD pattern of the precursor.

Figure 6.4 TEM (a, b) and HRTEM (c, d) images of the as-synthesized α -Fe₂O₃ microspheres.

To reveal the interior crystalline structure, the α -Fe₂O₃ microspheres, TEM was employed. Figure 6.4a is a bright field TEM image, which clearly approves the hollow and porous nanostructure of the α -Fe₂O₃ microspheres in good agreement with the SEM images (Figure 6.2b and c). The nanocrystalline structure of microspheres is identified from the selected area electron diffraction (SAED) pattern (inset of Figure 6.4a), which consists of as indicated from multiple discrete rings. In Figure 6.4b, it can be observed that the porous structure is formed by the randomly piling up of nanocrystals with average size of 30 nm. Furthermore, the

high-resolution TEM (HRTEM) images, Figure 6.4c and d (magnified from the square part in Figure 6.4c), show a single nanocrystal of α -Fe₂O₃ which can be verified by the fast fourier transform (FFT) pattern (inset of Figure 6.4d), in accordance with the XRD result (Figure 6.2d). As shown in Figure 6.4d, the fringes are shown to be separated by 0.29 nm, corresponding to the spacing between (210) planes of α -Fe₂O₃ nanocrystals.

Figure 6.5 BET isotherm plots and corresponding BJH pore size distributions (insets) of the α -Fe₂O₃ microspheres

Brunauer-Emmett-Teller gas-sorption measurement was conducted to study the porous nature and specific areas of the as-synthesized α -Fe₂O₃ microspheres. The typical type IV nitrogen adsorption-desorption isotherms and the inset of resultant pore size distribution profile are shown in Figure 6.5. The observed sharp capillary condensation step from high pressure ($p/p_0 > 0.8$) and the H1 type hysteresis loop showing the

both existence of the macro- and mesopores. The BET surface area of the α -Fe₂O₃ microspheres is calculated to be around 22.2 m² g⁻¹. On the word of the analysis of Barrett-Joyner-Halenda (BJH), the obvious property of the multimodal porosity is indicated. The relatively narrow distribution located centred at 10 nm is believed to be contributed by the presence of the mesoporous shell. Whereas, the wide distribution of large pores (45 nm-80 nm) is assumed to be associated with the interspace among the integrated α -Fe₂O₃ particles. The result above can also be confirmed by the image of SEM and TEM.

The electrochemical property of the as-obtained α -Fe₂O₃ microsphere was evaluated by the measurements of cyclic voltammetry (CV) and galvanostatic discharge-charge using the assembled CR2016 coin cells. As shown in Figure 6.6a, the detailed electrochemical reaction process can be thoroughly demonstrated in the profile of the corresponding CV test conducted at a rate of 0.5 mV s⁻¹.³²⁹⁻³³² In the cathodic process of the first cycle, a strong and three weak peaks are viewed and they are located at 0.62 V, 1.60 V, 1.33V and 0.95 V, respectively. The strong peak is attributed to the lithiation reaction of Fe₂O₃ and the irreversible decomposition of electrolyte. The other three small peaks are sequentially associated with the further lithium intercalation, the reduction process of Fe³⁺ to Fe²⁺ and the complete reduction reaction of Fe²⁺ to Fe⁰. However, in the subsequent cycle, the cathodic peak appears much broader and is shifted to 0.75 V, indicating the occurrence of the irreversible phase transformation and electrolyte decomposition. In the anodic part, an extensive anodic peak is observed and located at 1.7 V, related to the delithiation and the oxidation reaction of Fe⁰ to Fe³⁺. With more cycles, the anodic peak position and intensity are almost kept unchangeable, demonstrating the high reversibility of the oxidation reaction. Based on previous investigations, the electrochemical reaction mechanism is described as the following equation³²³⁻³²⁵:

Figure 6.6 First five cyclic voltammogram (CV) curves (at a scan rate of $0.5 \text{ mV} \cdot \text{s}^{-1}$) (a) and discharge and charge curves (b) of the as-prepared the as-obtained $\alpha\text{-Fe}_2\text{O}_3$ microspheres.

Figure 6.7 Cycling performance at a current of 0.2 C (a), rate capability (b) and high rate cycling performance at a current of 1 C (c) of the as-prepared $\alpha\text{-Fe}_2\text{O}_3$ microspheres.

The profile of galvanostatic discharge-charge was performed to measure the electrochemical properties of the hollow-porous α -Fe₂O₃ microspheres. The Figure 6.6b shows the discharge-charge profiles of the as-obtained α -Fe₂O₃ anode electrode of the first 3 cycles at the rate of 0.2 C (200 mA g⁻¹). At the first cathodic process, there exists plateaus at potentials of 1.47 V, 1.08 V and 0.88 V, respectively, followed by a continuous dropping of potential, corresponding to the reduction of metal oxides and electrolyte decomposition. In the following cycles, only a wide slope between 0.8 - 1.5 V is shown in the discharge curves. The drastic change demonstrates the occurrence of the irreversible reduction reaction and electrolyte decomposition in the first cycle.^{316, 333} In the charge process, a steady wide slope is located between 1.2 V and 2.5 V which is attributed by the reversible oxidation reaction of the active material. The test results above are in well agreement with Figure 6.6a.^{334, 335} The repective capacities of the initial discharge and charge are measured to be 1477.22 mAh g⁻¹ and 1125.33 mAh g⁻¹. The loss of the irreversible capacity (351.89 mAh g⁻¹) in the first cycle is likely attributed to the formation of SEI film and the reduction of oxide to metallic Fe with Li₂O matrix.³³⁶ The perfection of the as-synthesized α -Fe₂O₃ electrode's cyclability at a low rate (0.2 C) is shown in Figure 6.7a. In the range of the whole 50 cycles, the coulombic efficiency is kept stable above 98% except the initial one (76.18%). Meanwhile, the capacities remain a steady value of around 1150 mAh g⁻¹, which highly exceeds the theoretical capacity of the α -Fe₂O₃ (1005 mAh g⁻¹)¹⁶⁴. In the light of previous studies^{217, 299, 337}, the extra capacity is usually contributed to two parts. Firstly, the polymeric/ gel-like films could be reversibly formed/dissolved over the surface of active materials by the break-down of electrolyte. Secondly, the electrocatalysing cathodic reaction of C⁴⁺ from carbonate salt to other C species with low valences could be triggered by the fresh metal nanocrystals surface formed during the lithiation reaction. The great cycling performance is mainly

contributed by the merits of the unique structure. On the one hand, the intervals of the numerous nanocrystals consisting of the porous shell and the interior cavity of the microsphere offer the short diffusion length of the Li^+ ions and provide the reserved space for the volume change during lithiation-delithiation reaction. On the other hand, the hollow and porous structure significantly enhances the specific surface area of the active materials and consequently improves the reversible reaction.

The excellent rate capability of the $\alpha\text{-Fe}_2\text{O}_3$ electrode was further assessed by the multiple-step galvanostatic charge-discharge test. In Figure 6.7b, the reversible capacities are measured to be around 1200, 1150, 1000, 820, 650 and 450 mAh g^{-1} at six rates of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 5 C, respectively. The reversible capacity is still above 372 mAh g^{-1} , even when the rate is high up to 5 C. However, the reversible capacity immediately increases to 897 mAh g^{-1} and then reaches more than 1100 mAh g^{-1} after the rate is downs back to 0.1 C. Furthermore, the high rate capability under the current density of 1 C is demonstrated in Figure 6.7c. After 1000 cycles, the retention of the reversible capacity is measured to be 1150 mAh g^{-1} . It is worth to note that the capacity rapidly goes down at the beginning to around 550 mAh g^{-1} within 110 cycles and then slowly rises up to more than 1000 mAh g^{-1} subject to more cycles. This unusual phenomenon has been widely observed in different kinds of transition metal oxide based anode materials for LIBs. Based on related investigations, the reversible reaction of the polymeric/gel-like films formation is responsible for this capacity variation, which continuously conducts in the active materials' porous structure as the electrochemical reaction undergoes.^{217, 299} However, the detailed explanation for the electrochemical reaction process is needed to be further provided.

Figure 6.8 XRD patterns of the electrodes after (a) 110 cycles (sample 110) and (b) 500 cycles (sample 500).

In order to reveal the structural change of the Fe_2O_3 microspheres under high rate current density, ex-situ XRD measurement was performed to the electrodes obtained after 110 (labeled as sample 110) and 500 (labeled as sample 500) cycles at 1 C. As illustrated in Figure 6.8, both samples display weak peaks from 10° to 45° , reflected from the nanosized constituents of the active materials but strong peaks at 43.0° , 50.0° and 73.9° , generated from the metallic copper substrate indicating the occurrence of the structure destruction during cycling. By zooming in the patterns from 10° to 45° , the weak peaks of sample 110 at 23.9° , 26.3° and 30.4° , diffracted from (106), (116), (206) lattice planes, are clearly visible which is indexed to be $\gamma\text{-Fe}_2\text{O}_3$ (ICSD 172906) with lattice parameters of $a = 8.33 \text{ \AA}$ and $c = 25.11 \text{ \AA}$. Likewise, $\beta\text{-Fe}_2\text{O}_3$ (ICSD 36281) with lattice parameters of $a = 5.56 \text{ \AA}$ and $c = 22.55 \text{ \AA}$ is identified from the three peaks at 20.0° , 32.3° and 35.5° diffracted from the (0 1 2), (1 1 -1), (1 1 -4) lattice planes. Based on the analysis above, it is believed

that the crystal structure of the Fe_2O_3 microspheres undergoes the transformation in the order of $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \gamma\text{-Fe}_2\text{O}_3 \rightarrow \beta\text{-Fe}_2\text{O}_3$ with the increase of the cycling times, as indicated in Figure 6.7c.

Figure 6.9 TEM (a), HRTEM (b and c) and the FFT inverse (d) images of the 110 sample.

Figure 6.10 TEM (a), HRTEM (b and c) and the FFT inverse (d) images of the 500 sample.

The morphological and crystalline structural changes of microspheres subject to charge-discharge cycles were revealed using ex-situ TEM. One of microsphere from sample 110 shown in Figure 6.9a is seen to be covered by a thick SEI layer. The micro spherical particle appears amorphous-like structure but is embedded with some nanoparticles (Figure 6.9b). These nanoparticles are tiny with the size of $\sim 7\text{-}8\text{ nm}$ but crystalline (Figure 6.9c and d). With the increase of cycling up to 500 times, the SEI film that covers the surface of the integrated microsphere becomes much thicker as seen from Figure 6.10a. Meanwhile, the

average size of the nanocrystals embedded in the microsphere (Figure 6.10a) is reduced to 3 - 4 nm. It is worth to note that the respective HRTEM images of Figure 6.9c and Figure 6.10c are taken from Figure 6.9b and Figure 6.10b in the squared areas as marked. Figure 6.9d and Figure 6.10d are their corresponding atomic images after performing inverse FFT process. As indicated from Figure 6.9c, the spacing of the lattice fringes is measured to be 0.32 nm, which can be indexed as planes $\{1\ 3\ 1\}$ of $\gamma\text{-Fe}_2\text{O}_3$ along the zone axis of $\langle 1\ 1\ 4 \rangle$. Meanwhile, the HRTEM image of sample 500 (Figure 6.10c) shows a clear crystal lattice of $\beta\text{-Fe}_2\text{O}_3$ imaged along the $\langle 1\ 0\ 1 \rangle$ zone axis, based on the indexing of the inset FFT pattern.

Figure 6.11 Nyquist plots of the as-obtained $\alpha\text{-Fe}_2\text{O}_3$ microspheres before cycling and after 110 and 500 cycles.

Using ex-situ TEM, the phase transition among the three Fe_2O_3 phases ($\alpha \rightarrow \gamma \rightarrow \beta$) during high rate cycling as anode for lithium ion batteries was observed in the present study, which has been hardly reported elsewhere. This abnormal phase transition phenomenon is believed to be ascribed to the structural disorder with the decrease of the particle size³³⁸. Considering the effect of surface (or interface) energy contribution to the free energy for nanoparticles, smaller particle size causes the lattice modification³³⁹, which is consistent with an earlier interpretation that describes the size-induced lattice deformations using the protohematite-hydrohematite-Stoichiometric Hematite (SH) two-dimensional map³⁴⁰. Therefore, the phase transition ($\alpha \rightarrow \gamma \rightarrow \beta$) occurs at the structural disorder site under the driving force (electrochemical cycling).

In the present paper, the effect of Fe_2O_3 microspheres phase transition on their electrochemical performance as anode materials in lithium ion batteries was also revealed using electrochemical impedance spectroscopy (EIS). Figure 6.11 represents the Nyquist plot of the as-obtained Fe_2O_3 microspheres electrode along with different cycles. The EIS figures of all the electrodes are made up of one depressed semicircle located at the high and intermediate frequency, comprising of two semicircles, and a straight line, corresponding to the diffusion resistance. The semicircles in the high and intermediate frequency can be assigned to the migration of the lithium ion through the interfacial film and the charge transfer reaction on the electrode/electrolyte interface. It is evident that the charge transfers and ion diffusion resistance of the electrode increase after 110 cycles, which is verified by the diameter changes of the second semicircle and the decreasing line slope. The increasing resistance is likely attributed to the thickening SEI film during cycling which increases the lithium ions diffusion and electron exchange speed. However, when the 500th cycle is achieved on the electrode, it is interestingly seen that the charge transfer resistance drops to an even smaller number than the one of fresh

electrodes and the diffusion resistance gets slightly recovered from the value at 110th cycle, even though, the SEI film of electrode after 500 cycles turns to be thicker, compared with the one after 110 cycles (Figure 6.10a).

Figure 6.12 Crystal structures of (a) α - Fe_2O_3 , (b) γ - Fe_2O_3 , (c) β - Fe_2O_3 and their corresponding observation of the first crystal layer.

It has been well known that the intrinsic crystal structure shows the great effect on their lithium intercalation performance. The elemental interlayer, tunnels and holes in crystal structures can accommodate a large amount of lithium intercalation³⁴¹. According to Stokes–Einstein principle, the stokes radius of lithium ions ($r_{\text{Li}, \text{eff}}^+$) in organic electrolyte (EC, DEC or DMC) is calculated to be around $3.44 \sim 3.63 \text{ \AA}$ which is required to stabilize the crystal tunnels³⁴²⁻³⁴⁴. The crystal structures of α , γ and β phases Fe_2O_3 are shown in Figure 6.12. For the hematite structure (Figure 6.12a), each α - Fe_2O_3 crystal consists of basic FeO_6 octahedral units, which seems to be a rhombohedral centered hexagonal structure of the corundum type with a closed-packed lattice. Although there are no obvious interlayer spacing and tunnels through the whole structure, there

exist hexagonal holes (4.01 Å in diameter) on the crystal surface, which are suitable for cation accommodation. Figure 6.12b represents the crystal structure of γ -Fe₂O₃, which indicates the typical structure of spinel type. In the unit cell, the eight tetrahedral sites are occupied by Fe³⁺ cations. Meanwhile, 13/3 Fe³⁺ cations occupy the 16 octahedral sites. Similar to α -Fe₂O₃, the crystal holes of γ -Fe₂O₃ only exist in the surface lattice layer where edge-sharing tetrahedral units (2.98 Å) and octahedral units (3.17 Å) are linked to form trapezoid and triangle holes. Due to their narrow hole size, the progress of cation intercalation is conducted in γ -Fe₂O₃ worse than in α -Fe₂O₃. The presence of steric hindrance will increase the resistance of the electrochemical reaction as confirmed by EIS tests (Figure 6.11). With regard to β -Fe₂O₃ (Figure 6.12c), the hexagonal crystal structure has space group P3 (143 lattice structure with the parameters of $a=5.56$ Å and $c=22.55$ Å, which is comprised of distorted octahedral and tetrahedral units. In this structure, one-dimensional tunnel structures (3.2×7.5 Å) is viewed along the [1 0 0] direction which allows the rapid migration of lithium ions and consequently increases the specific contact area between electrolyte and active materials, giving rise to the higher performance after 500 cycles. As a result, we can emphasize that the crystal size induced Fe₂O₃ electrode phase transition ($\alpha \rightarrow \gamma \rightarrow \beta$) brings about its performance fluctuation during high rate cycling. The hole, interlayer and tunnel's variation of the crystal structure allows the penetration of more lithium ions for intercalation process in the electrochemical reaction.

6.3 Conclusions

In summary, we have rationally designed and fabricated hollow-porous α -Fe₂O₃ microspheres by a facile cation etching approach. Owing to merits from their intrinsic nanostructure, the α -Fe₂O₃ microspheres exhibit

excellent electrochemical performance (1100 mAh g^{-1} at 1 C) as anode materials for lithium ion batteries. Importantly, the occurrence of Fe_2O_3 phase transition process ($\alpha \rightarrow \gamma \rightarrow \beta$) along with the abnormal performance fluctuation during high rate cycling is observed using ex-situ TEM and XRD. The transformation process is believed to be activated by crystal size reduction followed by the generation of β phase, which not only increases the electrode's ion conductivity but also decreases the lithium ions diffusion path. This finding provides an effective approach to explain the activation process of transition metal oxides based anode materials. It may also be extended to open up new opportunities to construct novel anode materials with high performance.

Chapter 7

Conclusions and Future Work

In the research project, high performance carbon and MnO₂ based iron oxide hybrids are fabricated. Moreover, the phase transition of α -Fe₂O₃ electrode is discovered and explained. These studies' conclusions will make a huge scientific and technological contributions. In addition, the recommended future work is also discussed and planed.

7.1 Conclusions

In this thesis, systematic and in-depth investigation and studies on the controllable fabrication of various nanostructured iron oxide-based hybrids and their electrochemical behavior as anode for lithium ion batteries during cycling have been obtained. According to our research conclusions, the electrochemical performance of iron oxide-based hybrids anodes could be largely effected by their composites and morphology. Meanwhile, the precise control of the hybrids' morphology modification and effective improvement of the negative electrode performance have been achieved. Furthermore, the detailed crystal structure evolution of the as-prepared iron oxide electrode during electrochemical reaction was also completely revealed.

Iron oxides have attracted much attention as prospective anodes for LIBs, for their high theoretical capacity, low cost and environmental benignity. In order to improve iron oxides' cycling performance as anodes, various nanostructure such as porous, hollow and nanorods have been synthesized via different chemical and physical methods. By introducing suitable active or inactive secondary composite, large capacities and excellent cycling performance can be realized in the constructed nanostructured hybrids. The hierarchical three-dimensional Fe_3O_4 @porous carbon matrix (Fe_3O_4 @PCM) are synthesized by a facile annealing of MIL-53(Fe) templates. Benefiting from the active carbon matrix, the as-prepared hybrids anodes exhibit an initial capacity of 837 mAh g^{-1} and after 100 cycles, the cycling capacity of Fe_3O_4 @PCM gradually drops to 600 mAh g^{-1} (0.2 C). To further increase the nanostructured hybrids' cycling retention rate, the introduction of graphene oxide was conducted during the preparation of the MIL-53(Fe) templates. After calcination in the nitrogen, the heterostructured Fe_3O_4 @PCM/graphene anodes was successfully synthesized. In comparison with the Fe_3O_4 @PCM anode, the Fe_3O_4 @PCM/graphene electrode performed an enhanced electrochemical performance, whose capacity was as high as 1077 mAh g^{-1} after 100 cycles assigning to the intentionally

designed three-dimensional hierarchical nanostructure and the synergic effect between different components. Under a high rate condition (1 C), the retention capacity of the as-prepared $\text{Fe}_3\text{O}_4@\text{PCM}/\text{graphene}$ anode is up to more than 1000 mAh g^{-1} , after 500 cycles.

Despite the multiple advantages from the combination of iron oxides and carbon based secondary composites, for instance, the improvement of electric conductivity, mechanical strain buffering and structural integrity preservation, the carbon species' low theoretical capacity (372 mAh g^{-1}) leads to the limitation of the nanostructured hybrids' capacity improvement. Therefore, the alternative active secondary composites with high theoretical capacities are required to replace the carbon species. Herein, we demonstrate a facile method to prepare hollow-structured oxygen-vacancy-rich $\text{Fe}_2\text{O}_3/\text{MnO}_2$ nanorods, due to the high intrinsic capacity (1232 mAh g^{-1}) of MnO_2 . The method proposes the combination of MnO_2 coating on PVP decorated FeOOH nanorods and the subsequent annealing process. Through the ex-situ characterization, the oxygen vacancies are confirmed to be in-situ induced by nanoscale ion intermixing between Fe and Mn ions, during annealing process. The introduction of oxygen vacancies into MnO_2 could effectively boost the intrinsic conductivity of MnO_2 . As compared to the $\text{Fe}_3\text{O}_4@\text{PCM}/\text{graphene}$ anode, the hollow-structured $\text{Fe}_2\text{O}_3/\text{MnO}_2$ electrodes exhibit a higher reversible capacity and improved cycling performance (1167 mAh g^{-1} , 500 cycles, 1 C). At an even higher rate of 5 C, the final reversible capacity still can be measured to be as high as 706 mAh g^{-1} , after a long-term cycle (2000 times). The superior electrochemical performance is attributed to the unique nanostructure of the as-synthesized $\text{Fe}_2\text{O}_3/\text{MnO}_2$ hybrids. First of all, the internal hollow nanostructure could stabilize the structural integrity and facilitate the diffusion movement of Li ions. Secondly, the different composites of the nanostructured hybrids bring out synergistic effect between hollow Fe_2O_3 core (less volume change and structural destruction) and MnO_2 shell (high theoretical capacity). Most of all, the intrinsic electronic conductivity of the $\text{Fe}_2\text{O}_3/\text{MnO}_2$ electrode can be

enhanced by the formation of oxygen vacancies, giving rise to an enhanced rate capability. Moreover, the morphology modification of the $\text{Fe}_2\text{O}_3/\text{MnO}_2$ nanorods can be realized, via changing the annealing temperature. As the temperature changes from 300 °C to 600 °C, the internal core evolves from porous to hollow and solid nanostructure, meanwhile, the external layer converts from hierarchical to totally smooth nanostructure. The transition process is originated from the inward flow of MnO_2 layer, under heating treatment.

The abnormal performance fluctuation was observed in the as-prepared iron oxide-based hybrids such as $\text{Fe}_3\text{O}_4@\text{PCM}/\text{graphene}$ and hollow-structured $\text{Fe}_2\text{O}_3/\text{MnO}_2$, under the current density of 1 C. The similar phenomenon has also been widely discovered in the performance investigation of other transition metal oxide-based electrodes for LIBs. To further understand the detailed mechanism of the abnormal phenomenon, the comprehensive ex-situ characterization technique was performed on the cycled hollow-porous $\alpha\text{-Fe}_2\text{O}_3$ electrode in this thesis. At 1 C, the capacity of the as-prepared $\alpha\text{-Fe}_2\text{O}_3$ anode rapidly falls to around 550 mAh g⁻¹ within the initial 110 cycles and then slowly rises up to more than 1000 mAh g⁻¹. During the high rate cycling, the occurrence of Fe_2O_3 phase transition process ($\alpha \rightarrow \gamma \rightarrow \beta$) is revealed using ex-situ TEM and XRD. The transformation process is believed to be activated by crystal size reduction followed by the generation of β phase, leading to an increased ionic conductivity and the reduction of diffusion path. The result clearly certifies the activation process of transition metal oxides based anode materials. It would also expand our knowledge to construct some other novel anode materials with high performance.

7.2 Novel Contributions

According to the conclusions obtained in this dissertation, some novel scientific and technological contributions have been made to the iron oxides based anodes

for LIBs. The exhaustive content is described as following.

7.2.1 Scientific Contributions

1. Synthesis of iron oxide-carbon hybrids via a facile thermal annealing of metal organic frameworks. The morphology of the as-prepared hybrids was successfully modified by the introduction of graphene. The corresponding heterostructured hybrids demonstrate an improved electrochemical performance, as a result of the unique nanostructure, high surface area and the synergic effect of composites.
2. Iron oxide-manganese dioxide nanorod was synthesized via a facile two step method. The controllable tuning of the hybrid nanorods' nanostructure was conducted via changing the annealing temperature. The inward movement of Mn was observed, during thermal condition. The in-situ formation of the oxygen vacancies is responsible for the enhanced electrochemical performance as anode for LIBs.
3. Fundamental understanding the structure evolution of the iron oxide anode, during cycling, via comprehensive characterization on cycled electrode.

7.2.2 Technological Contributions

1. Providing a facile approach to introducing the oxygen vacancies via ionic intermixing under thermal condition.
2. Constructing a unique hybrid nanostructure made of Fe_3O_4 nanocrystals embedded within carbon frameworks using thermal decomposition of MIL-53(Fe) templates.

7.3 Future Work

Based on the content of our work in this thesis, the following research is

recommended for the future work to further investigate and develop a novel transition metal oxide-based material and the related electrochemical reaction mechanism as high performance anode for LIBs.

7.3.1 Fundamental Investigation of the Influence of the Substitute Cations on the Electrochemical Performance

Partial replacement of metallic elements in transition metal oxides with other metallic elements of different valences produces stoichiometric or even non-stoichiometric ternary transition metal oxides (mixed transition metal oxides). The merging ternary transition metal oxides comprising of two different metal cations show promising potentials as anode materials for LIBs.³⁴⁵⁻³⁴⁷ They have exhibited high and adjustable electrochemical activities corresponding to the complexity of elemental composition and the synergetic effect from constitutional cations. Furthermore, due to the advantages of the chemical composition complexity, the desirable electrochemical characteristics such as working potential, conductivity and theoretical capacity, of the ternary transition metal oxides can be obtained via tuning kinds, concentration and valence of the metallic cations.^{348, 349}

In the present work, the research on the effect of secondary composites in iron oxide-based hybrids anodes have been conducted. According to previous studies, partial replacement of Fe element forming ternary transition metal oxides is supposed to significantly affect the materials' electrochemical performance.³⁵⁰ It is believed that the optimum properties of the Fe-based ternary metal oxide are available through adjusting the substitute cation. However, even though numerous efforts have been devoted to exploring the electrochemical performance of various Fe-based ternary metal oxide mixed with different metallic elements (as seen in Table 7.1), the exact influence of the substitute cation on the electrochemical performance is still unclear. Therefore, more thorough and systematic studies should be given in the experimental and

theoretical terms. The illustration from the perspective of the fundamental studies would provide a clear-cut guideline for developing alternative high-performance anodes for LIBs.

Table 7.1 Current state of investigations for Fe-based ternary metal oxide anode for LIBs

Fe-based Ternary Metal Oxides Anodes	Current Density (mA g ⁻¹)	Cycling Number	Capacity (mAh g ⁻¹)	Ref
Yolk-shell Structured ZnFe ₂ O ₄ Powders	500	200	862	351
NiFe ₂ O ₄ Nanofibers	100	100	1000	352
Porous Hollow CoFe ₂ O ₄	5000	100	290	353
Mesoporous ZnFe ₂ O ₄ Nanorods	100	50	983	354
Ordered Mesoporous CoFe ₂ O ₄	200	30	702	355
Hollow CoFe ₂ O ₄ Nanospheres	90	50	1185	356
Mesoporous MnFe ₂ O ₄ Microspheres	186	50	712	357
FeCo ₂ O ₄ Nanoflakes	200	170	905	358
Porous MnFe ₂ O ₄ Microrods	4000	1000	420	359
Zn _{0.3} Mn _{0.7} Fe ₂ O ₄ Nanofibers	60	50	612	360
Porous Hollow MnFe ₂ O ₄	5000	100	447	353
NiFe ₂ O ₄ Nanorods	1000	300	520	361
CoFe ₂ O ₄ Nanorods	1000	300	800	361
Porous Hollow ZnFe ₂ O ₄	5000	100	390	353

7.3.2 Fundamental Studies of the Electrochemical Reaction Mechanism of the Fe-based Ternary Metal Oxide Anodes Using In-situ TEM

Figure 7.1 Schematic illustration of nanobatteries for in-situ TEM characterization.³⁶²

It is well known that the electrochemical reaction mechanism and structure evolution of electrode materials during cycling should be fundamentally understood, in order to effectively offer strategies to improve the cycling performance and mitigate the structural deterioration. Until now, lots of in-situ techniques have been employed and developed to elaborately demonstrate the textural modification of electrode materials during cycling, including optical microscopy, SEM, synchrotron XRD, synchrotron X-ray absorption spectroscopy (XAS), synchrotron transmission X-ray microscopy (TXM), Raman spectroscopy, Fourier transform-infrared spectroscopy (FTIR), mass spectroscopy (MS), nuclear magnetic resonance (NMR) spectroscopy and TEM.

Among those in-situ characterizations, optical microscopy and SEM can only offer a low spatial resolution revealing macrostructure evolution such as micro-breaking of electrode, during electrochemical reactions. The crystal and electronic structure can be provided in in-situ XRD and XAS measurements, respectively. Due to the advantages of ultrahigh resolution, in-situ TEM batteries have been extensively utilized in materials characterization to reveal their structural and properties' real time evolution until very recently.

To dates, there are two kind nanobattery cells for in-situ TEM (as seen in Figure 7.1), one filled with ionic liquid electrolytes of room temperature and the other assembled by all solid components. For the first one, the liquid electrolyte can be sealed in liquid cells comprising of top and bottom Si_3N_4 membranes.³⁶² Although the morphological and structural evolution of active materials can be observed, the spatial resolution will be limited owing to the presence of liquid phase. To further perform real time composition analysis, the all solid cell for in-situ TEM is attempted to be utilized. Until now, various alloy anode such as Si and Sn with different nanostructures have been investigated in terms of their structural evolution in real time of electrochemical lithiation.³⁶³⁻³⁶⁵

In this thesis, ex-situ TEM has been used to verify the phase transition of $\alpha\text{-Fe}_2\text{O}_3$ anodes. The conclusion provides a novel possibility to develop high performance metal oxide based anodes for LIBs. However, in the ex-situ characterization, the decomposition of the electrodes' surface might happen, because of the inevitable exposure to the ambient atmosphere. Therefore, it is reasonable to recommend the conduction of in-situ TEM on the Fe-based ternary metal oxide anodes as our future work. Deep comprehension of the lithium storage mechanism in the Fe-based ternary metal oxide anodes would be achieved from the obtained information of the transient state at a ultrahigh resolution.

7.3.3 Fabrication and Investigation of the Fe-based Ternary Metal Oxide Hybrids Electrode

Based on the conclusions of the thesis, construction of heterostructure can bring about an enhanced electrochemical performance of iron oxide anodes, owing to the synergetic effect between composites. The merits from the introduction of carbon based species and metal oxides have been validated in our work. For that reason, it is sensible that the hybridization of Fe-based ternary metal oxides with other active species could further optimize the electrode's performance.

So far, around the world, lots of efforts have been devoted to developing various Fe-based ternary metal oxide hybrids as anodes for LIBs (as listed in Table 7.2), which showing high electrochemical performance. In future work, the influence of nanostructure and composition on the electrode's performance will be thoroughly investigated. The structural evolution of the as-prepared nanostructured hybrids during cycling can be measured using in-situ TEM. The comparison of electrodes' structural stability will provide effective approaches to construct anode materials with desirable properties.

Table 7.1 Current state of investigations for Fe-based ternary metal oxide hybrids for LIBs

Fe-based Ternary Metal Oxide Hybrids	Current Density (mA g ⁻¹)	Cycling Number	Capacity (mAh g ⁻¹)	Ref
CoO/CoFe ₂ O ₄ Nanocomposites	1000	100	603	³⁶⁶
CoFe ₂ O ₄ -graphene Nanocomposites	100	50	910	³⁶⁷
Co ₃ O ₄ /CoFe ₂ O ₄ Nanocomposites	64	60	896	³⁶⁸
Core-Shell NiFe ₂ O ₄ @TiO ₂ Nanorods	2000	100	358	³⁶⁹
Mesoporous CoFe ₂ O ₄ /CNTs Nanocomposites	200	100	1046	³⁷⁰

NiFe ₂ O ₄ /C composite	114	40	780	371
CoFe ₂ O ₄ /graphene nanocomposites	1000	50	651	372
Carbon Coated ZnFe ₂ O ₄ Nanoparticles	40	100	1300	373
Porous ZnO/ZnFe ₂ O ₄ /C Hollow Octahedra	2000	100	988	374
MWCNT–ZnFe ₂ O ₄ Nanocomposites	60	50	1032	375

List of Publications

- 1 **Shiji Hao**, Bowei Zhang, Sarah Ball, Mark Copley, Zhichuan Xu, Madhavi Srinivasan, Kun Zhou, Subodh Mhaisalkar, and Yizhong Huang, 'Synthesis of Multimodal Porous ZnCo_2O_4 and Its Electrochemical Properties as an Anode Material for Lithium Ion Batteries', *Journal of Power Sources*, 294 (2015), 112-19.
- 2 **Shiji Hao**, Bowei Zhang, Sarah Ball, Bo Hu, Junsheng Wu, and Yizhong Huang, 'Porous and Hollow NiO Microspheres for High Capacity and Long-Life Anode Materials of Li-Ion Batteries', *Materials & Design*, 92 (2016), 160-65.
- 3 **Shiji Hao**, Bowei Zhang, Sarah Ball, Junsheng Wu, Madhavi Srinivasan, and Yizhong Huang, 'Phase Transition of Hollow-Porous $\alpha\text{-Fe}_2\text{O}_3$ Microsphere Based Anodes for Lithium Ion Batteries During High Rate Cycling', *Journal of Materials Chemistry A*, 4 (2016), 16569-75.
- 4 **Shiji Hao**, Bowei Zhang, Jianyong Feng, Yayuan Liu, Sarah Ball, Jisheng Pan, Madhavi Srinivasan, and Yizhong Huang, 'Nanoscale Ion Intermixing Induced Activation of $\text{Fe}_2\text{O}_3/\text{MnO}_2$ Composites for Application in Lithium Ion Batteries', *Journal of Materials Chemistry A*, 5 (2017), 8510-18.
- 5 NIE Lina, Guangfeng Liu, **Shiji Hao**, Zhichuan J Xu, and Rong Xu, 'Crystalline in-Sb-S Framework for Highly-Performed Lithium/Sodium Storage', *Journal of Materials Chemistry A* (2017).
- 6 Bowei Zhang, Bensong Chen, Junsheng Wu, **Shiji Hao**, Guang Yang, Xun Cao, Lin Jing, Minmin Zhu, Siu Hon Tsang, and Edwin Hang Tong Teo, 'The Electrochemical Response of Single Crystalline Copper Nanowires to Atmospheric Air and Aqueous Solution', *Small*, 13 (2017).
- 7 Bowei Zhang, **Shiji Hao**, Junsheng Wu, Xiaogang Li, and Yizhong Huang, 'Evidence of a Nanosized Copper Anodic Reaction in an Anaerobic Sulfide Aqueous Solution', *RSC Advances*, 6 (2016), 19937-43.
- 8 Bowei Zhang, **Shiji Hao**, Junsheng Wu, Xiaogang Li, Chaojiang Li,

Xiaowei Di, and Yizhong Huang, 'Direct Evidence of Passive Film Growth on 316 Stainless Steel in Alkaline Solution', *Materials Characterization* (2017).

9 Bowei Zhang, **Shiji Hao**, Dongrong Xiao, Junsheng Wu, and Yizhong Huang, 'Templated Formation of Porous Mn₂O₃ Octahedra from Mn-Mil-100 for Lithium-Ion Battery Anode Materials', *Materials & Design*, 98 (2016), 319-23.

10 Bowei Zhang, Junsheng Wu, Xiaogang Li, Hai Liu, Boluo Yadian, RV Ramanujan, Kun Zhou, Renbing Wu, **Shiji Hao**, and Yizhong Huang, 'Passivation of Nickel Nanoneedles in Aqueous Solutions', *The Journal of Physical Chemistry C*, 118 (2014), 9073-77.

References:

1. G. Gao, Q. Zhang, X.-B. Cheng, J. G. Shapter, T. Yin, R. Sun and D. Cui, *Sci Rep-Uk*, 2015, **5**.
2. H. Zhou, Y. Wang, H. Li and P. He, *Chemsuschem*, 2010, **3**, 1009-1019.
3. Y. Yu, L. Gu, C. Wang, A. Dhanabalan, P. A. van Aken and J. Maier, *Angewandte Chemie International Edition*, 2009, **48**, 6485-6489.
4. H. Kawai, M. Nagata, H. Tukamoto and A. R. Westa, *Electrochemical and Solid-State Letters*, 1998, **1**, 212-214.
5. G. Derrien, J. Hassoun, S. Panero and B. Scrosati, *Adv Mater*, 2007, **19**, 2336-2340.
6. H. Wang, L.-F. Cui, Y. Yang, H. Sanchez Casalongue, J. T. Robinson, Y. Liang, Y. Cui and H. Dai, *Journal of the American Chemical Society*, 2010, **132**, 13978-13980.
7. Z.-S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li and H.-M. Cheng, *Acs Nano*, 2010, **4**, 3187-3194.
8. W. M. Zhang, J. S. Hu, Y. G. Guo, S. F. Zheng, L. S. Zhong, W. G. Song and L. J. Wan, *Adv Mater*, 2008, **20**, 1160-1165.
9. S. H. Yu, S. H. Lee, D. J. Lee, Y. E. Sung and T. Hyeon, *Small*, 2015.
10. B. Koo, H. Xiong, M. D. Slater, V. B. Prakapenka, M. Balasubramanian, P. Podsiadlo, C. S. Johnson, T. Rajh and E. V. Shevchenko, *Nano Lett*, 2012, **12**, 2429-2435.
11. G. Zhou, D.-W. Wang, F. Li, L. Zhang, N. Li, Z.-S. Wu, L. Wen, G. Q. Lu and H.-M. Cheng, *Chem Mater*, 2010, **22**, 5306-5313.
12. Y. Chen, H. Xia, L. Lu and J. Xue, *Journal of Materials Chemistry*, 2012, **22**, 5006-5012.
13. E. Kang, Y. S. Jung, A. S. Cavanagh, G. H. Kim, S. M. George, A. C. Dillon, J. K. Kim and J. Lee, *Adv Funct Mater*, 2011, **21**, 2430-2438.
14. M. Sánchez, J. Gregori, C. Alonso, J. García-Jareño, H. Takenouti and F. Vicente, *Electrochimica Acta*, 2007, **52**, 7634-7641.
15. Y. Zhao, J. Li, Y. Ding and L. Guan, *Chemical Communications*, 2011, **47**, 7416-7418.
16. N. Liu, H. Wu, M. T. McDowell, Y. Yao, C. Wang and Y. Cui, *Nano Lett*, 2012, **12**, 3315-3321.
17. A. Magasinski, P. Dixon, B. Hertzberg, A. Kvit, J. Ayala and G. Yushin, *Nature materials*, 2010, **9**, 353-358.
18. Y. Yao, M. T. McDowell, I. Ryu, H. Wu, N. Liu, L. Hu, W. D. Nix and Y. Cui, *Nano Lett*, 2011, **11**, 2949-2954.
19. Y. S. Hu, R. Demir - Cakan, M. M. Titirici, J. O. Müller, R. Schlögl, M. Antonietti and J. Maier, *Angewandte Chemie International Edition*, 2008, **47**, 1645-1649.
20. X. Huang, J. Tu, B. Zhang, C. Zhang, Y. Li, Y. Yuan and H. Wu, *Journal of Power Sources*, 2006, **161**, 541-544.
21. Y. Shi, B. Guo, S. A. Corr, Q. Shi, Y.-S. Hu, K. R. Heier, L. Chen, R. Seshadri and G. D. Stucky, *Nano Lett*, 2009, **9**, 4215-4220.
22. X. Zhu, Y. Zhu, S. Murali, M. D. Stoller and R. S. Ruoff, *Acs Nano*, 2011, **5**, 3333-3338.

23. B. Guo, X. Wang, P. F. Fulvio, M. Chi, S. M. Mahurin, X. G. Sun and S. Dai, *Adv Mater*, 2011, **23**, 4661-4666.
24. B. Li, H. Cao, J. Shao, G. Li, M. Qu and G. Yin, *Inorganic chemistry*, 2011, **50**, 1628-1632.
25. W. Zhou, C. Cheng, J. Liu, Y. Y. Tay, J. Jiang, X. Jia, J. Zhang, H. Gong, H. H. Hng and T. Yu, *Adv Funct Mater*, 2011, **21**, 2439-2445.
26. A. L. M. Reddy, M. M. Shaijumon, S. R. Gowda and P. M. Ajayan, *Nano Lett*, 2009, **9**, 1002-1006.
27. J. Chen and F. Cheng, *Accounts of chemical research*, 2009, **42**, 713-723.
28. N. S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y. K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho and P. G. Bruce, *Angewandte Chemie International Edition*, 2012, **51**, 9994-10024.
29. J.-M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359-367.
30. M. Broussely, P. Biensan and B. Simon, *Electrochimica Acta*, 1999, **45**, 3-22.
31. J. Ribeiro, M. Silva, J. Carmo, L. Gonçalves, M. M. Silva and J. Correia, in *Scanning Probe Microscopy in Nanoscience and Nanotechnology 3*, Springer, 2012, pp. 575-619.
32. M. M. Thackeray, C. Wolverton and E. D. Isaacs, *Energ Environ Sci*, 2012, **5**, 7854-7863.
33. L. Fu, H. Liu, C. Li, Y. P. Wu, E. Rahm, R. Holze and H. Wu, *Solid State Sci*, 2006, **8**, 113-128.
34. C. K. Chan, H. Peng, G. Liu, K. Mcllwraith, X. F. Zhang, R. A. Huggins and Y. Cui, *Nature nanotechnology*, 2008, **3**, 31-35.
35. K. Tatsumi, N. Iwashita, H. Sakaebe, H. Shioyama, S. Higuchi, A. Mabuchi and H. Fujimoto, *J Electrochem Soc*, 1995, **142**, 716-720.
36. M. Armand and J.-M. Tarascon, *Nature*, 2008, **451**, 652-657.
37. B. Liang, Y. Liu and Y. Xu, *Journal of Power sources*, 2014, **267**, 469-490.
38. S. Xu, C. M. Hessel, H. Ren, R. Yu, Q. Jin, M. Yang, H. Zhao and D. Wang, *Energ Environ Sci*, 2014, **7**, 632-637.
39. Y. Yan, Y.-X. Yin, S. Xin, Y.-G. Guo and L.-J. Wan, *Chemical Communications*, 2012, **48**, 10663-10665.
40. G. Armstrong, A. R. Armstrong, P. G. Bruce, P. Reale and B. Scrosati, *Adv Mater*, 2006, **18**, 2597-2600.
41. B. Qiu, M. Xing and J. Zhang, *Journal of the American Chemical Society*, 2014, **136**, 5852-5855.
42. Y. Qiu, K. Yan, S. Yang, L. Jin, H. Deng and W. Li, *Acs Nano*, 2010, **4**, 6515-6526.
43. L. Kavan, M. Grätzel, J. Rathouský and A. Zukalb, *J Electrochem Soc*, 1996, **143**, 394-400.
44. H. Lindström, S. Södergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt and S.-E. Lindquist, *The Journal of Physical Chemistry B*, 1997, **101**, 7717-7722.
45. H. Han, T. Song, J.-Y. Bae, L. F. Nazar, H. Kim and U. Paik, *Energ Environ Sci*, 2011, **4**, 4532-4536.
46. S. Lee, J. Ha, J. Choi, T. Song, J. W. Lee and U. Paik, *Acs Appl Mater Inter*, 2013, **5**, 11525-11529.
47. B. Zhao, S. Jiang, C. Su, R. Cai, R. Ran, M. O. Tadé and Z. Shao, *J Mater Chem A*, 2013, **1**, 12310-12320.

48. K. Zaghib, M. Simoneau, M. Armand and M. Gauthier, *Journal of Power Sources*, 1999, **81**, 300-305.
49. K. Mukai, Y. Kato and H. Nakano, *The Journal of Physical Chemistry C*, 2014, **118**, 2992-2999.
50. G.-N. Zhu, Y.-G. Wang and Y.-Y. Xia, *Energ Environ Sci*, 2012, **5**, 6652-6667.
51. Y. Wang, H. Li, P. He, E. Hosono and H. Zhou, *Nanoscale*, 2010, **2**, 1294-1305.
52. H. Li and H. Zhou, *Chemical Communications*, 2012, **48**, 1201-1217.
53. M. Winter and J. O. Besenhard, *Electrochimica Acta*, 1999, **45**, 31-50.
54. M. Winter, J. O. Besenhard, M. E. Spahr and P. Novák, *Adv Mater*, 1998, **10**, 725-763.
55. W.-J. Zhang, *Journal of Power Sources*, 2011, **196**, 13-24.
56. U. Kasavajjula, C. Wang and A. J. Appleby, *Journal of Power Sources*, 2007, **163**, 1003-1039.
57. X. Wang, X. Cao, L. Bourgeois, H. Guan, S. Chen, Y. Zhong, D. M. Tang, H. Li, T. Zhai and L. Li, *Adv Funct Mater*, 2012, **22**, 2682-2690.
58. S.-M. Paek, E. Yoo and I. Honma, *Nano Lett*, 2008, **9**, 72-75.
59. X. Zhou, L. J. Wan and Y. G. Guo, *Adv Mater*, 2013, **25**, 2152-2157.
60. Y.-J. Kim, H. Lee and H.-J. Sohn, *Electrochemistry Communications*, 2009, **11**, 2125-2128.
61. P. G. Bruce, B. Scrosati and J. M. Tarascon, *Angewandte Chemie International Edition*, 2008, **47**, 2930-2946.
62. Y. Wang, H. C. Zeng and J. Y. Lee, *Adv Mater*, 2006, **18**, 645-649.
63. Y. Deng, C. Fang and G. Chen, *Journal of Power Sources*, 2016, **304**, 81-101.
64. D. Larcher, G. Sudant, J. Leriche, Y. Chabre and J. Tarascon, *J Electrochem Soc*, 2002, **149**, A234-A241.
65. X. W. Lou, D. Deng, J. Y. Lee, J. Feng and L. A. Archer, *Adv Mater*, 2008, **20**, 258-262.
66. L. Luo, J. Wu, J. Xu and V. P. Dravid, *Acs Nano*, 2014, **8**, 11560-11566.
67. J. Cabana, L. Monconduit, D. Larcher and M. R. Palacin, *Adv Mater*, 2010, **22**.
68. R. Malini, U. Uma, T. Sheela, M. Ganesan and N. Renganathan, *Ionics*, 2009, **15**, 301-307.
69. Y. Li, B. Tan and Y. Wu, *Nano Lett*, 2008, **8**, 265-270.
70. J. Wang, N. Yang, H. Tang, Z. Dong, Q. Jin, M. Yang, D. Kisailus, H. Zhao, Z. Tang and D. Wang, *Angew Chem-Ger Edit*, 2013, **125**, 6545-6548.
71. N. Godshall, I. Raistrick and R. Huggins, *Mater Res Bull*, 1980, **15**, 561-570.
72. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J. Tarascon, *Nature*, 2000, **407**, 496-499.
73. Z. Zhang, C. Boxall and G. Kelsall, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1993, **73**, 145-163.
74. G. Jain, M. Balasubramanian and J. J. Xu, *Chem Mater*, 2006, **18**, 423-434.
75. J. S. Chen, T. Zhu, X. H. Yang, H. G. Yang and X. W. Lou, *Journal of the American Chemical Society*, 2010, **132**, 13162-13164.
76. W. Wu, Z. Wu, T. Yu, C. Jiang and W.-S. Kim, *Science and technology of advanced materials*, 2015, **16**, 023501.
77. C. Boxall, G. Kelsall and Z. Zhang, *Journal of the Chemical Society, Faraday Transactions*, 1996, **92**, 791-802.

78. D. Larcher, C. Masquelier, D. Bonnin, Y. Chabre, V. Masson, J.-B. Leriche and J.-M. Tarascon, *J Electrochem Soc*, 2003, **150**, A133-A139.
79. M. Reddy, T. Yu, C.-H. Sow, Z. X. Shen, C. T. Lim, G. Subba Rao and B. Chowdari, *Adv Funct Mater*, 2007, **17**, 2792-2799.
80. X. Liu, W. Si, J. Zhang, X. Sun, J. Deng, S. Baunack, S. Oswald, L. Liu, C. Yan and O. G. Schmidt, *Sci Rep-Uk*, 2014, **4**.
81. L. Ji, M. Rao, S. Aloni, L. Wang, E. J. Cairns and Y. Zhang, *Energ Environ Sci*, 2011, **4**, 5053-5059.
82. S. Laruelle, S. Grugeon, P. Poizot, M. Dolle, L. Dupont and J. Tarascon, *J Electrochem Soc*, 2002, **149**, A627-A634.
83. L. Wang, Y. Yu, P. Chen, D. Zhang and C. Chen, *Journal of Power Sources*, 2008, **183**, 717-723.
84. Q. Su, D. Xie, J. Zhang, G. Du and B. Xu, *Acs Nano*, 2013, **7**, 9115-9121.
85. J. Li, H. Dahn, L. Krause, D.-B. Le and J. Dahn, *J Electrochem Soc*, 2008, **155**, A812-A816.
86. H. Wu, G. Chan, J. W. Choi, Y. Yao, M. T. McDowell, S. W. Lee, A. Jackson, Y. Yang, L. Hu and Y. Cui, *Nature nanotechnology*, 2012, **7**, 310-315.
87. E. Peled, *J Electrochem Soc*, 1979, **126**, 2047-2051.
88. Y.-B. He, M. Liu, Z.-D. Huang, B. Zhang, Y. Yu, B. Li, F. Kang and J.-K. Kim, *Journal of power sources*, 2013, **239**, 269-276.
89. J. Kim, M. K. Chung, H. K. Bok, J. H. Ku, S. Park, J. Ryu and S. M. Oh, *J Electrochem Soc*, 2010, **157**, A412-A417.
90. D. Larcher, D. Bonnin, R. Cortes, I. Rivals, L. Personnaz and J.-M. Tarascon, *J Electrochem Soc*, 2003, **150**, A1643-A1650.
91. J. Chen, L. Xu, W. Li and X. Gou, *Adv Mater*, 2005, **17**, 582-586.
92. C. Wu, P. Yin, X. Zhu, C. OuYang and Y. Xie, *The Journal of Physical Chemistry B*, 2006, **110**, 17806-17812.
93. Y.-M. Lin, P. R. Abel, A. Heller and C. B. Mullins, *The Journal of Physical Chemistry Letters*, 2011, **2**, 2885-2891.
94. Y. Nuli, P. Zhang, Z. Guo and H. Liu, *J Electrochem Soc*, 2008, **155**, A196-A200.
95. J. Yang, M. Winter and J. Besenhard, *Solid State Ionics*, 1996, **90**, 281-287.
96. L. Lu, X. Chen, X. Huang and K. Lu, *Science*, 2009, **323**, 607-610.
97. Y. Chen, B. Song, X. Tang, L. Lu and J. Xue, *Small*, 2014, **10**, 1536-1543.
98. S. Zeng, K. Tang, T. Li, Z. Liang, D. Wang, Y. Wang, Y. Qi and W. Zhou, *The Journal of Physical Chemistry C*, 2008, **112**, 4836-4843.
99. J. Zhou, H. Song, X. Chen, L. Zhi, S. Yang, J. Huo and W. Yang, *Chem Mater*, 2009, **21**, 2935-2940.
100. Z. Sun, K. Xie, Z. A. Li, I. Sinev, P. Ebbinghaus, A. Erbe, M. Farle, W. Schuhmann, M. Muhler and E. Ventosa, *Chemistry—A European Journal*, 2014, **20**, 2022-2030.
101. L. Ji, Z. Lin, M. Alcoutlabi and X. Zhang, *Energ Environ Sci*, 2011, **4**, 2682-2699.
102. H. Zhang, L. Zhou, O. Noonan, D. J. Martin, A. K. Whittaker and C. Yu, *Adv Funct Mater*, 2014, **24**, 4337-4342.
103. H. Kim, Y.-J. Kim, D. Kim, H.-J. Sohn and T. Kang, *Solid State Ionics*, 2001, **144**, 41-49.
104. Y.-U. Kim, C. K. Lee, H.-J. Sohn and T. Kang, *J Electrochem Soc*, 2004, **151**, A933-A937.

105. M. Reddy, G. S. Rao and B. Chowdari, *Journal of Materials Chemistry*, 2011, **21**, 10003-10011.
106. M. Reddy, L. Y. Tse, W. K. Z. Bruce and B. Chowdari, *Mater Lett*, 2015, **138**, 231-234.
107. Z. Chen, V. Chevrier, L. Christensen and J. Dahn, *Electrochemical and solid-state letters*, 2004, **7**, A310-A314.
108. O. Crosnier, X. Devaux, T. Brousse, P. Fragnaud and D. Schleich, *Journal of power sources*, 2001, **97**, 188-190.
109. W.-R. Liu, M.-H. Yang, H.-C. Wu, S. Chiao and N.-L. Wu, *Electrochemical and Solid-State Letters*, 2005, **8**, A100-A103.
110. Z. Chen, L. Christensen and J. Dahn, *Electrochemistry communications*, 2003, **5**, 919-923.
111. J. Li, R. Lewis and J. Dahn, *Electrochemical and Solid-State Letters*, 2007, **10**, A17-A20.
112. F. Maroni, S. Gabrielli, A. Palmieri, E. Marcantoni, F. Croce and F. Nobili, *Journal of Power Sources*, 2016, **332**, 79-87.
113. J. Liu, Q. Zhang, T. Zhang, J. T. Li, L. Huang and S. G. Sun, *Adv Funct Mater*, 2015, **25**, 3599-3605.
114. N. Yan, F. Wang, H. Zhong, Y. Li, Y. Wang, L. Hu and Q. Chen, *Sci Rep-Uk*, 2013, **3**, 1568.
115. J. Liu, H. Xia, D. Xue and L. Lu, *Journal of the American Chemical Society*, 2009, **131**, 12086-12087.
116. M. H. Park, K. Kim, J. Kim and J. Cho, *Adv Mater*, 2010, **22**, 415-418.
117. X. M. Yin, C. C. Li, M. Zhang, Q. Y. Hao, S. Liu, L. B. Chen and T. H. Wang, *The Journal of Physical Chemistry C*, 2010, **114**, 8084-8088.
118. R. Wu, X. Qian, F. Yu, H. Liu, K. Zhou, J. Wei and Y. Huang, *J Mater Chem A*, 2013, **1**, 11126-11129.
119. R. Liu, J. Duay and S. B. Lee, *Chemical Communications*, 2011, **47**, 1384-1404.
120. A. Yu, H. W. Park, A. Davies, D. C. Higgins, Z. Chen and X. Xiao, *The Journal of Physical Chemistry Letters*, 2011, **2**, 1855-1860.
121. D. Wang, D. Choi, J. Li, Z. Yang, Z. Nie, R. Kou, D. Hu, C. Wang, L. V. Saraf and J. Zhang, *Acs Nano*, 2009, **3**, 907-914.
122. T. Fang, J.-G. Duh and S.-R. Sheen, *J Electrochem Soc*, 2005, **152**, A1701-A1706.
123. B. Z. Jang, C. Liu, D. Neff, Z. Yu, M. C. Wang, W. Xiong and A. Zhamu, *Nano Lett*, 2011, **11**, 3785-3791.
124. D. Liu, Q. Wang, L. Qiao, F. Li, D. Wang, Z. Yang and D. He, *Journal of Materials Chemistry*, 2012, **22**, 483-487.
125. P.-L. Taberna, S. Mitra, P. Poizot, P. Simon and J.-M. Tarascon, *Nature materials*, 2006, **5**, 567-573.
126. M. F. Hassan, M. M. Rahman, Z. P. Guo, Z. X. Chen and H. K. Liu, *Electrochimica Acta*, 2010, **55**, 5006-5013.
127. E. Hammel, X. Tang, M. Trampert, T. Schmitt, K. Mauthner, A. Eder and P. Pötschke, *Carbon*, 2004, **42**, 1153-1158.
128. X. Zhang, H. Liu, S. Petnikota, S. Ramakrishna and H. J. Fan, 2014.
129. H. B. Wu, J. S. Chen, H. H. Hng and X. W. D. Lou, *Nanoscale*, 2012, **4**, 2526-2542.

-
130. B. Jang, M. Park, O. B. Chae, S. Park, Y. Kim, S. M. Oh, Y. Piao and T. Hyeon, *Journal of the American Chemical Society*, 2012, **134**, 15010-15015.
131. X. Lv, J. Deng, J. Wang, J. Zhong and X. Sun, *J Mater Chem A*, 2015, **3**, 5183-5188.
132. C. Wang, L. Yin, D. Xiang and Y. Qi, *Acs Appl Mater Inter*, 2012, **4**, 1636-1642.
133. C. Zhang, X. Peng, Z. Guo, C. Cai, Z. Chen, D. Wexler, S. Li and H. Liu, *Carbon*, 2012, **50**, 1897-1903.
134. P. Wu, N. Du, H. Zhang, J. Yu and D. Yang, *The Journal of Physical Chemistry C*, 2010, **114**, 22535-22538.
135. D. Y. Liu and J. R. Reynolds, *Acs Appl Mater Inter*, 2010, **2**, 3586-3593.
136. D. K. Bhat and M. S. Kumar, *J Mater Sci*, 2007, **42**, 8158-8162.
137. V. Gupta and N. Miura, *Electrochemical and Solid-State Letters*, 2005, **8**, A630-A632.
138. Y. Chen, S. Zeng, J. Qian, Y. Wang, Y. Cao, H. Yang and X. Ai, *Acs Appl Mater Inter*, 2014, **6**, 3508-3512.
139. J. M. Jeong, B. G. Choi, S. C. Lee, K. G. Lee, S. J. Chang, Y. K. Han, Y. B. Lee, H. U. Lee, S. Kwon and G. Lee, *Adv Mater*, 2013, **25**, 6250-6255.
140. S. Menkin, D. Golodnitsky and E. Peled, *Electrochemistry Communications*, 2009, **11**, 1789-1791.
141. Y. Liu, D. Lin, P. Y. Yuen, K. Liu, J. Xie, R. H. Dauskardt and Y. Cui, *Adv Mater*, 2016.
142. F. S. Li, Y. S. Wu, J. Chou, M. Winter and N. L. Wu, *Adv Mater*, 2015, **27**, 130-137.
143. H. Wu, G. Yu, L. Pan, N. Liu, M. T. McDowell, Z. Bao and Y. Cui, *Nat Commun*, 2013, **4**.
144. G. Zhang, S. Hou, H. Zhang, W. Zeng, F. Yan, C. C. Li and H. Duan, *Adv Mater*, 2015, **27**, 2400-2405.
145. X. Sun, W. Si, X. Liu, J. Deng, L. Xi, L. Liu, C. Yan and O. G. Schmidt, *Nano Energy*, 2014, **9**, 168-175.
146. W. Guo, W. Sun and Y. Wang, *Acs Nano*, 2015, **9**, 11462-11471.
147. M. Chen, W. Li, X. Shen and G. Diao, *Acs Appl Mater Inter*, 2014, **6**, 4514-4523.
148. B. Zhao, S.-Y. Huang, T. Wang, K. Zhang, M. M. Yuen, J.-B. Xu, X.-Z. Fu, R. Sun and C.-P. Wong, *Journal of Power Sources*, 2015, **298**, 83-91.
149. S.-K. Park, A. Jin, S.-H. Yu, J. Ha, B. Jang, S. Bong, S. Woo, Y.-E. Sung and Y. Piao, *Electrochimica Acta*, 2014, **120**, 452-459.
150. L. Hou, L. Lian, L. Zhang, G. Pang, C. Yuan and X. Zhang, *Adv Funct Mater*, 2015, **25**, 238-246.
151. D. H. Youn, C. Jo, J. Y. Kim, J. Lee and J. S. Lee, *Journal of Power Sources*, 2015, **295**, 228-234.
152. H. Jiang, Y. Hu, S. Guo, C. Yan, P. S. Lee and C. Li, *Acs Nano*, 2014, **8**, 6038-6046.
153. F. Han, L. Ma, Q. Sun, C. Lei and A. Lu, *Nano Res*, 2014, **7**, 1706-1717.
154. L. Hu and Q. Chen, *Nanoscale*, 2014, **6**, 1236-1257.
155. M.-C. Kim, Y.-W. Lee, S.-J. Kim, B.-M. Hwang, H.-C. Park, E.-T. Hwang, G. Cao and K.-W. Park, *Electrochimica Acta*, 2014, **147**, 241-249.
156. S. J. Yang, J. H. Im, T. Kim, K. Lee and C. R. Park, *Journal of hazardous materials*, 2011, **186**, 376-382.

157. A. Banerjee, R. Gokhale, S. Bhatnagar, J. Jog, M. Bhardwaj, B. Lefez, B. Hannoyer and S. Ogale, *Journal of Materials Chemistry*, 2012, **22**, 19694-19699.
158. S. Dou, X. Li, L. Tao, J. Huo and S. Wang, *Chemical Communications*, 2016, **52**, 9727-9730.
159. P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebric, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, P. N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur and R. Gref, *Nature materials*, 2010, **9**, 172-178.
160. W. S. Hummers Jr and R. E. Offeman, *Journal of the American Chemical Society*, 1958, **80**, 1339-1339.
161. Z. Pu, M. Cao, J. Yang, K. Huang and C. Hu, *Nanotechnology*, 2006, **17**, 799.
162. S. Xiong and H. C. Zeng, *Angewandte Chemie International Edition*, 2012, **51**, 949-952.
163. Y. Yu, X. Yin, A. Kvit and X. Wang, *Nano Lett*, 2014, **14**, 2528-2535.
164. Q. Xie, J. Li, Q. Tian and R. Shi, *J Mater Chem*, 2012, **22**, 13541-13547.
165. W. L. Bond, *Acta Crystallographica*, 1960, **13**, 814-818.
166. Powder X-ray Diffraction, https://chem.libretexts.org/Core/Analytical_Chemistry/Instrumental_Analysis/Diffraction_Scattering_Techniques/Powder_X-ray_Diffraction).
167. SEM Working Principle, https://www.researchgate.net/figure/261702149_fig1_Figure-1-Schematic-diagram-of-the-SEM-working-principle-32).
168. TEM Outline, http://www.hk-phy.org/atomic_world/tem/tem02_e.html).
169. XPS Working Principle, https://en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy).
170. TGA Working Principle, https://www.researchgate.net/post/How_to_interpret_the_TGA_and_DSC_analysis2).
171. Raman Spectra Working Principle, https://en.wikipedia.org/wiki/Raman_spectroscopy).
172. S. Han, X. J. Wang, Y. S. Huang, Y. P. Tang, Y. N. Ai, J. Z. Jiang and D. Q. Wu, *Rsc Adv*, 2015, **5**, 98399-98403.
173. Y. Jiang, Z. J. Jiang, L. F. Yang, S. Cheng and M. L. Liu, *J Mater Chem A*, 2015, **3**, 11847-11856.
174. L. S. Fan, B. J. Li, D. W. Rooney, N. Q. Zhang and K. N. Sun, *Chemical communications*, 2015, **51**, 1597-1600.
175. S. J. Sun, X. Y. Zhao, M. Yang, L. L. Wu, Z. Y. Wen and X. D. Shen, *Scientific reports*, 2016, **6**.
176. L. G. Guo, Y. Ding, C. Q. Qin, W. Li, J. Du, Z. B. Fu, W. L. Song and F. Wang, *Electrochim Acta*, 2016, **187**, 234-242.
177. J. Y. Liu, S. J. Kelly, E. S. Epstein, Z. Pan, X. J. Huang, J. H. Liu and P. V. Braun, *J Power Sources*, 2015, **299**, 40-48.
178. X. Yao, G. L. Guo, X. Ma, Y. Zhao, C. Y. Ang, Z. Luo, K. T. Nguyen, P. Z. Li, Q. Y. Yan and Y. L. Zhao, *Acs Appl Mater Inter*, 2015, **7**, 26085-26093.
179. M. Y. Wang, S. Li, Y. M. Zhang and J. G. Huang, *Chemistry-a European Journal*, 2015, **21**, 16195-16202.

180. R. Z. Hu, G. H. Waller, Y. K. Wang, Y. Chen, C. H. Yang, W. J. Zhou, M. Zhu and M. L. Liu, *Nano Energy*, 2015, **18**, 232-244.
181. Y. Qian, R. Liu, X. J. Jin, B. Liu, X. F. Wang, J. Xu, Z. R. Wang, G. Chen and J. F. Chao, *Front Optoelectron*, 2015, **8**, 220-228.
182. J. Wu, C. H. Chen, Y. Hao and C. L. Wang, *Colloid Surface A*, 2015, **468**, 17-21.
183. W. Yin, Y. Shen, F. Zou, X. L. Hu, B. Chi and Y. H. Huang, *Acs Appl Mater Inter*, 2015, **7**, 4947-4954.
184. F. Mattelaer, P. M. Vereecken, J. Dendooven and C. Detavernier, *Chem Mater*, 2015, **27**, 3628-3635.
185. K. Wen, G. H. Chen, F. Jiang, X. Y. Zhou and J. Yang, *Int J Electrochem Sc*, 2015, **10**, 3859-3866.
186. K. W. Qiu, H. L. Yan, D. Y. Zhang, Y. Lu, J. B. Cheng, M. Lu, C. L. Wang, Y. H. Zhang, X. M. Liu and Y. S. Luo, *J Solid State Electr*, 2015, **19**, 391-401.
187. G. M. Zhou, D. W. Wang, F. Li, L. L. Zhang, N. Li, Z. S. Wu, L. Wen, G. Q. Lu and H. M. Cheng, *Chem Mater*, 2010, **22**, 5306-5313.
188. X. Y. Li, X. L. Huang, D. P. Liu, X. Wang, S. Y. Song, L. Zhou and H. J. Zhang, *J Phys Chem C*, 2011, **115**, 21567-21573.
189. L. W. Ji and X. W. Zhang, *Electrochemistry Communications*, 2009, **11**, 795-798.
190. Y. Chen, H. Xia, L. Lu and J. M. Xue, *J Mater Chem*, 2012, **22**, 5006-5012.
191. W. Zhou, Y. R. Wang, L. P. Zhang, G. S. Song and S. Q. Cheng, *Int J Electrochem Sc*, 2015, **10**, 5942-5949.
192. J. J. Zhang and A. S. Yu, *Sci Bull*, 2015, **60**, 823-838.
193. C. K. Zhang, H. Q. Song, C. F. Liu, Y. G. Liu, C. P. Zhang, X. H. Nan and G. Z. Cao, *Adv Funct Mater*, 2015, **25**, 3497-3504.
194. G. X. Gao, H. B. Wu, B. T. Dong, S. J. Ding and X. W. Lou, *Adv Sci*, 2015, **2**.
195. K. Palanisamy, Y. Kim, H. Kim, J. M. Kim and W. S. Yoon, *J Power Sources*, 2015, **275**, 351-361.
196. L. Li, S. J. He, M. M. Liu, C. M. Zhang and W. Chen, *Analytical chemistry*, 2015, **87**, 1638-1645.
197. H. M. Ding, H. Jiang, Z. J. Zhu, Y. J. Hu, F. Gu and C. Z. Li, *Electrochim Acta*, 2015, **157**, 205-210.
198. P. P. Su, S. C. Liao, F. Rong, F. Q. Wang, J. Chen, C. Li and Q. H. Yang, *J Mater Chem A*, 2014, **2**, 17408-17414.
199. F. Zou, X. L. Hu, Z. Li, L. Qie, C. C. Hu, R. Zeng, Y. Jiang and Y. H. Huang, *Adv Mater*, 2014, **26**, 6622-6628.
200. H. Y. Yue, Z. P. Shi, Q. X. Wang, Z. X. Cao, H. Y. Dong, Y. Qiao, Y. H. Yin and S. T. Yang, *Acs Appl Mater Inter*, 2014, **6**, 17067-17074.
201. D. Q. Zhu, F. C. Zheng, S. H. Xu, Y. G. Zhang and Q. W. Chen, *Dalton transactions*, 2015, **44**, 16946-16952.
202. C. Y. Zhang, J. Dai, P. G. Zhang, S. Y. Zhang, H. Zhang, Y. H. Shen and A. J. Xie, *Ceram Int*, 2016, **42**, 1044-1049.
203. X. L. Ge, Z. Q. Li, C. X. Wang and L. W. Yin, *Acs Appl Mater Inter*, 2015, **7**, 26633-26642.
204. S. Hao, B. Zhang, S. Ball, M. Copley, Z. Xu, M. Srinivasan, K. Zhou, S. Mhaisalkar and Y. Huang, *Journal of Power Sources*, 2015, **294**, 112-119.
205. S. Hao, B. Zhang, S. Ball, B. Hu, J. Wu and Y. Huang, *Mater Design*, 2016, **92**, 160-165.

-
206. S. Hao, B. Zhang, S. Ball, J. Wu, M. Srinivasan and Y. Huang, *J Mater Chem A*, 2016, **4**, 16569-16575.
207. S. Hao, B. Zhang, J. Feng, Y. Liu, S. Ball, J. Pan, M. Srinivasan and Y. Huang, *J Mater Chem A*, 2017, **5**, 8510-8518.
208. B. Zhang, S. Hao, D. Xiao, J. Wu and Y. Huang, *Mater Design*, 2016, **98**, 319-323.
209. X. Qiu, X. Wang and Y. W. Li, *Chemical communications*, 2015, **51**, 3874-3877.
210. W. F. Dong, X. D. Liu, W. B. Shi and Y. M. Huang, *Rsc Adv*, 2015, **5**, 17451-17457.
211. P. Cui, J. Lee, E. Hwang and H. Lee, *Chemical Communications*, 2011, **47**, 12370-12372.
212. S. K. Mishra, S. N. Tripathi, V. Choudhary and B. D. Gupta, *Sensors and Actuators B: Chemical*, 2014, **199**, 190-200.
213. L. Stobinski, B. Lesiak, A. Malolepszy, M. Mazurkiewicz, B. Mierzwa, J. Zemek, P. Jiricek and I. Bieloshapka, *J Electron Spectrosc*, 2014, **195**, 145-154.
214. J. Z. Wang, C. Zhong, D. Wexler, N. H. Idris, Z. X. Wang, L. Q. Chen and H. K. Liu, *Chemistry-a European Journal*, 2011, **17**, 661-667.
215. J. S. Luo, J. L. Liu, Z. Y. Zeng, C. F. Ng, L. J. Ma, H. Zhang, J. Y. Lin, Z. X. Shen and H. J. Fan, *Nano Lett*, 2013, **13**, 6136-6143.
216. P. C. Lian, X. F. Zhu, H. F. Xiang, Z. Li, W. S. Yang and H. H. Wang, *Electrochim Acta*, 2010, **56**, 834-840.
217. K. M. Shaju, F. Jiao, A. Debart and P. G. Bruce, *Physical Chemistry Chemical Physics*, 2007, **9**, 1837-1842.
218. P. C. Lian, X. F. Zhu, S. Z. Liang, Z. Li, W. S. Yang and H. H. Wang, *Electrochim Acta*, 2011, **56**, 4532-4539.
219. L. L. Luo, J. S. Wu, J. Y. Luo, J. X. Huang and V. P. Dravid, *Scientific reports*, 2014, **4**.
220. J. Y. Luo, X. Zhao, J. S. Wu, H. D. Jang, H. H. Kung and J. X. Huang, *J Phys Chem Lett*, 2012, **3**, 1824-1829.
221. J. Qin, C. N. He, N. Q. Zhao, Z. Y. Wang, C. S. Shi, E. Z. Liu and J. J. Li, *Acs Nano*, 2014, **8**, 1728-1738.
222. Z. Xiao, Y. Xia, Z. Ren, Z. Liu, G. Xu, C. Chao, X. Li, G. Shen and G. Han, *Journal of Materials Chemistry*, 2012, **22**, 20566-20573.
223. L. Lang and Z. Xu, *Acs Appl Mater Inter*, 2013, **5**, 1698-1703.
224. R. Wang, C. Xu, J. Sun, L. Gao and C. Lin, *J Mater Chem A*, 2013, **1**, 1794-1800.
225. L. Li, A. Kovalchuk, H. Fei, Z. Peng, Y. Li, N. D. Kim, C. Xiang, Y. Yang, G. Ruan and J. M. Tour, *Adv Energy Mater*, 2015, **5**.
226. D. Chen, Q. F. Wang, R. M. Wang and G. Z. Shen, *J Mater Chem A*, 2015, **3**, 10158-10173.
227. S. H. Choi, J. K. Lee and Y. C. Kang, *Nanoscale*, 2014, **6**, 12421-12425.
228. X. H. Xia, J. P. Tu, Y. Q. Zhang, X. L. Wang, C. D. Gu, X. B. Zhao and H. J. Fan, *Acs Nano*, 2012, **6**, 5531-5538.
229. B. Zhao, S. Y. Huang, T. Wang, K. Zhang, M. M. F. Yuen, J. B. Xu, X. Z. Fu, R. Sun and C. P. Wong, *J Power Sources*, 2015, **298**, 83-91.
230. Z. Q. Zhang, F. X. Bao, Y. N. Zhang, L. K. Feng, Y. Ji, H. D. Zhang, Q. S. Sun, S. H. Feng, X. D. Zhao and X. Y. Liu, *J Power Sources*, 2015, **296**, 162-168.

231. A. S. Liu, R. Jones, L. Liao, D. Samara-Rubio, D. Rubin, O. Cohen, R. Nicolaescu and M. Panizza, *Nature*, 2004, **427**, 615-618.
232. S. T. Kochuveedu, Y. H. Jang and D. H. Kim, *Chemical Society reviews*, 2013, **42**, 8467-8493.
233. Z. J. Su, C. Yang, C. J. Xu, H. Y. Wu, Z. X. Zhang, T. Liu, C. Zhang, Q. H. Yang, B. H. Li and F. Y. Kang, *J Mater Chem A*, 2013, **1**, 12432-12440.
234. C. Wang, H. Xu, C. Liang, Y. M. Liu, Z. W. Li, G. B. Yang, H. Cheng, Y. G. Li and Z. Liu, *Acs Nano*, 2013, **7**, 6782-6795.
235. J. J. Yang, M. D. Pickett, X. M. Li, D. A. A. Ohlberg, D. R. Stewart and R. S. Williams, *Nat Nanotechnol*, 2008, **3**, 429-433.
236. A. C. T. van Duin, V. S. Bryantsev, M. S. Diallo, W. A. Goddard, O. Rahaman, D. J. Doren, D. Raymand and K. Hermansson, *Journal of Physical Chemistry A*, 2010, **114**, 9507-9514.
237. X. Sun, H. Zhang, L. Zhou, X. Huang and C. Yu, *Small*, 2016, **12**, 3732-3737.
238. Q. W. Tian, J. Q. Hu, Y. H. Zhu, R. J. Zou, Z. G. Chen, S. P. Yang, R. W. Li, Q. Q. Su, Y. Han and X. G. Liu, *J Am Chem Soc*, 2013, **135**, 8571-8577.
239. Y. X. Zhang, H. L. Ding, Y. Y. Liu, S. S. Pan, Y. Y. Luo and G. H. Li, *J Mater Chem*, 2012, **22**, 10779-10786.
240. H. Zhang, X. Sun, X. Huang and L. Zhou, *Nanoscale*, 2015, **7**, 3270-3275.
241. S. Kim, B. Fisher, H. Y. Eisler and M. G. Bawendi, *Abstr Pap Am Chem S*, 2002, **224**, U443-U443.
242. H. Jiang, Y. J. Hu, S. J. Guo, C. Y. Yan, P. S. Lee and C. Z. Li, *Acs Nano*, 2014, **8**, 6038-6046.
243. Y. Yang, D. S. Kim, M. Knez, R. Scholz, A. Berger, E. Pippel, D. Hesse, U. Gosele and M. Zacharias, *J Phys Chem C*, 2008, **112**, 4068-4074.
244. C. L. Zhu, S. W. Chou, S. F. He, W. N. Liao and C. C. Chen, *Nanotechnology*, 2007, **18**.
245. D. Deng and J. Y. Lee, *Chem Mater*, 2008, **20**, 1841-1846.
246. G. D. Li and Z. Y. Tang, *Nanoscale*, 2014, **6**, 3995-4011.
247. M. Cargnello, M. Grzelczak, B. Rodriguez-Gonzalez, Z. Syrgiannis, K. Bakmutsky, V. La Parola, L. M. Liz-Marzan, R. J. Gorte, M. Prato and P. Fornasiero, *J Am Chem Soc*, 2012, **134**, 11760-11766.
248. L. Zhou, H. Xu, H. Zhang, J. Yang, S. B. Hartono, K. Qian, J. Zou and C. Yu, *Chemical communications*, 2013, **49**, 8695-8697.
249. J. X. Wang, Q. B. Zhang, X. H. Li, B. Zhang, L. Q. Mai and K. L. Zhang, *Nano Energy*, 2015, **12**, 437-446.
250. C. Guan, X. H. Xia, N. Meng, Z. Y. Zeng, X. H. Cao, C. Soci, H. Zhang and H. J. Fan, *Energy & Environmental Science*, 2012, **5**, 9085-9090.
251. S. J. Hao, B. W. Zhang, S. Ball, M. Copley, Z. C. Xu, M. Srinivasan, K. Zhou, S. Mhaisalkar and Y. Z. Huang, *Journal of Power Sources*, 2015, **294**, 112-119.
252. S. J. Hao, B. W. Zhang, S. Ball, B. Hu, J. S. Wu and Y. Z. Huang, *Mater Design*, 2016, **92**, 160-165.
253. B. W. Zhang, S. J. Hao, D. R. Xiao, J. S. Wu and Y. Z. Huang, *Mater Design*, 2016, **98**, 319-323.
254. Y. Zhao, J. X. Li, Y. H. Ding and L. H. Guan, *Chemical communications*, 2011, **47**, 7416-7418.

-
255. A. P. Yu, H. W. Park, A. Davies, D. C. Higgins, Z. W. Chen and X. C. Xiao, *J Phys Chem Lett*, 2011, **2**, 1855-1860.
256. K. Zhao, M. Wen, Y. Dong, L. Zhang, M. Yan, W. Xu, C. Niu, L. Zhou, Q. Wei and W. Ren, *Adv Energy Mater*, 2016.
257. Y. M. He, W. J. Chen, X. D. Li, Z. X. Zhang, J. C. Fu, C. H. Zhao and E. Q. Xie, *Acs Nano*, 2013, **7**, 174-182.
258. X. H. Lu, M. H. Yu, G. M. Wang, T. Zhai, S. L. Xie, Y. C. Ling, Y. X. Tong and Y. Li, *Adv Mater*, 2013, **25**, 267-272.
259. Z. N. Yu, B. Duong, D. Abbitt and J. Thomas, *Adv Mater*, 2013, **25**, 3302-3306.
260. L. F. Chen, Z. H. Huang, H. W. Liang, Q. F. Guan and S. H. Yu, *Adv Mater*, 2013, **25**, 4746-4752.
261. S. M. Dong, X. Chen, L. Gu, X. H. Zhou, L. F. Li, Z. H. Liu, P. X. Han, H. X. Xu, J. H. Yao, H. B. Wang, X. Y. Zhang, C. Q. Shang, G. L. Cui and L. Q. Chen, *Energ Environ Sci*, 2011, **4**, 3502-3508.
262. D. Z. Kong, J. S. Luo, Y. L. Wang, W. N. Ren, T. Yu, Y. S. Luo, Y. P. Yang and C. W. Cheng, *Adv Funct Mater*, 2014, **24**, 3815-3826.
263. T. Zhai, S. L. Xie, M. H. Yu, P. P. Fang, C. L. Liang, X. H. Lu and Y. X. Tong, *Nano Energy*, 2014, **8**, 255-263.
264. L. Li, X. H. Feng, Y. Nie, S. G. Chen, F. Shi, K. Xiong, W. Ding, X. Q. Qi, J. S. Hu, Z. D. Wei, L. J. Wan and M. R. Xia, *Acs Catal*, 2015, **5**, 4825-4832.
265. D. J. Davis, T. N. Lambert, J. A. Vigil, M. A. Rodriguez, M. T. Brumbach, E. N. Coker and S. J. Limmer, *J Phys Chem C*, 2014, **118**, 17342-17350.
266. J. L. Kang, A. Hirata, L. J. Kang, X. M. Zhang, Y. Hou, L. Y. Chen, C. Li, T. Fujita, K. Akagi and M. W. Chen, *Angew Chem Int Edit*, 2013, **52**, 1664-1667.
267. T. R. Zhang, F. Y. Cheng, J. Du, Y. X. Hu and J. Chen, *Adv Energy Mater*, 2015, **5**.
268. A. P. Miller, *Am J Public Health N*, 1941, **31**, 1324-1324.
269. F. Bodino, G. Baud, M. Benmalek, J. P. Besse, H. M. Dunlop and M. Jacquet, *Thin Solid Films*, 1994, **241**, 21-24.
270. K. Endo, C. Inoue, N. Kobayashi and M. Aida, *J Phys Chem Solids*, 1994, **55**, 471-478.
271. J. A. Taylor, G. M. Lancaster and J. W. Rabalais, *Appl Surf Sci*, 1978, **1**, 503-514.
272. Y. Cheng, B. Zou, C. Wang, Y. Liu, X. Fan, L. Zhu, Y. Wang, H. Ma and X. Cao, *Crystengcomm*, 2011, **13**, 2863-2870.
273. L. Li, R. M. Li, S. L. Gai, S. J. Ding, F. He, M. L. Zhang and P. P. Yang, *Chem-Eur J*, 2015, **21**, 7119-7126.
274. V. Dicastro and G. Polzonetti, *J Electron Spectrosc*, 1989, **48**, 117-123.
275. M. Oku, K. Hirokawa and S. Ikeda, *J Electron Spectrosc*, 1975, **7**, 465-473.
276. M. Zhi, G. Zhou, Z. Hong, J. Wang, R. Gemmen, K. Gerdes, A. Manivannan, D. Ma and N. Wu, *Energ Environ Sci*, 2011, **4**, 139-144.
277. S. Zhan, D. Zhu, M. Qiu, H. Yu and Y. Li, *Rsc Adv*, 2015, **5**, 29353-29361.
278. Z. Sun, H. Yuan, Z. Liu, B. Han and X. Zhang, *Adv Mater*, 2005, **17**, 2993-2997.
279. T. Ohta, M. Yamada and H. Kuroda, *Bulletin of the Chemical Society of Japan*, 1974, **47**, 1158-1161.
280. D. Sarma and C. Rao, *J Electron Spectrosc*, 1980, **20**, 25-45.
281. C. Wagner, D. Zatko and R. Raymond, *Analytical Chemistry*, 1980, **52**, 1445-1451.

-
282. A. Quesada, M. García, P. Crespo and A. Hernando, *J Magn Magn Mater*, 2006, **304**, 75-78.
283. P. Torelli, F. Sirotti and P. Ballone, *Physical Review B*, 2003, **68**, 205413.
284. H. J. Fan, U. Gösele and M. Zacharias, *small*, 2007, **3**, 1660-1671.
285. V. A. Coleman, M. Buda, H. H. Tan, C. Jagadish, M. R. Phillips, K. Koike, S. Sasa, M. Inoue and M. Yano, *Semiconductor science and technology*, 2006, **21**, L25.
286. H. Sumida, H. Asahi, S. J. Yu, K. Asami, S. i. Gonda and H. Tanoue, *Appl Phys Lett*, 1989, **54**, 520-522.
287. V. Vonk, J. Huijben, D. Kukuruznyak, A. Stierle, H. Hilgenkamp, A. Brinkman and S. Harkema, *Physical Review B*, 2012, **85**, 045401.
288. R. Würschum, P. Farber, R. Dittmar, P. Scharwaechter, W. Frank and H.-E. Schaefer, *Physical review letters*, 1997, **79**, 4918.
289. J. Wang, R. Limas-Ballesteros, T. Lopez, A. Moreno, R. Gomez, O. Novaro and X. Bokhimi, *The Journal of Physical Chemistry B*, 2001, **105**, 9692-9698.
290. J. Pan, S.-M. Hühne, H. Shen, L. Xiao, P. Born, W. Mader and S. Mathur, *The Journal of Physical Chemistry C*, 2011, **115**, 17265-17269.
291. A. M. Cao, J. S. Hu, H. P. Liang and L. J. Wan, *Angewandte Chemie International Edition*, 2005, **44**, 4391-4395.
292. L. Li, A. R. O. Raji and J. M. Tour, *Adv Mater*, 2013, **25**, 6298-6302.
293. B. Sun, J. Horvat, H. S. Kim, W. S. Kim, J. Ahn and G. X. Wang, *J Phys Chem C*, 2010, **114**, 18753-18761.
294. Z. Cao and B. Wei, *Acs Appl Mater Inter*, 2013, **5**, 10246-10252.
295. J. A. Dawson, H. Chen and I. Tanaka, *Acs Appl Mater Inter*, 2015, **7**, 1726-1734.
296. Y.-Y. Hu, Z. Liu, K.-W. Nam, O. J. Borkiewicz, J. Cheng, X. Hua, M. T. Dunstan, X. Yu, K. M. Wiaderek and L.-S. Du, *Nature materials*, 2013, **12**, 1130-1136.
297. K. Zhong, X. Xia, B. Zhang, H. Li, Z. Wang and L. Chen, *Journal of Power Sources*, 2010, **195**, 3300-3308.
298. P. Balaya, H. Li, L. Kienle and J. Maier, *Adv Funct Mater*, 2003, **13**, 621-625.
299. S. Laruelle, S. Grugeon, P. Poizot, M. Dolle, L. Dupont and J. M. Tarascon, *Journal of the Electrochemical Society*, 2002, **149**, A627-A634.
300. H. Sun, G. Xin, T. Hu, M. Yu, D. Shao, X. Sun and J. Lian, *Nat Commun*, 2014, **5**, ncomms5526.
301. J. Li, S. Xiong, Y. Liu, Z. Ju and Y. Qian, *Acs Appl Mater Inter*, 2013, **5**, 981-988.
302. J. Zang, J. J. Chen, C. L. Zhang, H. Qian, M. S. Zheng and Q. F. Dong, *J Mater Chem A*, 2014, **2**, 6343-6347.
303. J. K. Hu, C. F. Sun, E. Gillette, Z. Gui, Y. H. Wang and S. B. Lee, *Nanoscale*, 2016, **8**, 12958-12969.
304. X. Gu, L. Chen, Z. C. Ju, H. Y. Xu, J. Yang and Y. T. Qian, *Adv Funct Mater*, 2013, **23**, 4049-4056.
305. Z. Y. Wang, L. Zhou and X. W. Lou, *Adv Mater*, 2012, **24**, 1903-1911.
306. L. F. Cui, Y. Yang, C. M. Hsu and Y. Cui, *Nano Lett*, 2009, **9**, 3370-3374.
307. M. S. Wu and H. W. Chang, *J Phys Chem C*, 2013, **117**, 2590-2599.
308. F. Cheng, T. Zhang, Y. Zhang, J. Du, X. Han and J. Chen, *Angewandte Chemie International Edition*, 2013, **52**, 2474-2477.
309. J. Huang, A. S. Poyraz, S.-Y. Lee, L. Wu, Y. Zhu, A. C. Marschilok, K. J. Takeuchi and E. S. Takeuchi, *Acs Appl Mater Inter*, 2016.

-
310. K. S. Lee, S. Park, W. Lee and Y. S. Yoon, *Acs Appl Mater Inter*, 2016, **8**, 2027-2034.
311. J. S. Luo, X. H. Xia, Y. S. Luo, C. Guan, J. L. Liu, X. Y. Qi, C. F. Ng, T. Yu, H. Zhang and H. J. Fan, *Adv Energy Mater*, 2013, **3**, 737-743.
312. G. Wang, Y. H. Sun, D. B. Li, W. Wei, X. L. Feng and K. Mullen, *Small*, 2016, **12**, 3914-3919.
313. I. Hong, M. Angelucci, R. Verrelli, M. G. Betti, S. Panero, F. Croce, C. Mariani, B. Scrosati and J. Hassoun, *J Power Sources*, 2014, **256**, 133-136.
314. X. H. Ma, X. Y. Feng, C. Song, B. K. Zou, C. X. Ding, Y. Yu and C. H. Chen, *Electrochim Acta*, 2013, **93**, 131-136.
315. X. O. Wang, L. S. Gao, H. G. Zheng, M. R. Ji, T. Shen and Z. Zhang, *J Cryst Growth*, 2004, **269**, 489-492.
316. X. L. Wu, Y. G. Guo, L. J. Wan and C. W. Hu, *J Phys Chem C*, 2008, **112**, 16824-16829.
317. L. Chun, X. Z. Wu, X. M. Lou and Y. X. Zhang, *Electrochim Acta*, 2010, **55**, 3089-3092.
318. B. A. Zhang, Z. D. Huang, S. W. Oh and J. K. Kim, *J Power Sources*, 2011, **196**, 10692-10697.
319. F. Zhang, K. X. Wang, G. D. Li and J. S. Chen, *Electrochemistry Communications*, 2009, **11**, 130-133.
320. S. L. Chou, J. Z. Wang, H. K. Liu and S. X. Dou, *J Power Sources*, 2008, **182**, 359-364.
321. S. B. Yang, H. H. Song and X. H. Chen, *Electrochemistry Communications*, 2006, **8**, 137-142.
322. P. Arora, M. Doyle, A. S. Gozdz, R. E. White and J. Newman, *J Power Sources*, 2000, **88**, 219-231.
323. R. C. Jin, Y. S. Guan, H. Liu, J. H. Zhou and G. Chen, *Chempluschem*, 2014, **79**, 1643-1648.
324. B. T. Hang, I. Watanabe, T. Doi, S. Okada and J. I. Yamaki, *J Power Sources*, 2006, **161**, 1281-1287.
325. X. J. Zhu, Y. W. Zhu, S. Murali, M. D. Stollers and R. S. Ruoff, *Acs Nano*, 2011, **5**, 3333-3338.
326. K. Z. Cao, L. F. Jiao, H. Q. Liu, Y. C. Liu, Y. J. Wang, Z. P. Guo and H. T. Yuan, *Adv Energy Mater*, 2015, **5**.
327. K. A. Kwon, H. S. Lim, Y. K. Sun and K. D. Suh, *J Phys Chem C*, 2014, **118**, 2897-2907.
328. J. X. Zhu, Z. Y. Yin, D. Yang, T. Sun, H. Yu, H. E. Hoster, H. H. Hng, H. Zhang and Q. Y. Yan, *Energ Environ Sci*, 2013, **6**, 987-993.
329. S. Chaudhari and M. Srinivasan, *J Mater Chem*, 2012, **22**, 23049-23056.
330. C. T. Cherian, J. Sundaramurthy, M. Kalaivani, P. Ragupathy, P. S. Kumar, V. Thavasi, M. V. Reddy, C. H. Sow, S. G. Mhaisalkar, S. Ramakrishna and B. V. R. Chowdari, *J Mater Chem*, 2012, **22**, 12198-12204.
331. M. S. Wu, Y. H. Ou and Y. P. Lin, *Electrochim Acta*, 2010, **55**, 3240-3244.
332. X. W. Li, L. Qiao, D. Li, X. H. Wang, W. H. Xie and D. Y. He, *J Mater Chem A*, 2013, **1**, 6400-6406.
333. Z. Y. Cao and B. Q. Wei, *J Power Sources*, 2013, **241**, 330-340.
334. W. Y. Hsien, Z. L. Dong, C. F. Li and S. K. Yen, *Surf Coat Tech*, 2013, **216**, 52-59.

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335. N. P. Liu, J. Shen and D. Liu, *Electrochim Acta*, 2013, **97**, 271-277.
336. F. L. Lou, H. T. Zhou, T. D. Tran, M. E. M. Buan, F. Vullum-Bruer, M. Ronning, J. C. Walmsley and D. Chen, *ChemSusChem*, 2014, **7**, 1335-1346.
337. L. W. Su, Z. Zhou, X. Qin, Q. W. Tang, D. H. Wu and P. W. Shen, *Nano Energy*, 2013, **2**, 276-282.
338. I. V. Chernyshova, M. F. Hochella and A. S. Madden, *Physical Chemistry Chemical Physics*, 2007, **9**, 1736-1750.
339. S. Sakurai, A. Namai, K. Hashimoto and S. Ohkoshi, *J Am Chem Soc*, 2009, **131**, 18299-18303.
340. M. Z. Dang, D. G. Rancourt, J. E. Dutrizac, G. Lamarche and R. Provencher, *Hyperfine Interact*, 1998, **117**, 271-319.
341. X. C. Duan, J. Q. Yang, H. Y. Gao, J. M. Ma, L. F. Jiao and W. J. Zheng, *Crystengcomm*, 2012, **14**, 4196-4204.
342. P. V. S. S. Prabhu, T. P. Kumar, P. N. N. Namboodiri and R. Gangadharan, *J Appl Electrochem*, 1993, **23**, 151-156.
343. P. Porion, Y. R. Dougassa, C. Tessier, L. El Ouatani, J. Jacquemin and M. Anouti, *Electrochim Acta*, 2013, **114**, 95-104.
344. Y. R. Dougassa, J. Jacquemin, L. El Ouatani, C. Tessier and M. Anouti, *Journal of Physical Chemistry B*, 2014, **118**, 3973-3980.
345. T. Y. Wei, C. H. Chen, H. C. Chien, S. Y. Lu and C. C. Hu, *Adv Mater*, 2010, **22**, 347-351.
346. G. Zhang, L. Yu, H. B. Wu, H. E. Hoster and X. W. D. Lou, *Adv Mater*, 2012, **24**, 4609-4613.
347. L. Zhou, D. Zhao and X. W. Lou, *Adv Mater*, 2012, **24**, 745-748.
348. F. Cheng, J. Shen, B. Peng, Y. Pan, Z. Tao and J. Chen, *Nature chemistry*, 2011, **3**, 79-84.
349. Y. Liang, H. Wang, J. Zhou, Y. Li, J. Wang, T. Regier and H. Dai, *Journal of the American Chemical Society*, 2012, **134**, 3517-3523.
350. A. Tavares, M. Cartaxo, M. da Silva Pereira and F. Costa, *J Electroanal Chem*, 1999, **464**, 187-197.
351. J. M. Won, S. H. Choi, Y. J. Hong, Y. N. Ko and Y. C. Kang, *Sci Rep-Uk*, 2014, **4**.
352. C. T. Cherian, J. Sundaramurthy, M. Reddy, P. Suresh Kumar, K. Mani, D. Pliszka, C. H. Sow, S. Ramakrishna and B. Chowdari, *Acs Appl Mater Inter*, 2013, **5**, 9957-9963.
353. H. Yu, H. Fan, B. Yadian, H. Tan, W. Liu, H. H. Hng, Y. Huang and Q. Yan, *Acs Appl Mater Inter*, 2015, **7**, 26751-26757.
354. X.-B. Zhong, Z.-Z. Yang, H.-Y. Wang, L. Lu, B. Jin, M. Zha and Q.-C. Jiang, *Journal of Power Sources*, 2016, **306**, 718-723.
355. Z. Li, T. Zhao, X. Zhan, D. Gao, Q. Xiao and G. Lei, *Electrochimica Acta*, 2010, **55**, 4594-4598.
356. Y. Wang, D. Su, A. Ung, J.-h. Ahn and G. Wang, *Nanotechnology*, 2012, **23**, 055402.
357. Z. Zhang, Y. Wang, Q. Tan, Z. Zhong and F. Su, *J Colloid Interf Sci*, 2013, **398**, 185-192.
358. S. G. Mohamed, C.-J. Chen, C. K. Chen, S.-F. Hu and R.-S. Liu, *Acs Appl Mater Inter*, 2014, **6**, 22701-22708.

-
359. N. Wang, X. Ma, Y. Wang, J. Yang and Y. Qian, *J Mater Chem A*, 2015, **3**, 9550-9555.
360. P. F. Teh, S. S. Pramana, Y. Sharma, Y. W. Ko and S. Madhavi, *Acs Appl Mater Inter*, 2013, **5**, 5461-5467.
361. N. Wang, H. Xu, L. Chen, X. Gu, J. Yang and Y. Qian, *Journal of Power Sources*, 2014, **247**, 163-169.
362. X. H. Liu and J. Y. Huang, *Energ Environ Sci*, 2011, **4**, 3844-3860.
363. Q. Li, P. Wang, Q. Feng, M. Mao, J. Liu, S. X. Mao and H. Wang, *Chem Mater*, 2014, **26**, 4102-4108.
364. X. H. Liu, S. Huang, S. T. Picraux, J. Li, T. Zhu and J. Y. Huang, *Nano Lett*, 2011, **11**, 3991-3997.
365. C.-M. Wang, X. Li, Z. Wang, W. Xu, J. Liu, F. Gao, L. Kovarik, J.-G. Zhang, J. Howe and D. J. Burton, *Nano Lett*, 2012, **12**, 1624-1632.
366. M. Li, Y.-X. Yin, C. Li, F. Zhang, L.-J. Wan, S. Xu and D. G. Evans, *Chemical Communications*, 2012, **48**, 410-412.
367. H. Xia, D. Zhu, Y. Fu and X. Wang, *Electrochimica Acta*, 2012, **83**, 166-174.
368. A. K. Rai, J. Gim, T. V. Thi, D. Ahn, S. J. Cho and J. Kim, *The Journal of Physical Chemistry C*, 2014, **118**, 11234-11243.
369. G. Huang, F. Zhang, X. Du, J. Wang, D. Yin and L. Wang, *Chemistry—A European Journal*, 2014, **20**, 11214-11219.
370. Z. Zhang, Y. Wang, M. Zhang, Q. Tan, X. Lv, Z. Zhong and F. Su, *J Mater Chem A*, 2013, **1**, 7444-7450.
371. Y. Ding, Y. Yang and H. Shao, *Journal of Power Sources*, 2013, **244**, 610-613.
372. S. Li, B. Wang, J. Liu and M. Yu, *Electrochimica Acta*, 2014, **129**, 33-39.
373. D. Bresser, E. Paillard, R. Klopech, S. Krueger, M. Fiedler, R. Schmitz, D. Baither, M. Winter and S. Passerini, *Adv Energy Mater*, 2013, **3**, 513-523.
374. F. Zou, X. Hu, Z. Li, L. Qie, C. Hu, R. Zeng, Y. Jiang and Y. Huang, *Adv Mater*, 2014, **26**, 6622-6628.
375. J. Sui, C. Zhang, D. Hong, J. Li, Q. Cheng, Z. Li and W. Cai, *Journal of Materials Chemistry*, 2012, **22**, 13674-13681.