Controlled synthesis of reduced graphene oxide-based metal compound hybrids for lithium-ion batteries application

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NANYANG
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**CONTROLLED SYNTHESIS OF REDUCED
GRAPHENE OXIDE-BASED METAL COMPOUND
HYBRIDS FOR LITHIUM-ION BATTERIES
APPLICATION**

ZHU JIXIN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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COMPOUND HYBRIDS FOR LITHIUM-ION BATTERIES APPLICATION**

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BASED METAL COMPOUND HYBRIDS FOR LITHIUM-ION
BATTERIES APPLICATION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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2012

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Abstract:

Lithium ion battery, as an effective electrochemical energy storage device, has attracted much interest recently. Advanced preparation processes of electrode materials have been developed with controlled size, morphology and composition. In order to enhance the capacity, stability and rate performance, the electrode materials will generally need to be able to (1) accommodate the strain generated during the lithium insertion/extraction and prevent significant structural collapse; (2) possess large surface area and high electrode/electrolyte contact area; (3) remain nanostructures to offer short Li ion diffusion path; (4) exhibit high electrical conductivity and also (5) maintain stable electrical contact with the current collector. Hence, the design of advanced electrode materials is of prime importance and remains as a key challenge that needs to be addressed and constitute one of the motivations behind this study.

In this work, we aim to develop scalable, low-cost and environmentally friendly approaches to prepare electrode materials with advanced electrochemical properties. The chemical and physical mechanisms of these electrode materials were then investigated.

Firstly, to identify the ideal carbon supports for active nanoparticles (NPs), we prepared SnO₂ NPs with different carbonaceous materials, e.g. amorphous carbon, carbon nanotubes (CNT) and reduced graphene oxide (rGO). With the similar SnO₂ mass loading, the electrochemical test showed that SnO₂/rGO electrode delivered the highest reversible capacities, which are mainly due to its large surface area and high electrical conductivity. In addition, the mass loading of SnO₂ was optimized in this part of the work. However, the SnO₂ NPs tended

to agglomerate during the charge-discharge process, and hence affected the long-term cyclability.

Therefore, to achieve high capacity and cyclability at high current density, the agglomeration of SnO_2 NPs should be prevented. Amorphous Fe_2O_3 NPs were introduced into SnO_2/rGO composite to form ternary phase $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ nanocomposite with tailored weight ratio of three components. Electrochemical test demonstrated that the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrode showed good capacity and cycling stability, especially at high current densities. The amorphous Fe_2O_3 NPs are believed to effectively prevent the agglomeration of SnO_2 .

Based on above results, it indicated that MO/rGO nanocomposite structure could be excellent electrode materials. Then, we further investigated the effects of grain size, structure, surface area, and phases on their electrochemical performance. Cobalt oxides nanowalls arrays on rGO nanosheets were fabricated. The results showed structural-process-dependent performances, where smaller grain size and higher surface area can lead to higher capacity and better cycling stability.

However, the lithiation process of many metal oxides involves both the insertion and conversion processes, which involves structural change of the active materials and affects the fast Li diffusion in the electrodes as well as the high-C-rate performance. In order to achieve better electrochemical performance at high C rates, we prepared organic molecular, ferrocene, decorated rGO nanohybrids. In this case, the ferrocene greatly improves the specific capacity while the rGO serves as the light-weight flexible platform to anchor the ferrocene

molecules to prevent them from dissolving into the aprotic electrolyte. These ferrocene/rGO nanohybrids showed excellent high-C-rate performances.

Based on all the above work, the strategy on preparation of nanocomposites for electrode materials of Li ion battery is proposed.

Table of Contents

Acknowledgements	I
Abstract:	II
Table of Contents	V
Chapter 1: Literature Review	1
1.1 The energy storage challenge	1
1.2 Development of batteries	2
1.3 Redox-reactions for anode materials in LIB	5
1.4 Nanostructured anode materials	9
1.5 Transition metal oxide based anode materials for LIB	11
1.5.1 Iron oxides	12
1.5.2 Tin oxides	14
1.5.3 Cobalt oxides	17
1.5.4 Other transition metal oxides	18
1.6 Synthesis methods of electrode materials for LIB	21
1.6.1 Hydrothermal route	21
1.6.2 Solvothermal route	24
1.6.3 Microwave route	25
1.6.4 Electrospinning	26
1.6.5 Chemical vapor deposition (CVD)	26
1.6.6 Electrochemical deposition	27
1.6.7 Other routes	28
1.7 Summary	29
Chapter 2: Objectives	32
Chapter 3: Experiments	35
3.1 Preparation of carbon based-SnO ₂ hybrids with controlled carbon source and mass loading for LIB	35

3.2 Preparation of rGO based-Fe ₂ O ₃ and SnO ₂ /Fe ₂ O ₃ hybrids with controlled mass loading and composition for LIB	37
3.4 Preparation of rGO based-Co ₃ O ₄ nanowalls and CoO nanowalls/nanoparticles with controlled phase, grain size and porosity for LIB ...	38
3.4 Preparation of rGO based-ferrocene nanoclusters with controlled shape for LIB.....	40
3.6 Characterizations:	41
Chapter 4: Results & Discussion	43
4.1 Preparation of carbon based-SnO ₂ hybrids with controlled carbon source and mass loading for LIB	43
4.2 Preparation of rGO based-Fe ₂ O ₃ and SnO ₂ /Fe ₂ O ₃ hybrids with controlled mass loading and composition for LIB	57
4.4 Preparation of rGO based-Co ₃ O ₄ nanowalls and CoO nanowalls/nanoparticles with controlled phase, grain size and porosity for LIB ...	78
4.5 Preparation of rGO based-ferrocene nanoclusters with controlled shape for LIB.....	102
Chapter 5 Conclusion	114
Chapter 6: Future Work.....	116
List of Publications	118
References	120

Chapter 1: Literature Review

1.1 The energy storage challenge

Hydrocarbon fossil fuels such as petroleum oil, coal and natural gas are accounted for the most significant portion of the global electricity generation. However, the increasing consumption and the rapid depletion of fossil fuels has driven the major research focus to exploitation and utilization of renewable energy such as wind energy, tidal energy and solar energy for the past few decades. To provide widespread usage of renewable energies, efficient energy storage and conversion technologies are required. Among these applications, portable electric vehicles and hybrid electric vehicles have been significantly developed to the need of our information-rich, mobile society. Based on the reversible redox reactions, the electrochemical systems available for energy storage and conversion include Li-ion batteries, electrochemical capacitors and metal-air batteries (Figure 1.1) etc.¹⁻⁵

Figure 1.1 Schematic representation and operating principles of (a) Li-ions batteries, (b) Li-Air batteries and (c) supercapacitor

Li-ion battery (LIB) is a type of rechargeable battery which consists of the anode, cathode and electrolyte materials. The lithiation processes in LIB are highly reversible that Li ions are extracted from the cathode electrode (e.g. LiCoO_2) and simultaneously inserted into the anode electrode (e.g. graphitic carbon) during the charging process. When discharging process, Li ions are

reversibly extracted from the anode electrode and simultaneously inserted into the cathode electrode.⁶ Metal-air battery, launched by Abraham et al. in 1996, consists of a Li (or Zn, etc.) metal as anode, a Li^+ conductive organic polymer electrolyte membrane and a carbon composite electrode. It was revised by Bruce and coworkers/et. al. in 2006 due to their high energy density and, hence, has the potential to become alternative energy resources.^{1,6} This battery mainly involves the reactions that oxygen is reduced on discharging to form Li_2O_2 or Li_2O . Then, the lithium oxides are electrochemically decomposed to Li and O_2 on charging.¹ Supercapacitor, also known as electrochemical capacitor or ultracapacitor, can quickly store and release energy through a simple charge separation between two closely spaced electrode layers. Such electrochemical energy storage devices have attracted growing interest to achieve high power and high energy density for possible applications in electric vehicles. Among these, LIB is of particular interest as a power-storage device because of its good energy densities and cyclability, which has been used widely in the world. The review in this chapter will be limited and focused on LIBs.

1.2 Development of batteries

In the past decades, lead-acid, nickel-cadmium, nickel-metal hydride batteries have been developed and were associated with the advances in engineering and technologies (Figure 1.2).⁷ For the first generation of batteries, electrodes are made using bulk or millimeter sized-particles, which can only offer high energy density but not high charge/discharge rate. Owing to the limit of the intrinsic diffusivity of charge carriers in solid state (ca. $10^{-8} \text{ cm}^2/\text{s}$),³ the charge/discharge rates in millimeter sized-electrodes are inevitably limited. As a

result, the first generation of batteries cannot keep pace with the critical requirements of power supply.

Figure 1.2 Development of battery chemistry over the years.⁷

Present-day battery technologies are being outpaced by the ever increasing power demands from new applications. Apart from being inherently safe, batteries of the future will have to integrate the concept of environmental sustainability.⁷ From Figure 1.3a, it can be observed that LIB, as the second generation of batteries, has higher volumetric and gravimetric energy density than that of lead acid and Ni-MH batteries,⁸ which are attractive for the electric vehicles. In the future, other lithium-based batteries, such as lithium-organic, lithium-air batteries will be continued to develop for energy storage and conversion applications.

Figure 1.3 (a) Comparison of the different battery technologies in terms of volumetric (Y axis) and gravimetric (X axis) energy density and (b) Voltage versus capacity for positive and negative electrode materials used or under considerations in Li-based cells.⁸

High energy and power density are the two important requirements to be achieved for energy storage systems. The electrical energy per mass or per unit volume of a LIB is greatly dependent on the chemistry of the system, while the power is crucially dependent on the charge transport rate of the electrode materials.⁷ The conventional and commercially used anode material, graphite, has a theoretical capacity of 372 mAh/g based on the formation of LiC₆, which only delivers a practical value of 350 mAh/g.⁸ Furthermore, the capacity of LiCoO₂, a common material used for the cathode for LIB, is also lower than 150 mAh/g leading to low power density.⁹ Improving these values is the key to develop LIB with higher energy densities. Besides, low power density generated from the high level of polarization at high charge-discharge rates should be addressed. Also, due to safety considerations, the intercalation voltage should be more positive than the redox potential of Li/Li⁺ to minimize the risks generated from deposition of metallic Li on the surface of electrode.^{8,10} In addition, the combustible and oxidizing materials (e.g. organic electrolyte) in LIBs may pose as fire or explosion hazards. Hence, to improve the performance of LIB, electrode materials with high capacities, long-term stabilities and high

charge/discharge rates are required. In this regard, great efforts have been dedicated on the exploration of electrode materials (seeing Figure 1.3b), especially the nanostructured electrode materials.

1.3 Redox-reactions for anode materials in LIB

Figure 1.4 A schematic representation of the different reaction mechanisms observed in electrode materials for lithium batteries. Black circles: voids in the crystal structure, blue circles: metal, yellow circles: lithium.²³

Lithiation reactions between electrolyte and anode materials mainly involved insertion reaction, electrochemical alloying and conversion reaction (Figure 1.4).²³ For example, metallic or semi-metallic anode materials, e.g. Sn, Si, involve alloying reaction, while transition metal compounds, M_aX_b (M = transition metal, X = O, S, F, P, N. . .) involve conversion reaction to yield metallic nanoparticles embedded in a matrix of Li_nX .²³

Based on redox-reactions, metallic or semi-metallic materials can alloy with large amounts of Li per formula unit to yield high specific capacities. For

example, one mole of Si, Ge or Sn can each react with 4.4 mole of Li according to the equation, $M + 4.4 \text{ Li}^+ + 4.4 \text{ e}^- \rightarrow \text{Li}_{4.4}\text{M}$ (where M is Si, Ge and Sn) to yield theoretical capacities of 4200, 1625 and 994 mAh/g, respectively. Sb can react with 3 Li, $\text{Sb} + 3 \text{ Li}^+ + 3.0 \text{ e}^- \rightarrow \text{Li}_3\text{Sb}$ and has a theoretical capacity of 660 mAh/g.^{2,24-26} However, large volume swing is inevitable resulted during this alloying or dealloying processes, leading to low capacities and poor stability. In order to accommodate volume change and improve the stability of the anode, carbon coating and hybridization with other materials are adopted. For example, high reversible capacities and stability were obtained after thin carbon layer was coated. The carbon coated Si@C composites delivered high capacities of 1,500 mAh/g at 1C, which is much larger than the pure Si.²⁷ Heterostructured TiSi_2 nanonets coated with Si obtained specific capacities as high as 1026 mAh/g and showed excellent capacity retention even at a high current density of 8400 mA/g.²⁷ ZnSb nanoparticles imbedded in carbon matrix to form a quasi-intercalation composite, exhibited long cyclability, fast rate capability and high energy density.²⁸ Here, the carbon can effectively accommodate the volume change and prevent active materials from agglomeration and structure collapse.

Metal compounds, such as metal phosphides (MP_x), nitride (MN_x) and sulfides (MS_x), also triggered great interest as potential alternative anode materials. Numerous approaches have been developed to fabricate these materials with nanostructure and study their performance.^{29,30} For example, metal phosphides have received research attention because of their lower intercalation potential and higher degree of electron delocalization than their nitrides and sulfides.³¹ The lithiated reactions in MP_x can be ascribed as: $\text{MP}_x \leftrightarrow \text{Li}_y\text{MP}_x$ (Li^+ intercalation) or $\text{MP}_x \leftrightarrow \text{M} (\text{Li}_y\text{M}) + \text{Li}_y\text{P}$ (metallization or metal

alloying). Here, the P lithiates with several lithium ions and resulted in high capacity. Actually, these phosphides show rapid capacity fading due to the irreversible decomposition of the Li_xP and metal. For instances, MnP_4 nanoparticles can react with 7 lithium to yield Li_7MnP_4 , which exhibits first discharge and charge capacities as high as 1150 mAh/g and 700 mAh/g, respectively. However, the discharging capacity quickly decreases from 1150 to 350 mAh/g after a few cycles.³¹ Similar to MnP_4 , other metal phosphides, such as FeP_2 , CoP_3 , Cu_3P , VP_4 , and Sn_3P_4 , also decompose which is attributed to the pulverization of the particles and formation of low conductivity Li_xP .³¹⁻³⁷ Moreover, high toxicity of phosphides has limited the usage of these materials. So, further efforts are required to improve the electrochemical performances of these electrode materials.

Layer-structured sulfides are expected to be used as electrode materials for LIBs. Sulfides can deliver high capacities when reacted with Li to yield Li_2S . Recently, Jinwoo Cheon and his co-workers have prepared ZrS_2 nanodiscs with different size and used them as anode materials. The results showed that the nanodiscs with 20 nm delivered higher capacity of about 600 mAh/g than that of its bulk counterpart (200 mAh/g).³⁸ With similar layered-structure, high initial capacities of 500 and 600 mAh/g were depicted by FeS and FeS_2 , respectively. However, poor reversibility was observed for both FeS_2 and FeS due to the formation of a variety of lithium polysulfide intermediates, which are soluble in the electrolyte and resulted in low conductivity.^{39,40} Mixing sulfides with graphene have been reported to improve their electrochemical performances. The discharging capacity as high as 1187 mAh/g over 100 cycles have been achieved through tuning the composition of layered MoS_2 /graphene composites,

where pure MoS_2 exhibited poor cyclic stability and its reversible capacity decreases to 256 mAh/g after 100 cycles.⁴¹

For metal nitrides electrode materials such as VN, CoN, Co_3N , Fe_3N , Mn_4N , the lithiated reactions are mostly conversion reactions.⁴²⁻⁴⁵ For example, sputtered VN thin film showed a high capacity of 800 mAh/g and retained this value after 50 cycles, which was possibly attributed to the formation of high lithiated states of Li_3N .⁴⁴ Pereira et al. studied reaction mechanism of Zn_3N_2 with lithium, which involved a conversion reaction of Zn_3N_2 into LiZn alloy imbedded in a matrix of $\beta\text{-Li}_3\text{N}$. Interestingly, they also reported that a similar conversion reaction of Ge_3N_4 with Li. The Ge_3N_4 electrodes exhibited good cycle life and excellent rate capabilities.^{46,47}

Metal oxides have high theoretical capacities and high energy density, which are more attractive as alternative anode materials. The lithiation/delithiation reactions in transition metal oxides are mainly ascribed to conversion reactions, which involve the reduction of metal oxide to metal nanoparticles and the formation of Li_2O . For example, the redox-reactions of $\alpha\text{-Fe}_2\text{O}_3$ and lithium ions are expressed as follows, $\alpha\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Li}_x\text{Fe}_2\text{O}_3 \rightarrow \text{cubic Li}_2\text{Fe}_2\text{O}_3 \rightarrow \text{Fe} + \text{Li}_2\text{O}$.⁴⁸ Unfortunately, large volume expansion is inevitably generated during conversion reactions coupling with formation of non-conductive Li_2O in metal oxides electrodes. This generally leads to low capacity, poor stability and inferior rate capability. Consequently, improvement of electrical conductivity and accommodation of volume change are two key requirements for the successful utilization of metal oxide electrodes. Hence, much efforts and attention have been paid on these problems. For example, iron oxide nanotube arrays derived from sacrificial template showed better electrochemical performances due to its

large electrode/electrolyte contact area.⁴⁹ It delivered a capacity of 700 mA h/g at the first 60 cycles and maintained a reversible capacity of as high as 659 mA h/g even after 150 cycles. On the other hand, metal oxide electrodes with porous structure may allow effective diffusion of Li ions into the active materials, which may result in higher capacities and better stabilities.^{20,50-52} For example, 3D porous SnO₂ thin film retained a capacity of 689 mAh/g at a current density of 0.5C after 100 cycles, which was better than dense SnO₂ film.²⁰

1.4 Nanostructured anode materials

Nanostructured anode materials have many merits for LIB applications. Firstly, based on the equation of $t=L^2/D$, the time t is largely dependent on the diffusion length of L , where D is the diffusion constant. Thus, high-rate capability of lithium insertion/extraction could be achieved when the dimensions of electrode materials are reduced to nanoscale leading to shorter lithium ion transport distance.¹¹ Secondly, nanostructured electrode materials with high surface area can increase the contact area with the electrolyte, allowing more efficient reactions at the interface. Thirdly, the reaction potential for lithium ions can possibly be tuned by reducing the electrode materials to nanosize. For example, reversible lithium intercalation into mesoporous β -MnO₂ without destruction of the rutile structure.¹² Finally, nanostructured electrode materials can help to accommodate the structural strain generated during lithiation/delithiation process.³ Based on the abovementioned reasons, various approaches have been proposed and developed to design nanostructured electrode materials with specific structure, morphology and composition.

Figure 1.5 Different heterogeneous nanostructured electrode materials based on structural complexity.¹³

For example, heterogeneous nanostructured materials can be constructed at zero-dimension (e.g. core-shell nanospheres),^{14,15} one-dimension (e.g. coaxial nanorods),^{16,17} two-dimension (e.g. graphene based hybrids),^{18,19} three-dimension (e.g. mesoporous metal oxide based composites)^{20,21} or more complex nanostructured materials (Figure 1.5).^{13,22} Combining the merits of each component, for example, the high energy densities of metal oxides and high electrical conductivity of graphene, is a promising approach to develop advanced electrode materials for rechargeable LIBs.

In general, nanoelectrode materials are widely accepted to be able to better alleviate the volume strain generated in lithium ions insertion/extraction, enable higher redox reactivity, offer larger electrode/electrolyte contact area and shorten transport path of electrons and Li ion compared with their counterpart bulk materials. However, nanomaterials are certainly not a panacea.⁵³ For example,

nanostructured electrode materials without protection tend to agglomerate and undergo structural collapse during the charge/discharge process.^{16,49,54,55} Furthermore, nanostructured electrode materials also demonstrated low electrical conductivity and large volume change. To circumvent these obstacles, either engineering of nanoelectrodes themselves with controlled size, morphology and composition,^{14,22,56} such as porous structure,⁵⁷ or combination with amorphous carbon/carbon nanotubes/graphene,^{15,17,50,58-60} can effectively improve their electrochemical performances. Moreover, much effort has been made on developing binary hybrids with strong synergistic interactions between different metal oxide species to enhance their capacity and stability,^{61,62} e.g. $\text{SnO}_2/\text{In}_2\text{O}_3$. The electrochemical properties of metal oxides will be discussed in detail in the following parts

1.5 Transition metal oxide based anode materials for LIB

Transition metal oxides (MOs) have shown higher theoretical Li-ion storage capacities (>600 mA h/g) than that of conventional graphite anodes (372 mA h/g) and have been widely investigated as promising anode materials for LIB.⁶³⁻⁶⁶ Moreover, M_xO_y electrodes have attracted increasing attention because of their low cost, low toxicity and widespread availability. However, these materials usually suffer from low reversible capacities and poor stability due to the large volume expansion and structural collapse occurred during charge/discharge processes, which leads to agglomeration of electrode materials and the lost of contact between the electrode and current collector.⁶⁷⁻⁷⁰ Drastic improvements in cyclability and specific capacity through nanostructuring of transition MOs have been reported.^{13,71} For example, hybridizing the M_xO_y nanoparticles (NPs) with conducting matrices, e.g. amorphous carbon shell, carbon nanotubes or

graphene sheets, has been reported to be an effective route to overcome these problems.^{16,17,55,72,73} In particular, metal oxides combined with graphene or its derivatives with high electrical conductivity, high surface-to-volume ratio and ultra-thin thickness. rGO also serves as the conductive matrix to maintain the electrical contact between metal oxides and the current collector.

However, preservation of high capacities after long cycles at high current density remains as a critical challenge.^{67,74-77} Therefore, further efforts have been devoted to improve Li ion storage performances with nanostructured metal oxide electrodes. The merits and demerits of various metal oxides will be introduced below. Meanwhile, some strategies adopted to improve their Li ion storage performance are also addressed.

1.5.1 Iron oxides

There are three types of iron oxides with different oxidation states, e.g. FeO, Fe₂O₃ and Fe₃O₄, where Fe₂O₃ can be divided into α - and γ - crystalline Fe₂O₃. Due to their high theoretical capacity (1007 mA h/g for Fe₂O₃, and 926 mA h/g for Fe₃O₄), low cost and low toxicity, Fe₂O₃ and Fe₃O₄ have been widely studied as alternative anode candidates. Among these iron oxides, hematite (α -Fe₂O₃), being the most stable n-type semiconducting oxide, has been prepared with controlled size, composition, and morphology for LIB.^{48,49,54,64,67,78-89} Chowdari and his co-workers prepared α -Fe₂O₃ nanoflakes on Cu foil by a simple hotplate technique. When used as anode materials, the nanoflakes showed a stable capacity of 680 mAh/g at a current density of 0.1C. Here, its superior performance was ascribed to the sustainable connection between the Fe₂O₃ flakes and current collectors during the lithium insertion/extraction process.⁸⁹

Furthermore, high rate capability and high capacity have been achieved by decreasing grain size of the Fe_2O_3 nanoparticles. Nanosized Fe_2O_3 particles were prepared using a solvothermal method reported by Chen and his co-workers. The grain size of Fe_2O_3 particles was tuned by changing the annealing temperature. The discharge capacity was as high as 1100 mAh/g at a current density of 0.2 mA/cm² for the samples obtained at 400 °C.⁸⁶ Moreover, hybridizing nanostructured Fe_2O_3 , e.g. mixing with a conductive matrix, was also proposed to enhance its electrochemical performance. Hollow structured $\alpha\text{-Fe}_2\text{O}_3$ /carbon nanocomposite with a high surface area was synthesized using a spray pyrolysis method by Chou and his co-workers.⁸⁴ This porous structured $\alpha\text{-Fe}_2\text{O}_3$ /carbon nanocomposite demonstrated a high capacity of 1210 mAh/g at a current density of 0.1C and sustained a capacity of 720 mAh/g up to 200 cycles at a current density of 2C. These improvements were attributed to both the high electrical conductivity of amorphous carbon and high surface area of Fe_2O_3 (260 m²/g). Carbon and high surface are usually required to maintain the contact between the hosts and electrolyte as well as to enhance the transport of lithium ions and electrons. Based on this concept, iron oxide/CNTs arrays were derived by using ZnO as the sacrificial template, where the carbon coating was formed through carbonization of glucose added in the precursor solution. A high capacity of 659 mAh/g was achieved at a current density of 0.2 C and sustained over 150 cycles.⁴⁹ Even at high C rates, it still retained excellent capacity, e.g. 463 mAh/g at 1.5 C and 457 mAh/g at 3 C, which is possibly ascribed to the uniform carbon coated layer covering the hollow tubes.

In the case of Fe_3O_4 , electrochemical performances can be enhanced after engineering their structures or introducing other composition.^{54,87,90-93} Recently,

Fe_3O_4 nanorods were directly deposited on Cu and a factor of six enhancement in power density over planar electrodes has been achieved. A capacity of 80% of the total capacity at 8C over 100 cycles was delivered.⁹³ In order to improve stability, Fe_3O_4 nanospindles with carbon coating obtained have been fabricated by partial reduction of $\text{Fe}_2\text{O}_3/\text{C}$ composite. The $\text{Fe}_3\text{O}_4 @ \text{C}$ nanospindles showed stable cyclability and high rate capability e.g. 700 mAh/g at 0.2 C and 600 mAh/g at 0.5 C compared with their counterparts (e.g. pure Fe_2O_3 faded to 200 mAh/g or Fe_3O_4 faded to 300 mAh/g). Here, the uniform and continuous carbon layers can effectively sustain the integrity of structure and enhance the electrical conduction of the electrodes.⁵⁴ Otherwise, highly conductive graphene nanosheets were also adopted as matrices to support the Fe_3O_4 nanoparticles. Fe_3O_4 nanoparticles were wrapped in rGO by the annealing process. This composite depicted a reversible capacity of 1026 mAh/g after 30 cycles at 35 mA/g and 580 mAh/g after 100 cycles at 700 mA/g, respectively. The flexible graphene nanosheets largely improved electron transport and isolated the Fe_3O_4 nanoparticles during the charge/discharge process.⁹⁰

Improved electrochemical performances of iron oxides have been achieved by either designing their structure/size/shape/composition, or hybridizing them with highly conductive matrix.

1.5.2 Tin oxides

Electrochemically active metal oxides such as SnO_2 , Fe_2O_3 , and Co_3O_4 have long been considered as anode materials for LIB because of their high theoretical capacities. In line with this, tin oxide is proposed as alternative anode material for LIB due to its high energy densities.⁷¹ During the charge/discharge

process, there are two typical electrochemical processes took place in SnO_2 : $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O}$ (1); $\text{Sn} + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{Sn}$ ($0 \leq x \leq 4.4$) (2).^{71,94} Based on the second reaction, SnO_2 exhibited attractive theoretical reversible capacity (e.g. 790 mAh /g) compared to that of current graphitic material (e.g. 372 mAh/g). However, a large volume swing (about 358%) occurred during the charge-discharge process in SnO_2 ,⁹⁵ leading to the pulverization of Sn particles. As a result of this, SnO_2 suffered from poor stability caused by the loss of the electrical contact from the current collector.^{94,96-98}

To solve this issue, advanced preparation processes of SnO_2 have been developed with controlled size, morphology and composition.^{14,22,56} Following the strategy that nanomaterials with hollow structures were able to, manifest large improvements in electrochemical performance., SnO_2 hollow nanostructures were reported by Lou *et.al.*⁹⁹ using template-free solvothermal route. The SnO_2 hollow nanospheres have a surprisingly large initial discharge of 1140 mAh/g at a current density of 160 mA/g. However, the stability of SnO_2 hollow nanospheres is low, which is possibly ascribed to its large volume swing generated during the Li insertion/extraction processes. In consideration of this, SnO_2 hollow spheres with carbon layer and coaxial SnO_2 @carbon hollow nanospheres were further prepared by Lou and his co-workers using two-steps method.^{15,100} The capacity can stabilize around 460mAh/g for more than 100 cycles. After 100 cycles, the hollow spheres can still deliver a stable capacity of about 210mAh/g at a high rate of 4.8 C. Here, simultaneously combing hollow interior space and carbon nanopainting in this structure are the main reasons for its super performance.

On the other hand, maintaining the electrical contact to the current collectors is another desirable design rationale to achieve high-energy anode materials. SnO_2 has been attached onto conductive materials, e.g. carbon nanotubes and reduced graphene oxide (rGO) sheets,^{15,17,50,58-60} to maintain the electrical contact and have showed enhanced reversible capacities at reasonable C rates. An in situ chemical route was reported to prepare SnO_2/rGO nanocomposite by Wang etc..¹⁰¹ A discharge capacity of 520 mAh/g was sustained over 100 cycles for the SnO_2/rGO nanocomposite, while the capacities of pure SnO_2 nanoparticle faded to 50 mAh/g in the 20th cycle. Sn powder, graphene oxide, NH_4OH and hydrazine were used as precursors to prepare SnO_2/rGO composite as reported by Kang and his co-workers.¹⁰² During the reaction, tin particles were etched and oxidized to tin oxide (SnO_2). This method is not widely accepted for use because of the highly toxicity of hydrazine, although a high reversible capacity of 634 mAh/g was delivered after 50 cycles. In addition, improvements can also be achieved by changing the morphologies of SnO_2 from nanoparticles to nanosheets grown on graphene.¹⁰³ The rGO-supported SnO_2 nanosheets delivered a much higher reversible capacity of 518 mAh/g over 50 cycles, while the bare SnO_2 nanosheets and SnO_2/rGO composite can only deliver a capacity in the range of 300-350 mAh/g.

There are efforts to mix SnO_2 with other metal oxides, e.g. In_2O_3 , to increase the electrical conductivity.^{61,62} However, high reversible capacities, in particular at high C rates, are still desired in these SnO_2 based advanced anodes although improved Li storage performances have been demonstrated. To achieve high reversible capacities at large current densities, it generally requires the material system to (1) remain nanostructures without significant agglomeration to

facilitate the fast Li diffusion process and (2) further expanding this concept to achieve high Li storage performance at higher C rates is demanded.

1.5.3 Cobalt oxides

Cobalt oxides (CoO and Co₃O₄) are also listed among the most promising alternative anode materials. Conversion reactions in these metal oxides involved the formation/decomposition of Li₂O accompanying with the reduction/oxidation of metal nanoparticles during lithiation/delithiation process. One of the key issues for these anode materials is to enable the integrity of the electrodes over cycling process and keep good contact with current collector. These are greatly dependent on their structures and morphologies.^{51,53,55,68,104-113} For example, CoO and Co₃O₄ particles obtained from ball milling showed low capacities e.g. CoO, 600 mAh/g and Co₃O₄ 380 mAh/g and the capacities quickly faded to 300 and 100 mAh/g, respectively.¹⁰⁴ However, multilayered CoO and Co₃O₄ nanosheets delivered higher reversible capacity and better cyclability, e.g. 800 mAh/g for CoO and 600 mAh/g for Co₃O₄ sustained over 100 cycles at a current density of 100 mA/g.¹⁰⁹ These multilayered CoO and Co₃O₄ nanosheets were prepared through pyrolysis of Co(OH)₂. Meanwhile, small pores were generated in CoO and Co₃O₄ nanoplatelets, which is desirable to favor lithium ions insertion/extraction and accommodate the volume change. In agreement with this, macroporous Co₃O₄ platelets exhibited higher reversible capacity, better cyclability and larger rate capability than that of its nanoparticles or rod-like nanoclusters.⁵¹ The macroporous Co₃O₄ platelets maintained high capacities of 930 mAh/g over 30 cycles, while Co₃O₄ nanoparticles and rod-like nanoclusters quickly faded to 200 and 400 mAh/g, respectively.

Besides engineering their structure, size and morphologies, the electrochemical performances of cobalt oxides can also be improved by combining them with another phase to increase electrical conductivity etc. For example, the Co_3O_4 nanoparticles were attached on the highly electrical conductive and flexible rGO nanosheets by a solvothermal route.⁵⁵ The composites delivered a capacity as high as 935 mAh/g after 30 cycles at 50 mA/g and 500 mAh/g at 500 mA/g. When the Co_3O_4 nanospheres encapsulated in rGO, the composite showed higher reversible capacity of 1100 mAh/g during the first few cycles and retained the capacity as high as 1000 mA/g after 130 cycles at a current density of 74 mA/g.¹¹³ In such anode materials, rGO in the composite can significantly increase the electric conductivity and ensured the contact of host with electron collector.

1.5.4 Other transition metal oxides

Besides iron oxides, tin oxides and cobalt oxide, manganese oxides, chromium oxide, nickel oxide and copper oxide etc., have also been widely investigated as alternative anode materials for LIB due to their own unique chemical and physical properties.^{16,66,114-118} Among them, MnO_2 has the highest theoretical capacity (1233 mAh/g in theory). However, the conversion reaction is not that reversible for MnO_2 .¹¹⁹ Hence, great efforts have to be put forth for developing various approaches to improve it. For example, the capacity of MnO_2 nanoparticles was largely enhanced after wrapping the MnO_2 nanoparticles in carbon nanotubes, where the carbon nanotube shell constrained the volume change generated during the insertion/extraction of lithium.¹⁶ Low electrical conductivity ($\sim 10^{-7}$ - 10^{-8} S/cm) of Mn_3O_4 limited its capacity below the theoretical capacity (936 mAh/g). Consequently, Mn_3O_4 nanoparticles encapsulated in

highly conductive graphene was used to improve the Li ion storage performance. The composites delivered a stable specific capacity of 900 mAh/g at 40 mA/g and 390 mAh/g at 1600 mA/g, which was much better than the pure Mn_3O_4 nanoparticles.¹²⁰

NiO with a theoretic capacity of 718 mAh/g, usually shows poor cycling performance as compared to that of CoO, Fe_2O_3 and CuO. But NiO is less expensive than CoO. The cyclability of NiO can be improved by introducing Ni to increase the electrical conductivity of the composite. The NiO-Ni composite delivered a capacity as high as 750 mAh/g and retained good capacity retention.¹²¹ Moreover, nanostructured NiO obtained from direct thermal oxidation of Ni foams in air was reported and excellent electrochemical performance, especially at high C rates, was manifested. Reversible capacities of 700 mAh/g and 400 mAh/g were exhibited at a current density of 0.2C and 10C, respectively.¹¹⁵ Short diffusion path for lithium ions, 3D porous structure and good electrical contact of NiO with Ni skeleton are proposed to contribute to these excellent electrochemical performances.

Cu_2O and CuO have theoretical capacities of 375 mAh/g and 674 mAh/g, respectively. In addition, the cost and toxicity of such metal oxides are low. Therefore, CuO is a promising alternative anode material, while Cu_2O is not suitable for LIBs due to its low theoretical capacity. The electrochemical properties of CuO were greatly improved through well-controlled structure and morphology, e.g. urchin-like CuO showed much higher capacity and longer cyclability than that of its hollow cubes and spheres. Urchin-like CuO maintained high capacity of 560 mAh/g up to 50 cycles, while the capacities of hollow cubes and sphere CuO decreased to 79 and 91 mAh/g, respectively.⁶⁶ Moreover, Li

storage performance of CuO can be improved through hybridizing CuO with conductive CNT. The capacity of CuO/CNT composite was stabilized at about 500 mAh/g with good retention of capacity, while the capacity of pure CuO quickly faded to 296 mAh/g.¹¹⁷

There are also many other transition metal oxides reported as alternative anode materials. For example, Cr₂O₃ has a very high theoretical capacity of 1058 mAh/g, but it is more toxic. When used as anode material, molybdenum oxide (MoO₃) usually suffers from poor cycling stability. However, decreasing particle size of MoO₃ to nanoscale can enhance its electrochemical properties. Nanosized MoO₃ can deliver a high capacity of 630 mAh/g at 0.5 C and sustain a good capacity retention even after 150 cycles.¹²²

Electrode Materials	Theoretical Capacity(mA/g)	Advantages	Disadvantages	Reference
Iron oxides	Fe ₂ O ₃ /Fe ₃ O ₄ (1007/926)	high theoretical capacity, energy density, low cost and low toxicity	poor electrical conductivity, high volume change, low first Coulombic efficiency	1-4
Cobalt oxides	Co ₃ O ₄ /CoO (891/716)	high theoretical capacity, energy density,	Poor electrical conductivity, high volume change, high cost, low first Coulombic efficiency	5,6
Tin oxide	SnO ₂ (790)	high theoretical capacity, energy density, low toxicity	poor electrical conductivity, high volume change, poor stability, low first Coulombic efficiency	7,8
Manganese oxide	MnO ₂ (1233)	high theoretical capacity, energy density, low cost	poor electrical conductivity, low first Coulombic efficiency	9-11
Nickel oxide	NiO (718)	high theoretical capacity, energy density	poor electrical conductivity, high cost, low first Coulombic efficiency	12,13
Copper oxides	Cu ₂ O/CuO (375/ 674)	low cost	poor electrical conductivity, low theoretical capacity, low first Coulombic efficiency	9,10

Metal oxides are very promising as alternative anode materials due to their high reversible capacity, low cost and toxicity, and stable cyclability after either

engineering themselves structure or mixing with other materials, e.g. amorphous carbon, CNT and graphene. Therefore, developing efficient approaches to design metal oxide with controlled structure, composition, size and morphology plays important roles in scientific studies and industrial engineering.

1.6 Synthesis methods of electrode materials for LIB

The properties of nanomaterials are greatly dependent on their morphologies, size, composition and structure, which have driven us to develop new, facile and environmental friendly approaches to design such nanostructured materials. Variety of synthetic methods will be introduced in the next section and their merits and demerits will be discussed in detail as well.

1.6.1 Hydrothermal route

Hydrothermal route, which precipitates substances from high-temperature aqueous solutions at high vapor pressures, is a versatile and environmental friendly approach. To date, hydrothermal route is one of the most widely used approaches to synthesize various materials, e.g. metal, metal oxide, carbon, and so on.¹³⁵⁻¹³⁹ Nanomaterials have been designed with different structure, size, composition and phases by well-controlled nucleation and growth processes.^{52,140-142} An impressive example is the hydrothermal synthesis of single crystalline α -Fe₂O₃ nanotubes in the presence of sodium sulfate and sodium phosphate (Figure 1.6). The formation of α -Fe₂O₃ nanotubes is controlled by the synergistic interaction of sulfate and phosphate ions. Firstly, nucleation seeds of Fe₂O₃ nanocrystals were formed and surrounded within the sulfate and phosphate ions. Then, the growth direction is induced through preferential adsorption of the phosphate ions on the corresponding crystal

planes. Finally, excess of phosphate and sulfate ions lead the dissolution of the growing Fe_2O_3 spindles from the unprotected tips and hence result in the formation of nanotube.¹⁴³

Figure 1.6 Left: Reaction scheme illustrating the influence of the phosphate and sulfate concentration on the formation of hematite nanotubes. Right: SEM images of $\alpha\text{-Fe}_2\text{O}_3$ nanotubes synthesized with different phosphate concentrations: a) 0.1 mm, b) 0.36 mm, c) 0.5 mm, and d) 0.6 mm (the concentrations of Fe^{3+} and sulfate ions were kept constant at 20 mm and 0.55 mm, respectively)¹⁴³

In the hydrothermal process, seeds are often introduced to moderate the nucleation and growth of crystals with unique structure. Plenty of functional groups on graphene oxide can complex with various metal ions. This was widely proposed to act as heterogeneous nucleation seeds and to facilitate the growth of small crystal grains, e.g. $\text{Co}_3\text{O}_4/\text{rGO}$, $\text{Fe}_2\text{O}_3/\text{rGO}$.^{55,101,102,144,145} Sometimes, surfactant was introduced to driven the formation of metal oxide/rGO.¹¹³ The surface of Co_3O_4 nanospheres was modified by aminopropyl trimethoxysilane (APS), after which, graphene oxide sheets was grafted on its surface through mutual electrostatic interactions, followed by chemical reduction.

Nanomaterials with special structure and composition also can be designed via two-step process, e.g. core-shell structure and binary phase.^{15,52,58,147,148} An instructive example is the hydrothermal preparation of hollow metal oxides microspheres using polysaccharides (Figure 1.7).¹⁴⁶ Abundant hydrophilic groups, e.g. COOH, OH, on the surface of carbon spheres can complex with metal ions. A variety of hollow oxide spheres (Fe_2O_3 , NiO , Co_3O_4 , CeO_2 , MgO , and CuO) were yielded after pyrolysis of carbon sphere.

Figure 1.7 Hydrothermal formation of metal oxide hollow spheres from a polysaccharide-assisted approach.¹⁴⁶

A selective oxalic acid etching process was proposed by Lou, etc. to prepare porous Fe_2O_3 (Figure 1.8).¹⁴⁹ The direction of oxalic acid etching process is constrained to $[001]$ because of phosphate ions (H_2PO_4^-) preferred to adsorb on the (110) planes of $\alpha\text{-Fe}_2\text{O}_3$. So, the formation of $\alpha\text{-Fe}_2\text{O}_3$ nanosheets is ascribed to the synergistic interaction of $\text{H}_2\text{C}_2\text{O}_4^-$ and H_2PO_4^- .

In brief, nanomaterials with unique size, phase, composition and morphologies can be achieved through the facile hydrothermal route. The cost of this method is also low.

Figure 1.8 FESEM image (A) and TEM images (B, C) of the α -Fe₂O₃ nanocrystals before etching. FESEM image (D) and TEM image (E) of the α -Fe₂O₃ nanodiscs obtained after etching. (F) High resolution TEM image of the region marked by white square in (E). The insets in (C) and (E) are SAED patterns of the corresponding sample. (G) Schematic illustration of the etching process.¹⁴⁹

1.6.2 Solvothermal route

Solvothermal route, which involves high pressure and high temperature (e.g. beyond the critical point) reaction in organic solution, is another most commonly used approach to prepare nanomaterials.^{137-139,150,151} Solvothermal route has been extensively developed to synthesize nanocrystals with new structures, especially for monodispersed nanocrystals. Among organic solvents, fatty acids (oleic acid and linoleic acid), are preferentially used as reaction solvent and surfactant to facilitate the growth of nanocrystals. These organic molecules usually adsorbed on the surface of nanocrystals to prevent them from undergoing agglomeration.¹⁵¹

For example, TiO₂ nanocrystals with different shapes and dopings have been prepared in the mixture of triethylamine and cyclohexane. The nucleation and growth process were well controlled during the hydrolysis reaction of Ti(OBu)₄.¹⁵² Surfactants are important to control the shape of nanocrystals. Simply speaking, different morphologies of silver nanocrystals can be fabricated by tuning the ratio of silver precursor to poly-(vinylpyrrolidone) (PVP, the capping agent).^{153,154} In

this case, the surfactant molecules adsorbed on the special facets of the seeds during the nucleation process and then induced the growth of the nanocrystals to the designed shape. In addition, the composition and shape are also dependent on the type of precursors. CoO nanoparticles attached on rGO were prepared using $\text{Co}(\text{CH}_3\text{COO})_2$, while $\text{Co}(\text{OH})_2$ nanowall arrays on rGO was fabricated with $\text{Co}(\text{NO}_3)_2$.^{155,156}

In short, solvothermal route is an efficient method to prepare various metal oxide nanocrystal with small size. The structure and composition can also be tuned after introducing surfactants.¹³⁶

1. 6.3 Microwave route

Microwave route renders a reaction in a rapid heating manner, which is an efficient method to prepare nanocrystals. In the microwave process, the nanocrystals are mostly formed at the nucleation stage and the growth of nanocrystal is less involved. Consequently, the resulted nanocrystals exhibit small particle size and narrow size distributions, which is attributed to the uniform and rapid heating process. This approach offers an alternative method to prepare nanomaterials with high crystallinity in a very short reaction time.¹³⁸ A variety of nanomaterials including oxides, metals and bimetallic alloys with controlled size and morphologies were synthesized using this method.¹⁵⁷ For example, graphene oxide can be quickly reduced in different solvents in a short time. Small nanoparticles (e.g. Pd, Cu and PdCu) were simultaneously formed on the reduced graphene oxide nanosheets in a microwave process.^{158,159} Recently, microwave-assisted hydrothermal or solvothermal routes are greatly developed to fabricate nanocrystals.¹⁶⁰⁻¹⁶² Single crystalline tin dioxide nanoparticles with uniform particles size distribution were fabricated using

microwave technique within 10 min.¹⁶³ High surface area tin oxide nanopowders synthesized by microwave flash synthesis were reported by Jouhannaud etc.¹⁶⁴ Furthermore, synthesis of binary and ternary metal oxide nanoparticles such as Fe_3O_4 , CoO , MnO , ZnO , Mn_3O_4 , and BaTiO_3 using microwave method have also been reported.¹⁶⁵

1.6.4 Electrospinning

Electrospinning route is a useful method to prepare one-dimensional (1D) materials, which was used to construct nanowire or nanorods networks with large surface area.¹⁶⁶⁻¹⁷¹ Moreover, the diameter, composition and porosity of 1D materials can be precisely controlled via electrospinning method.¹⁷¹ For example, porous nanowires can be fabricated after pyrolysis of the polymer and precursors, where polymer is used as either binder or source of porosity.^{172,173} Furthermore, hollow and core-shell structured fibers, such as co-electrospun PCL shell-PEO core, can also be prepared via such facile method.¹⁷⁴ Besides polymers, carbon@ SnO_2 core-shell hybrid nanofibers can also be prepared by single-spinneret electrospinning followed heat treatment.¹⁷⁵ These 1D materials can further undergo functionalizations to broaden their applications.

1.6.5 Chemical vapor deposition (CVD)

Chemical vapor deposition has been used to grow nanostructured materials, such as Si, Ge, SnO_2 , NiO and their binary phased materials, via a vapor-liquid-solid (VLS) mechanism.^{25,26,115,176-180} In addition, CVD route also offers an option to fabricate core-shell structured nanomaterials, such as Ge @ C or Si @ C through growth of Ge or Si and then formation of carbon coating. Moreover, nanomaterials with designed structure, such as core-shell structure can also be

fabricated via CVD route combining with other techniques.⁷³ For example, MnO_2/CNT hybrid coaxial nanotube was synthesized through electrodeposition and CVD methods.¹⁶

Similarly, binary and ternary structured nanomaterials, such as Sn or Sn/Sb @ C nanorods were prepared via CVD method introducing one or two metal oxides precursors under C_2H_2 gas environment.¹⁷⁷ Heterostructured coaxial $\text{SnO}_2\text{-In}_2\text{O}_3$ nanowires with high conductivity were prepared by one-step, which greatly enhanced its lithium ion storage capability.⁶¹ Branched Si/TiSi₂ nanowires obtained from CVD method delivered the capacity as high as 1000 mAh/g at a current density of 8400 mA/g.²⁷ Furthermore, seed-assisted CVD method is more efficiently to grow 1D nanomaterials.^{25,26} Therefore, CVD is a useful route to generate 1D single phased nanocrystals and binary heterostructured nanomaterials, including core-shell, branched and tetrapod structure.

1.6.6 Electrochemical deposition

Electrochemical deposition is another useful route to prepare nanostructured materials, especially 1D nanomaterials. With the help of templates (e.g. AAO), nanorods or nanowires can be quickly deposited.¹⁸¹ In addition, the cost of instruments, reaction temperature and pressures of this method are lower than that of hydrothermal and solvothermal approaches. For example, ZnSb nanoparticles, nanoflowers and nanowires can be fabricated by controlling the deposition potential, solvent and concentration of precursors.¹⁸² Furthermore, dual phased nanomaterials with controlled structure can also be achieved by two steps, e.g. core-shell structured $\text{MnO}_2@\text{CNT}$ (Figure 1.9)¹⁶ or multisegmented nanorods Au-Pt. The MnO_2 nanorods were prepared by electrochemical deposition and then the carbon shell was introduced by chemical vapor

deposition (CVD) route. Finally, coaxial nanotubes were obtained after removal of the template.

Figure 1.9 Schematic diagram showing the fabrication of MnO₂/CNT hybrid coaxial nanotube arrays inside AAO template using a combination of simple vacuum infiltration and chemical vapor deposition techniques.¹⁶

Multisegmented rods, e.g. Pt-Au or Pt-Au-Pt, can be easily fabricated through changing reaction electrolytes and controlling its deposition potentials.^{152,165,183} Metals, semiconductors, conducting polymers and their compounds can be more efficiently synthesized through this route.

1.6.7 Other routes

There are also many other routes that can be used to prepare materials for lithium ion battery applications, such as ball milling,^{184,185} melt spinning,¹⁸⁶ and ionothermal route.¹²³

Throughout my PhD study, I mainly focused on the hydrothermal and solvothermal routes to synthesize reduced graphene oxide-based transition metal oxide hybrids for LIB applications. Here, polyol and ethanol, which have

low ionic strength, weak reducing capability, low toxicity and low cost, are employed as the main solvents in the chemical synthesis.

1.7 Summary

In order to improve properties of anode materials, various strategies have been developed to favorite the Li ions insertion/extraction and shorten their diffusion path, e.g. the insertion of 0.6 Li per nanometer-scale Fe_2O_3 hematite particles (20 nm) is larger than that of its bulk with larger hematite particles (2 μm , 0.05 Li).¹¹ On the other hand, improvement in electron transfer and reduce the mechanical strain upon volume expansion for metal oxide nanocrystals can be achieved through confining them in highly conductive carbonaceous matrix, such as amorphous carbon, CNT or graphene sheets.^{50,55,59,141} The volume strain of SnO_2 hollow spheres can be significantly constrained after introducing carbon coating.¹⁵ A stable capacity of about 630 mAh/g was produced at 0.8C during 80th cycle. Highly electrical conductivity and stable electrical contact of active materials with the current collectors can be achieved after attaching metal oxides on rGO sheets. Co_3O_4 /graphene composite was synthesized by pyrolysis of as-prepared $\text{Co}(\text{OH})_2$ /graphene composites. The Co_3O_4 /graphene composite electrodes delivered a high reversible capacity of 800 mAh/g, which is much larger than that of its bulk counterpart.⁵⁵ Besides downsizing and hybridizing strategies, binary or ternary metal oxides are also able to achieve good performance through introducing other phase. In regard to SnO_2 - In_2O_3 core-shell structure, the core material offers energy density while the shell provides electrical conductivity and mechanical constraint on structural changes during conversion reactions.⁷¹ In addition, heterostructured metal oxides are also proposed as alternative electrode materials.¹³

However, the lithiation/delithiation processes in transition metal oxides are mainly conversion reactions, involving the reduction of metal oxides to metal nanoparticles and the formation of non-conductive Li_2O . Nevertheless, large volume change is generated during the cycling process coupling with the reduction in electrical conductivity due to the agglomeration and structural collapse of the metal oxides. In some cases, the transportation of Li ions and electrons are constrained as the result of losing contact between the active metal oxides and the current collector. Thus, metal oxides normally suffer from low capacities and poor stabilities, especially at high current densities.

On the other hand, these methods for preparation of anode materials are relatively complicated and not easily adapted for large scale production. Sometimes, introducing amorphous carbon in metal oxides possibly leads to structural collapse and results in impurities during CVD or carbonization of polysaccharides or polymers processes.¹⁸⁷ Furthermore, the preparation of these rGO-based composites mainly contains two steps, which require the reduction of graphite oxide sheets by thermal annealing or adding toxic hydrazine^{59,141} and a subsequent thermal treatment of the nanoparticles to form the proper nanocrystals. Sometimes, surfactants or polymers have to be added to maintain good dispersion of GO in solution, which may decrease the electrical conductivity of the samples.¹⁸⁸ In the case of binary metal oxides,^{61,189} they often deliver multi-plateaus corresponding to both metal oxides during the discharge process, which is an obstacle to the application of LIB. As a result, either pure metal oxides or their derivatives could not maintain high capacities and good stabilities at high charge/discharge rates. Therefore, there is still space for improving the anode performances. Decreasing particle size, sustaining

structure integrity, enhancing electrical conductivity and keeping contact between active materials with current collector are proposed to improve the electrical performances of anode materials. In addition, feasible approaches are required to prepare available anode materials with improved electrochemical performance. Therefore, there is still space for improving the anode performances. Decreasing particle size, sustaining structure integrity, enhancing electrical conductivity and keeping contact between active materials with current collector are proposed to improve the electrical performances of anode materials. In addition, feasible approaches are required to prepare available anode materials with improved electrochemical performances.

In this thesis, highly electrical conductivity, high surface area and high flexibility of rGO combined with metal oxides have been prepared through various approaches and their performance-dependent-structure, size, composition and shape was studied.

Chapter 2: Objectives

Nowadays, rapid depletion of fossil fuels has raised global attention. In order to reduce our dependence on these non-renewable resources, exploration and utilization of alternative energy are important in tackling the energy crisis. In line with this, LIB has been invented for use in rechargeable energy storage application and energy conversion technologies. In the past decade, using LIB as the hybrid electric vehicle power generator was a technological breakthrough in the automotive industry. To build a lighter and smaller hybrid electric vehicle, high energy and power density become the major application requirements need to be met. However, the development and application of LIB are largely limited due to their low capacity, poor cyclability, slow charge/discharge rates, and high cost electrode materials. As a result, exploration and development of alternative electrode materials have attracted considerable interests in the fields of scientific research and engineering technology. Meanwhile, facile, environmental-friendly and low-cost synthetic approaches are also highly desirable for preparation of promising alternative electrode materials.

The capacities of available cathode materials are typically lower than 150 mAh/g. The total capacity of a full cell will increase rapidly when the capacities of anode materials increase from 300 mAh/g to around 1000 mAh/g. Afterwards, the total capacity reaches a plateau and maintains a relatively constant value even with further increased in anode specific capacity (Figure 7a). This indicates that commercially used graphite anode should be replaced with alternative materials having capacities between 500 mAh/g to 1000 mAh/g so as to improve the overall capacity. Under these considerations, Sb, Ge, Sn, metal oxides and

their derivatives are attractive to be used as the alternative anode materials, especially those metal oxides having high capacities (Figure 7b).

Figure 7a Total capacity of a Li-ion cell as a function of anode capacity (CA), including the masses of other required internal components and the case;¹⁹⁰ **Figure 7b** Theoretical capacities of different compounds obtained from literature.²⁹

For example, Sb, Sn, and Fe₂O₃, which possess high theoretical capacities, (660, 994, and 1007mAh/g, respectively) are explored for batteries application. The lithiation/delithiation processes in these anode materials are mainly alloying and conversion reactions. Normally, large volume change generated during the cycling process leads to poor cyclability due to structural collapse. Furthermore, Li ions and electrons transfer will be constrained by the loss contact of active materials with the current collector, which will result in low capacity. Thus, these materials significantly suffer from low capacities and poor stabilities, especially at high current densities.

However, many of the reported studies are mainly focus on the engineering process to improve the capacities and/or stabilities. Optimization of the individual rGO/MO hybrid system is required in order to achieve its ideal Li storage performances. This should involve adjusting their phases, grain sizes, composition, structure and even porosity of MO nanostructures in the rGO/MO

hybrids, which have not been well investigated. Therefore, the detailed study on the factors that could affect the electrochemical performance based on the understanding of the effects of all the parameters, rational design of the improvement on electrode materials is pursued. Furthermore, feasible approaches are required to prepare available anode materials with designable size, structure and composition.

In this thesis, we will investigate the effects of individual factors on the performance of LIB electrode using hybrid nanostructures:

- (1) Effects of the shape and size of the nanostructures
- (2) Effects of types of carbon layers
- (3) Effects of ratio between the metal oxides and carbon matrix
- (4) Effects of interaction between different phases in the nanostructures.
- (5) Effects of phase, porosity and annealing temperature.
- (6) Effects of interaction between various type of active anode materials and carbon matrix

Based on the understanding of the above effects, the strategy on preparation of advanced nanocomposite for electrode materials of Li ion battery will be then proposed.

Chapter 3: Experiments

3.1 Preparation of carbon based-SnO₂ hybrids with controlled carbon source and mass loading for LIB

The following describe the experimental procedures for the synthesis of SnO₂ with various carbon sources.

Synthesis of the graphite oxide: Graphite oxide was synthesized from natural graphite (SP-1) by a modified Hummer's method.¹⁹¹⁻¹⁹³ In brief, 1.5 g graphite powder was added into a mixture of 10 mL 98% H₂SO₄, 1.25 g K₂S₂O₈, and 1.25 g P₂O₅, and the solution was maintained at 80 °C for 4.5 h. The resulting pre-oxidized product was cleaned using water and dried in a vacuum oven at 50 °C. After it was mixed with 60 mL 98% H₂SO₄, 7.5 g KMnO₄ was slowly added at a temperature below 20 °C, and then followed by 125 mL H₂O. After 2 h, additional 200 mL H₂O and 10 mL 30% H₂O₂ were slowly added into the solution to completely react with the excess KMnO₄. After 10 minutes, a bright yellow solution was obtained. The resulting mixture was washed with diluted HCl aqueous (1/10 v/v) solution and H₂O. The graphite oxide was obtained after drying in a vacuum oven at 30 °C. In the following experiments, rGO nanosheets used for preparation of rGO-based hybrids were obtained through this process.

Synthesis of SnO₂/amorphous carbon (AC): 2 g of sucrose was dissolved in 24ml 0.04 M SnCl₂ solution, and then the solution was added into 46 ml 99.9% ethanol. Finally, the mixture was transferred and sealed in a Teflon-lined autoclave and maintained at 180 °C for 3 h. After it was cooled down to room temperature, the precipitation, e.g. SnO₂/C, was collected and washed with ethanol.

Synthesis of SnO₂/carbon nanotubes (CNT): 30 mg Multiwalled carbon nanotubes was dispersed in 46 ml 99.9% ethanol and then was mixed with 24ml 0.04 M SnCl₂ solution. Finally, the mixture was sealed into a Teflon-lined autoclave and maintained at 180 °C for 3 h. After it was cooled down to room temperature, the precipitation, e.g. SnO₂/CNT, was collected and washed with ethanol.

Synthesis of SnO₂/reduced graphene oxide (rGO): 50 mg graphite oxide was dispersed in 46 ml 99.9% ethanol to get graphene oxide by sonication and then was mixed with 24ml 0.04 M SnCl₂ solution. Finally, the mixture was sealed into a Teflon-lined autoclave and maintained at 180 °C for 3 h. After it was cooled down to room temperature, the precipitation, e.g. SnO₂/RGO, was collected and washed with ethanol.

Electrochemical Measurements: The electrochemical measurements were carried out using two-electrode Swagelok cells with pure lithium metal as both the counter electrode and the reference electrode at room temperature. The working electrode consisted of active material (e.g., SnO₂/AC), a conductive agent (carbon black, Super-P-Li), and a polymer binder [poly(vinylidene difluoride), PVDF, Aldrich] in a 80:10:10 weight ratio. The electrolyte used was 1.0 M LiPF₆ in a 50:50 weight ratio mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The charge/discharge tests were performed using a NEWARE battery tester at a current density 0.2 C (160 mA/g) within a voltage window of 0.01 V - 2.0 V.

3.2 Preparation of rGO based-Fe₂O₃ and SnO₂/Fe₂O₃ hybrids with controlled mass loading and composition for LIB

Synthesis of Fe₂O₃/rGO hybrids. In a typical procedure, 50 mg graphite oxide was dispersed in 70 mL 99.9% ethanol by sonication to get graphene oxide (GO). Then, 0.5 mmol FeCl₂ and 50 μ L 37% ammonia were added into the solution. The mixture was sealed into a Teflon-lined autoclave and maintained at 170 °C for 5 h. After it was cooled down to room temperature, the precipitation, e.g. Fe₂O₃/rGO, was collected and washed with ethanol.

Synthesis of SnO₂-Fe₂O₃/rGO hybrids. In a typical procedure, 50 mg graphite oxide was dispersed in 70 mL 99.9% ethanol by sonication to get graphene oxide (GO) sheets. Then, x mg SnCl₂ and y mg FeCl₂ were added into the solution (detailed x and y were listed in Table 1). The mixture was sealed in a Teflon-lined autoclave and maintained at 170 °C for 4 h. After it was cooled down to room temperature, the precipitation, e.g. SnO₂-Fe₂O₃/rGO, was collected and washed by ethanol. The weight ratio of precursors and resultant samples were calculated from TGA analysis and EDX results, and the results are presented in supporting information Table 1.

Electrochemical Measurements:

The metal oxides/rGO (MO/rGO) hybrids were dried at 150 °C for 30 min under Ar atmosphere. Then, 80 wt% active material (SnO₂/rGO or SnO₂-Fe₂O₃/rGO), 10 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed into N-methyl-2-pyrrolidinone (NMP). The obtained slurry was coated onto Cu foil using a doctor blade to achieve a uniform film, which were then dried in vacuum at 50 °C for 12 h to remove the solvent, and finally used as working electrodes. Electrochemical measurements

were carried out on CR2032 (3 V) coin-type cells with lithium metal as the counter/reference electrode, Celgard 2400 membrane as the separator, and electrolyte solution obtained by dissolving 1M LiPF₆ into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 50 : 50 w/w). The coin cells were assembled in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The charge/discharge tests were performed with a NEWARE battery tester at a voltage window of 0.001-3.0 V for SnO₂/rGO and SnO₂-Fe₂O₃/rGO samples. Cyclic voltammetry (0.001-3 V, 0.5 mV s⁻¹) was performed with an electrochemical workstation (CHI 660C).

3.4 Preparation of rGO based-Co₃O₄ nanowalls and CoO nanowalls/nanoparticles with controlled phase, grain size and porosity for LIB

Synthesis of cobalt precursor nanowalls: 30 mg graphite oxide was dispersed in 40 mL 99.9% ethanol by ultrasonication to obtain graphene oxide (GO). Then, 292 mg Co(NO₃)₂·6H₂O and 100 μ L 25% ammonia were added into the solution. The mixture was sealed in a 50 ml Teflon-lined autoclave and maintained at 170 °C for 5 hours. After it was cooled down to room temperature, the precipitate was collected and washed with ethanol.

Synthesis of Co₃O₄ or CoO/rGO nanowalls Co₃O₄/rGO nanowalls were obtained by thermal pyrolysis of the as-prepared cobalt precursor at selected temperatures (e.g. 250, 350, 450 °C) for 30 minutes at a heating rate 10 °C/min in air. The obtained Co₃O₄/rGO hybrids were correspondingly named as Co₃O₄/rGO-250, Co₃O₄/rGO-350 and Co₃O₄/rGO-450 according to the reaction temperatures of 250, 350 and 450 °C. CoO/rGO nanowalls were obtained at the same conditions except for the replacement of air for Ar gas. The CoO/rGO

hybrids were named as CoO/rGO-250, CoO/rGO-350 and CoO/rGO-450, respectively according to the reaction temperatures of 250, 350 and 450 °C.

Synthesis of CoO nanoparticles 50 mg graphite oxide was dispersed in 70 mL 99.9% ethanol by sonication to get graphene oxide (GO). Then, 2 mmol $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 100 μL 37% ammonia were added into the solution. The mixture was sealed into a Teflon-lined autoclave and maintained at 170 °C for 5 h. After it was cooled down to room temperature, the precipitation, e.g. CoO/rGO, was collected and washed by ethanol.

Electrochemical Measurements: 80 wt% active material ($\text{Co}_3\text{O}_4/\text{rGO}$ or CoO/rGO), 10 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed into N-methyl-2-pyrrolidinone (NMP). The obtained slurry was coated onto Cu foil disks to form the working electrodes, which were then dried in vacuum at 50 °C for 12 h to remove the solvent. Electrochemical measurements were carried out on the CR2032 (3 V) coin-type cells with lithium metal as the counter/reference electrode, Celgard 2400 membrane as the separator, and electrolyte solution obtained by dissolving 1 M LiPF_6 into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 50:50 wt/wt). The coin cells were assembled in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The charge/discharge tests were performed with a NEWARE battery tester at a voltage window of 0.01-3.0 V for both samples. Cyclic voltammetry (0.01-3 V, 0.5 mV/s) was performed with an electrochemical workstation (CHI 660C). Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 10 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 10 mV with the help of an impedance spectrum analyzer

(Solatron, SI 1255B Impedance/grain-phase analyzer and computer software ZView).

3.4 Preparation of rGO based-ferrocene nanoclusters with controlled shape for LIB

Synthesis of ferrocene nanocluster/rGO: In a typical procedure, 50 mg graphite oxide was dispersed in 70 mL 99.9% ethanol by sonication to get graphene oxide (GO) sheets. Then, 50 mg or 100 mg ferrocene was added into the solution under sonication. The mixture was sealed in a Teflon-lined autoclave and maintained at 170 °C for 4 h. After it was cooled down to room temperature, the precipitation, e.g. ferrocene/rGO, was collected and washed by ethanol. The weight ratio of ferrocene to rGO was calculated from TGA analysis results

The pure rGO was obtained under the same synthetic conditions without adding ferrocene.

Electrochemical Measurements: 80 wt% active material (rGO or ferrocene/rGO), 10 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) binder were mixed into N-methyl-2-pyrrolidinone (NMP). The obtained slurry was coated onto Cu foil using a doctor blade to achieve a uniform film, which were then dried in vacuum at 50 °C for 12 h to remove the solvent, and finally used as working electrodes. Electrochemical measurements were carried out on CR2032 (3 V) coin-type cells with lithium metal as the counter/reference electrode, Celgard 2400 membrane as the separator, and electrolyte solution obtained by dissolving 1M LiPF₆ into a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 50 : 50 w/w). The coin cells were assembled in an Ar-filled glovebox with concentrations of moisture

and oxygen below 1.0 ppm. The charge/discharge tests were performed with a NEWARE battery tester at a voltage window of 0.05-3.0 V for rGO and ferrocene/rGO samples. Cyclic voltammetry (0.05-3 V, 0.5 mV s⁻¹) was performed with an electrochemical workstation (CHI 660C). Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 10 kHz to 0.1 Hz at open circuit potential with an ac perturbation of 10 mV with the help of an impedance spectrum analyzer (Solatron, SI 1255B Impedance/grain-phase analyzer and computer software ZView).

3.6 Characterizations:

The morphology of the as-synthesized samples was investigated by using a field emission SEM (JEOL JSM-6340F).

For TEM observation, the suspension was dropped onto carbon coated copper grids and dried at room temperature. A TEM (JEOL JEM-2010) operating at 200 kV was used to characterize the nanostructures.

Crystal phases were identified using a Scintag PAD-V X-ray diffractometer with Cu K α irradiation.

Raman spectra were obtained with a WITec CRM200 confocal Raman microscopy system with a laser wavelength of 488 nm and a laser spot size of 0.5 mm. The Si peak at 520 cm⁻¹ was used as a reference for wave number calibration.

The IR spectra were measured with a Fourier transform infrared spectrometer (PerkinElmer) equipped with a DGTS detector and a ZnSe-window.

Thermogravimetry analysis (TGA, Q500) were carried out in the temperature range of 25 to 700 °C at a heating rate of 10 K/min in air.

X-ray Photoelectron Spectroscopy (XPS) of the resulting composites was performed with an X-ray photoelectron spectrometer (Kratos AXIS Ultra) using monochromatic Al K α (1486.71 eV) X-ray radiation (15 kV and 10 mA); 160 eV pass energy was used for survey scan, whereas 40 eV was used for the high-resolution scan.

Nitrogen adsorption/desorption isotherms were measured on a Micromeritics TriStar 3000 porosimeter (mesoporous characterization) and Micromeritics ASAP 2020 (microporous characterization) at 77 K. All samples were outgassed at 100 °C for 6 h under vacuum before measurements were recorded. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method.

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) spectra were performed on an Axima TOF2 mass spectrometry (Shimazu/Kratos, Singapore). Each mass spectrometer uses a nitrogen laser at 337 nm (Pulse 10 ns, 10 Hz) for desorption of analytes. The spectrum was recorded by adding 100 laser shots using a laser energy of 56.80 μ J. The accelerating voltage is 20 kV, and the operating pressure is 10⁻⁶ mbar.

Chapter 4: Results & Discussion

4.1 Preparation of carbon based-SnO₂ hybrids with controlled carbon source and mass loading for LIB

1. Introduction

Lithium ion battery, as an effective electrochemical energy storage device, has attracted much interest recently. Great efforts have been devoted to develop different types of materials with high reversible capacity, long cycle life, and low cost.^{10,22,26,53,55,59,67} Transition metal oxides (MOs) have been widely investigated as promising anode materials for high energy density lithium-ion batteries. These MO (M = Fe, Co, Ni, or Cu) electrodes have shown higher theoretical Li-ion storage capacities (>600 mA h/g) than that of conventional graphite anodes (372 mA h/g).⁶³⁻⁶⁶ Moreover, due to their low cost, low toxicity and widespread availability, the MO electrodes have attracted increasing attention. However, these materials suffer from poor capacity retention due to the pulverization process.⁶⁷⁻⁷⁰ Although improvements have been reported on the cyclability and specific capacity through nanostructuring the transition MOs,⁷¹ preservation of high capacities after numerous charge-discharge cycles remains an important challenge due to the aggregation of the nanostructures and the collapse of their crystal structures during the insertion and extraction of Li ions.^{67,74-77} Hybridizing the MO nanoparticles (NPs) with conducting matrixes, e.g. amorphous carbon shell, carbon nanotubes or graphene sheets, to form complex structures has been reported to be an effective route to overcome these problems.^{16,17,55,72,73} Amorphous carbon can be formed from CVD method or carbonization of glucose or polymers to prevent MO nanoparticles from agglomeration.^{114,230,231} However, during high temperature annealing process, the metal oxides could be reduced

to metal and structural collapse occurred.¹⁸⁷ In addition, although its cost is low, the electrical conductivity of amorphous carbon is much lower than CNT and graphene.

Owing to the high electrical conductivity, high surface-to-volume ratio and ultra-thin thickness, graphene sheets have attracted great interests for hybridizing with different nanocrystals to produce nanohybrids that showed excellent cyclability and high specific capacity. For example, Co_3O_4 anchored on graphene sheets exhibits a high reversible capacity of 800 mA h/g at a discharge current density of 50 mA/g,⁵⁵ Fe_3O_4 -graphene composite shows a reversible specific capacity approaching 1026 mA h/g after 30 cycles at a discharge current density of 35 mA/g,²³² and a steady specific capacity of 625 mA h/g for SnO_2 -graphene nanocomposite is obtained at a current density of 10 mA/g after over 100 cycles.⁵⁰ However, many of the reported studies are mainly focus on the engineering process to improve the capacities and/or stabilities. Therefore, the detailed study on the factors that could affect the electrochemical performance is pursued to understand the effects of all the parameters. Furthermore, rational design of the advanced electrode materials requires fundamental understanding of individual parameter.

Based on previous studies, the lithium ion storage performance of metal oxides can be improved through combining them with different carbonaceous carbon, such as amorphous carbon (AC), carbon nanotubes (CNT) and reduced graphene oxide (rGO). However, the detailed study on the effects of carbon layers and mass loading of active metal oxides on carbon layer was not achieved. In this section, SnO_2 with high theoretical capacity and low cost was selected as active anode materials to study its electrochemical performances. To

identify the ideal carbon supports for active metal oxides, SnO₂ NPs with different carbonaceous materials, e.g. amorphous carbon, carbon nanotubes (CNT) and reduced graphene oxide (rGO) were prepared to investigate the effect of carbon layer on their electrochemical performance. Finally, the effect of mass loading of SnO₂ in SnO₂/rGO composites on its electrochemical performance was also studied here.

2. Results and Discussion

As known, carbon coating inducing into the host nanomaterials can largely enhance its capacity and stability, which is mainly attributed to accommodation of volume change during the insertion/extraction of Li⁺. Otherwise, the carbon coating is not only used as a buffer layer, but also favors both ions and electrons transport from the host to current collector.^{15,16,49,54,58,92} However, the electrical conductivity is very low even after high temperature annealing process, which is often accompanied by collapse of structure and impurities induced during the process.¹⁸⁷ Base on these obstacles, we synthesize SnO₂ decorated on different carbonaceous materials and study the synergistic effects between SnO₂ and carbon source to get the optimize system for lithium ions batteries.

Figure 4.1 TEM images: (a-b) SnO₂/AC; (c-d) SnO₂/CNT; (e-f) Sn₂O/RGO

From Figure 4.1, it is observed that the SnO₂ nanoparticles (NPs) were well embedded in amorphous carbon (AC) matrix, attached onto carbon nanotubes (CNT) or reduced graphene oxide (RGO) nanosheets. The nanoparticles size is around 5-8 nm, which can be observed from the high resolution TEM images (Figure 4.1 (b), (d) & (f)).

The phase of the composite was further confirmed through XRD measurements, which indicate the formation of tetragonal SnO₂ phase (JCPDS 77-0452) and without any impurity detected, where the broad hump observed at 20-30 degree is contributed to carbon (Figure 4.2). The crystal size of SnO₂ was estimated to be 3-4 nm from the width of peaks in the XRD patterns using Scherrer's equation, which was consistent with the HRTEM observations (see Figure 4.1).

Figure 4.2 XRD patterns of SnO₂/AC, SnO₂/CNT and SnO₂/rGO

The Raman spectroscopy reveals the formation of amorphous carbon and the increase in the intensity ratio between the D band (located at 1350 cm⁻¹) and G band (located at 1580 cm⁻¹) in SnO₂/rGO demonstrates the reduction of graphene oxide through the hydrothermal process and agreed well with previous reports.²³³ Upon hydrothermal reaction, the sucrose was transferred into amorphous carbon, while graphene oxide nanosheets were reduced (Figure 4.3).

Figure 4.3 Raman shift spectrum of SnO₂/AC, SnO₂/CNT and SnO₂/rGO

To study the Li-ion storage performance of these SnO₂ and carbon composite nanostructures, a series of electrochemical measurements were carried out based on the half-cell configuration.^{48,234} The cyclic voltammetry (CV) curves of these samples (see Figure 4.4) were obtained at a scanning rate of 0.5 mV/s over the voltage range of 0.001-3.0 V. Three of the composites exhibit the similar CV profiles. For example, in the case of SnO₂/rGO, the first cathodic scans of the SnO₂/rGO composite nanostructures showed an obvious reduction peaks, which was consistent with previous reports.^{15,101} The peak at 0.76 V was attributed to the reduction of SnO₂ to Sn and Li₂O.⁹⁵ The reduction peak in the range of 0 to 0.7 V was mainly associated with the insertion of Li into metallic Sn and carbon materials^{15,101} corresponding to the following reactions: (1) $\text{Sn} + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{Sn}$ ($0 \leq x \leq 4.4$) and (2) $x\text{Li}^+ + \text{C (graphene)} + xe^- \leftrightarrow \text{Li}_x\text{C}$.

Figure 4.4 Representative CVs of the SnO₂/C at a scan rate of 0.5 mV/s for the first three cycles and their cycling performance within a voltage window of 0.01-2.0 V and a current density of 160 mA/g (0.2 C). CV of SnO₂/AC was carried out at a scan rate of 0.5 mV/s with a voltage window of 0.01-3.0 V for the first three cycles to check redox-reactions.

The charge-discharge cycling performance of SnO₂/C samples was also investigated at a current density of 160 mA/g (0.2C). It was found that SnO₂/RGO shows the best electrochemical performance, which is larger than that of SnO₂/C and SnO₂/CNT. SnO₂/RGO depicts a capacity as high as 390 mAh/g after 50 cycles, while SnO₂/AC can only give a capacity of 120 mAh/g. Here, the improvement of SnO₂/RGO is attributed to the high electrical conductivity, which also can effectively separate the nanoparticles from agglomeration during the insertion/extraction Li⁺.

Figure 4.5 Nyquist plots of SnO_2/C composites electrodes obtained by applying a sine wave with amplitude of 10.0 mV over the frequency range 10 kHz–0.1 Hz. In the case of a series connection of the resistance and capacitance, the impedance is given by: $Z(j\omega) = R + 1/j\omega C = R - j/\omega C$. The result may be represented graphically using two types of plots: complex plane (also known as Argand or Nyquist plots) and Bode plots. The complex plane plot is a plot of Z'' versus Z' , that is, the imaginary versus the real components, plotted for various frequencies.

Electrochemical impedance spectroscopy was used to understand the relevance of carbon source and capacity of the synthesized SnO_2/AC , SnO_2/CNT and SnO_2/RGO with the electrochemical performance in terms of the total internal electrochemical impedances of a cell. The characteristic impedance curves (Nyquist plots) for the SnO_2/C samples are shown in Figure 4.5. The SnO_2/RGO composites show the lowest diameter of semicircle, while the SnO_2/AC composites display the largest diameter. Here, the main reason for this is attributed to the highest electrical conductivity of RGO and the AC shows the lowest conductivity in short. In impedance spectroscopy, high frequency activity is attributed to charge transfer phenomenon whereas low frequency region of the spectrum is ascribed to the mass transfer process.^{235,236} The Nyquist plots for

the samples of SnO_2/CNT and SnO_2/RGO were similar except for the diameters of the semicircles, while SnO_2/AC shows two semicircles. This means that the diameter of the semicircle is strongly dependent on the synthesis temperature, surface area and grain/grain interfaces, which may have a direct impact on the Li storage performance.²³⁷⁻²⁴²

Figure 4.6 (a-b) Low magnification and (c) SAED pattern of SnO_2 NPs; (d) high magnification TEM images of the SnO_2/rGO hybrid.

Here, it is worthwhile to point out that the mass loading of the metal oxide NPs on rGO sheets may affect their energy storage performance as indicated in previous report.²⁴³ Reacting SnCl_2 with GOs in the solvothermal process led to the formation of composite nanostructures with NPs decorated onto thin GO sheets as revealed by TEM observations (see Figure 4.6). Fine particles with the size of 2-4 nm were uniformly attached onto the surface of the GO nanosheets (see Figure 4.6a-b) which was induced by the heterogeneous nucleation process

of NPs on the graphene oxide sheets. The SAED and HRTEM results revealed the formation of tetragonal SnO_2 phase (JCPDS 77-0452).

Figure 4.7 Raman spectra of graphene oxide and SnO_2/rGO

The reduction of the GOs to reduced graphene oxide (rGO) was confirmed by Raman spectroscopy (see Figure 4.7). The Raman spectroscopy results showed an increase in the intensity ratio ($I_{\text{D:G}}$) between the D band (located at 1350 cm^{-1}) and G band (located at 1580 cm^{-1}), e.g. $I_{\text{D:G}} = 0.90$ for GO sheets increased to $I_{\text{D:G}} = 1.33$ for SnO_2/rGO sample. This confirmed the reduction of GOs through the solvothermal process, which agreed well with previous reports.¹⁵⁵ The ring patterns (see Figure 4.6c) obtained in the selected area electron diffraction (SAED) measurements revealed that the NPs on the rGO sheets were tetragonal SnO_2 (JCPDF77-0452), which was consistent with the HRTEM observation (see Figure 4.6d) and XRD result (see Figure 4.8).

Figure 4.8 XRD patterns of samples prepared from SnCl₂ and GOs with $I_{\text{SnCl}_2:\text{GO}}=3.64:1$ and Thermogravimetry analyses (TGA) of SnO₂ /rGO hybrids with different ratios measured from 25 to 700 °C at a heating rate of 10 °C/min in air; weight percentage was calculated between 300 °C and 700 °C and weight loss before 300 °C was attributed to the loss of water

The mass loading of the SnO₂ on the rGO sheets (defined as the weight ratio of SnO₂ and rGO, $I_{\text{SnO}_2:\text{rGO}}$) could be tailored by changing the weight ratio between SnCl₂ and GOs in the solvothermal process as indicated by the TGA results (see Figure 4.8). For example, $I_{\text{SnO}_2:\text{rGO}}$ could be tuned from 0.39 : 1 to 1.78 : 1 by changing the weight ratio of SnCl₂ : GOs from 1.10 : 1 to 7.28 : 1 as revealed by the TGA measurements. Increasing the mass loading of the SnO₂ on rGO sheets led to the partial agglomeration of the NPs (see Figure 4.9d-f). Here, it is worthwhile to point out that the mass loading of the metal oxide NPs on rGO sheets may affect their energy storage performance as indicated in previous report.²⁴³

Figure 4.9 TEM images of SnO₂/rGO (a-b) $I_{\text{SnO}_2:\text{rGO}} = 0.39 : 1$ and (c-d) $I_{\text{SnO}_2:\text{rGO}} = 1.78 : 1$ obtained using the same synthesis conditions as $I_{\text{SnO}_2:\text{rGO}} = 0.96 : 1$

To study the Li-ion storage performance of these SnO₂/rGO composite nanostructures, a series of electrochemical measurements were carried out based on the half-cell configuration.^{155,234} Cyclic voltammetry (CV) curves of these samples (see Figure 4.10) were obtained at a scanning rate of 0.5 mV/s over the voltage range of 0.001-3.0 V. The first cathodic scans of the SnO₂/rGO composite nanostructures with $I_{\text{SnO}_2:\text{rGO}} = 0.96 : 1$ showed four reduction peaks (see Figure 4.10a), which was consistent with previous reports^{15,101}. The peaks at around 2.27 V and 1.39 V were ascribed to the formation of the solid electrolyte interface (SEI) while of the peak at 0.76 V was attributed to the reduction of SnO₂ to Sn and Li₂O.⁹⁵ The reduction peak in the range of 0 to 0.7 V was mainly associated with the insertion of Li into metallic Sn and carbon materials^{15,101} corresponding to the following reactions: (1) $\text{Sn} + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{Sn}$ ($0 \leq x \leq 4.4$) and (2) $x\text{Li}^+ + \text{C (graphene)} + x\text{e}^- \leftrightarrow \text{Li}_x\text{C}$. The broad reduction peak at around 0.17 V was ascribed to the formation of Li_xSn .^{98,244}

Figure 4.10 Typical cyclic voltammetry (CV) curve of SnO₂/rGO with $I_{\text{SnO}_2:\text{rGO}} = 0.96:1$ at a scanning rate of 0.5 mV/s in the voltage range of 0.001 - 3.0 V and Cycling performance of the SnO₂/rGO electrode at current density of 0.5 C (395 mA h/g) within a voltage window of 0.001 - 3.0 V.

The charge-discharge cycling performances of the SnO₂/rGO composite nanostructures were investigated at a current density of 395 mA/g (0.5 C) within a voltage range of 0.001 to 3.0 V (see Figure 4.11). For SnO₂/rGO composite nanostructures with different $I_{\text{SnO}_2:\text{rGO}}$ values, the cycling performance varied (see Figure 4.11). For example, SnO₂/rGO composite nanostructures with $I_{\text{SnO}_2:\text{rGO}} = 0.96:1$ showed a discharge capacity of 816 mAh/g at 0.5 C during the 12th. The capacities of the sample with $I_{\text{SnO}_2:\text{rGO}} = 0.96:1$ at 0.5 C decreased gradually and reached 420 mAh/g during the 100th cycle. Samples with a lower $I_{\text{SnO}_2:\text{rGO}}$ value, e.g. 0.39 : 1, showed a lower discharge capacity of 445 mAh/g at 0.5 C during the 12th cycle, which remained relatively stable at 270 mAh/g during the 100th cycle. For SnO₂/rGO samples with a higher $I_{\text{SnO}_2:\text{rGO}}$ value (e.g. 1.78 : 1), the specific capacity at 0.5 C was 833 mAh/g during the 12th cycle, which dropped rapidly and reached 274 mAh/g during the 100th cycle. The relatively stable cycling performance for samples with lower $I_{\text{SnO}_2:\text{rGO}}$ values (e.g 0.39 : 1 or 0.96 : 1) was mainly attributed to less agglomeration of the SnO₂ NPs during

the charge-discharge cycling process, which maintained the large surface area of the SnO₂ NPs to facilitate the effective Li ion diffusion. However, the low mass loading of SnO₂ in the samples with $I_{\text{SnO}_2:\text{rGO}} = 0.39 : 1$ led to low effective specific capacities^{58,97} because the theoretical capacity of SnO₂ is much higher than that of rGO sheets. On the other hand, high mass loading of SnO₂ in samples with $I_{\text{SnO}_2:\text{rGO}} = 1.78 : 1$ could result in a high effective specific capacity. However, the high density of SnO₂ NPs on rGO sheets tends to agglomerate during charge-discharge cycling process and led to the rapid drop in the reversible capacities. Samples with proper $I_{\text{SnO}_2:\text{rGO}}$ ratio (e.g. 0.96 : 1) showed better Li storage performance than the other two samples with either higher or lower $I_{\text{SnO}_2:\text{rGO}}$ values.

In this section, the effects of carbon layer and mass loading of active materials on their electrochemical performance have been studied. Based on results, it can be concluded that the SnO₂/rGO composites show the best improvement in electrochemical performances among the composites investigated. Here, the rGO sheets with high surface area and electrical conductivity in the SnO₂/rGO composite nanostructures serve the following purpose. Firstly, it acts as a conductive scaffolds¹⁰ to maintain the reliable electrical contacts between SnO₂ with the current collectors. Secondly, rGO can also prevent SnO₂ NPs from agglomeration. Finally, the weight ratio of SnO₂ and rGO ($I_{\text{SnO}_2:\text{rGO}}$ ratio, e.g. 0.96 : 1) was found to be the optimum. However, the stability and capacity are not good enough and further improvement is still desired.

4.2 Preparation of rGO based-Fe₂O₃ and SnO₂/Fe₂O₃ hybrids with controlled mass loading and composition for LIB

1. Introduction

The effects of carbon layers and mass loading active SnO₂ on their electrochemical performance were studied in section 4.1. The results revealed that rGO-based composite with 50% SnO₂ manifested the best performances. However, during the charge/discharge process, there are two typical electrochemical processes taking place in SnO₂: (1) $\text{SnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Sn} + 2\text{Li}_2\text{O}$; (2) $\text{Sn} + x\text{Li}^+ + x\text{e}^- \leftrightarrow \text{Li}_x\text{Sn}$ ($0 \leq x \leq 4.4$).^{71,94} The stability and capacity is not good enough, which is possibly due to a large volume swing (about 358%) occurs during the Li intercalation process in SnO₂.⁹⁵ This led to the pulverization of Sn particles and the rapid capacity decay because of the loss of electrical contact with the current collector.^{94,96-98}

To solve this issue, advanced preparation processes of SnO₂ have been developed with controlled size, morphology and composition.^{14,22,56,245} There are also efforts to mix SnO₂ with other metal oxides, e.g. In₂O₃, to induce synergistic effects.^{61,62} However, high reversible capacities, in particular at high C rates, are still not achieved in these SnO₂ based anodes. To achieve high reversible capacities at large current densities, the electrode material is generally required to (1) remain as nanostructures to facilitate the fast Li diffusion process, (2) introduce inhibitor to prevent significant agglomeration and (3) maintain electrical contact with the current collectors. Based on this concept, further studies on improvement in rGO/SnO₂ coupling with rational design are required. Herein, amorphous Fe₂O₃ NPs were introduced into SnO₂/rGO to prepare ternary phased SnO₂-Fe₂O₃/rGO composite structures. The effects of phase, synergetic

interactions between different phases, and ratio of different phases on their Li storage performances were studied.

2. Results and Discussion

Figure 4.11 (a-b) Low magnification and (c) high magnification TEM images of the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ hybrid; (h) high magnification TEM image of the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ hybrid; (d) SAED pattern of $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ NPs

Reacting SnCl_2 , FeCl_2 with GOs in the solvothermal process led to the formation of composite nanostructures with NPs decorated onto thin GO sheets as revealed by TEM observations (see Figure 4.11). It was observed that nanoparticles with size of 2-4 nm were uniformly attached onto the surface of rGO sheets (Figure 4.11b and d). The well-crystallized SnO_2 lattice could be identified in the HRTEM image (see Figure 4.11). However, the ring pattern obtained in the selected area electron diffraction (SAED) measurements (see Figure 4.11c) corresponded only to that of the tetragonal SnO_2 (JCPDF77-0452) without detectable Fe containing phases.

Figure 4.12 XRD patterns of samples prepared from SnCl_2 , FeCl_2 and GOs. There is no detectable Fe containing phase except for SnO_2 .

This was also confirmed by the XRD measurements (see Figure 4.12). The XRD patterns of Fe containing SnO_2/rGO samples showed only peaks corresponding to the tetragonal SnO_2 phase. The crystal size of SnO_2 was estimated to be 2-3 nm from the width of peaks in the XRD patterns using Scherrer's equation, which was consistent with the HRTEM observations (see Figure 4.11d).

The Raman spectroscopy results showed an increase in the intensity ratio ($I_{\text{D}:\text{G}}$) between the D band (located at 1350 cm^{-1}) and G band (located at 1580 cm^{-1}), e.g. $I_{\text{D}:\text{G}} = 0.90$ for GO sheets increased to $I_{\text{D}:\text{G}} = 1.17$ for $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ sample (see Figure 4.12). This confirmed the reduction of GOs through the solvothermal process, which agreed well with previous reports.¹⁵⁵

Figure 4.12 Raman spectra of GO sheets (black curve), samples prepared with a precursor weight ratio of $\text{SnCl}_2 : \text{FeCl}_2 : \text{GO} = 3.64 : 2 : 1$ (blue curve). The intensity ratio between D band and G band, $I_{D:G}$ are 0.98 and 1.02 for GO sheets (black curve) and sample prepared with $\text{SnCl}_2 : \text{FeCl}_2 : \text{GO}$ (blue curve), respectively.

Figure 4.13 Elemental mapping images of composite nanostructures prepared from SnCl_2 , FeCl_2 and GOs with $I_{\text{SnCl}_2:\text{FeCl}_2:\text{GO}} = 3.64 : 2 : 1$. It indicated the homogeneous distribution of Sn and Fe in the composite nanostructure.

The EDX elemental mapping results of Sn and Fe (see Figure 4.13) indicated the homogeneous distribution of Fe and Sn elements on the rGO sheets.

In order to obtain insights into the Fe compound formation, we acquired core-level XPS spectra (see Figure 4.14) from samples prepared with a precursor weight ratio of $\text{SnCl}_2 : \text{FeCl}_2 : \text{GOs} = 3.64 : 2 : 1$.

Figure 4.14 XPS spectra for $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ sample with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11 : 1 : 13$ showing core-level (a) C 1s, (b) Sn 3d, (c) Sn 3p and Fe 2p, (d) Fe 3p. The spectra have been normalized to equal height. The rough lines (black in each figure) stand for the raw data, and the smooth lines are the result of a curve fitting into various components.

The C 1s sub-band (Figure 4.14a) showed a strong peak of sp^2 carbon and a weak peak of carbonyl groups, which corresponded well with those reported for rGO sheets.^{158,247} The formation of SnO_2 was revealed by Sn $3\text{d}_{3/2}$ and $3\text{d}_{5/2}$ bands at 494.0 and 485.5 eV, which agreed with the SAED and XRD results. Both the Fe 2p bands (e.g. the Fe $2\text{p}_{3/2}$ at 711 eV and Fe $2\text{p}_{1/2}$ at 724 eV see Figure 4.14c) and Fe 3p band at 56.06 eV (see Figure 4.14d) indicated the formation of Fe_2O_3 .^{31,32,248}

Figure 4.15 EDX images of samples annealed at 150 °C for 30 min under Ar atmosphere. The samples are prepared from SnCl_2 , FeCl_2 and GOs with (a) $I_{\text{SnCl}_2:\text{FeCl}_2:\text{GO}} = 3.64 : 2 : 1$, (b) $I_{\text{SnCl}_2:\text{FeCl}_2:\text{GO}} = 1.82 : 2 : 1$ and (c) $I_{\text{SnCl}_2:\text{FeCl}_2:\text{GO}} = 0.78 : 2 : 1$.

Here, it was noted that there was no detectable chlorine element in the EDX spectra of the annealed Fe containing SnO_2/rGO samples (see Figure 4.15), which excluded the possible formation of FeCl_3 on the rGO sheets.

Based on the above results, it was concluded that amorphous Fe_2O_3 nanoparticles were formed in the samples prepared from SnCl_2 , FeCl_2 and GOs. The morphologies of the resultant sample had no obvious change (see Figure 4.16) as compared to that of SnO_2/rGO samples.

Figure 4.16 (a) TEM and (b) HRTEM images of $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ samples with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 2.82 : 1 : 5.27$; (c) TEM and (d) HRTEM images of $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ samples with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 1.32 : 1 : 1.68$.

The weight ratio of SnO_2 , Fe_2O_3 and rGO, $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}}$, in the final samples were characterized by TGA and EDX (see Figure 4.15 and 4.17 summarized in Table I), which closely related to the weight ratios of the precursors. For example, samples with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11 : 1 : 13$ were obtained with precursor weight ratio of $\text{SnCl}_2 : \text{FeCl}_2 : \text{GOs} = 3.64 : 2 : 1$. Changing the precursor weight ratio to $\text{SnCl}_2 : \text{FeCl}_2 : \text{GOs} = 0.78 : 4 : 1$ led to the formation of samples with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 1.32 : 1 : 1.68$.

Figure 4.17 Thermogravimetry analyses (TGA) of $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ composite nanostructures prepared with different precursor weight ratios. The calculated weight ratio of SnO_2 , Fe_2O_3 and rGO ($I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}}$) are indicated in the plot, which is also summarized in Table I. The measurements were carried out at a heating rate of 10 K/min in air. The weight loss before 100 °C was attributed to the loss of water.

Table I: The weight ratios of the resultant samples calculated from TGA analysis and EDX results.

Weight ratios	Precursors		
	x mg SnCl ₂	y mg FeCl ₂	GO
$I_{\text{SnO}_2:\text{rGO}} = 0.39 : 1$	55 mg	0	50 mg
$I_{\text{SnO}_2:\text{rGO}} = 0.96 : 1$	182 mg	0	50 mg
$I_{\text{SnO}_2:\text{rGO}} = 1.78 : 1$	364 mg	0	50 mg
$I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11 : 1 : 13$	182 mg	100 mg	50 mg
$I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 2.82 : 1 : 5.27$	91 mg	200 mg	50 mg
$I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 1.32 : 1 : 1.68$	39 mg	200 mg	50 mg

To study the Li-ion storage performance of these SnO₂-Fe₂O₃/rGO composite nanostructures, a series of electrochemical measurements were carried out based on the half cell configuration.^{155,234}

Figure 4.18 Cyclic voltammetry (CV) curves of SnO₂-Fe₂O₃/rGO samples at a scanning rate of 0.5 mV/s in the voltage range of 0.001 - 3.0 V.

The cyclic voltammetry (CV) curves of these samples (see Figure 4.18) were obtained at a scanning rate of 0.5 mV/s over the voltage range of 0.001-3.0 V. The first cathodic scans of the SnO₂-Fe₂O₃/rGO composite nanostructures with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11:1:13$ showed five reduction peaks (see Figure 4.18a), which was consistent with previous reports.^{15,101} The peaks at around 2.27 V and 1.39 V were ascribed to the formation of the solid electrolyte interface (SEI) while of the peak at 0.76 V was attributed to the reduction of SnO₂ to Sn and Li₂O.⁹⁵ The broad reduction peak at around 0.17 V was ascribed to the formation of Li_xSn.^{98,244} The peaks at 1.67, 1.27 and 0.84V were attributed to the insertion of Li⁺ into Fe₂O₃.⁶⁷

The charge-discharge cycling performance of SnO₂-Fe₂O₃/rGO samples was investigated. It was found that incorporating only small amounts of amorphous Fe₂O₃ NPs into the composite nanostructures led to much improved Li storage performance. For example, SnO₂-Fe₂O₃/rGO samples with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{GO}} = 11 : 1 : 13$ showed a high reversible capacity of 976 mAh/g (Figure 4.19a) during the second cycle at 0.5 C (395 mA/g), which also showed excellent cycling stability and maintained at 958 mAh/g during the 100th cycle. Such performance was much better than our measured data for SnO₂/rGO electrodes as well as those reported for SnO₂ based electrodes^{20,95,98,244} at relatively high current densities, e.g. 395 mA/g (0.5 C). It is also worthwhile to point out that such Li ion storage properties were also better than those reported for Fe₂O₃ based Li ion battery anodes.^{49,64,67,81,89}

Figure 4.19 (a) Cycling performance of the SnO₂-Fe₂O₃/rGO electrode at current density of 0.5 C (395 mA h/g) within a voltage window of 0.001 - 3.0 V; (b) Cycling performance of the SnO₂-Fe₂O₃/rGO with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11 : 1 : 13$ at various C rates. Here, 1C is equal to 790 mA h/g. (c-d) Charge-Discharge voltage profiles of the SnO₂-Fe₂O₃/rGO with different $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}}$ for the first three cycles at a current density of 0.5 C (395 mA h/g)

When increasing the amount of amorphous Fe₂O₃ in the sample, we found that the reversible capacities of the SnO₂-Fe₂O₃/rGO electrodes decreased. For example, samples with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 2.82 : 1 : 5.27$ and $1.32 : 1 : 1.68$ depicted specific capacities of 825 mAh/g and 797 mAh/g, respectively, during the second charge-discharge cycle at 0.5 C (395 mA/g). Here, the decreased specific capacities measured in these samples with higher weight percentage of

amorphous Fe_2O_3 were mainly due to the low specific capacities of amorphous Fe_2O_3 . Although specific capacities decreased, the samples with increased amount of Fe_2O_3 still showed excellent cyclability upon charge-discharge process, e.g. samples with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 2.82 : 1 : 5.27$ and $1.32 : 1 : 1.68$ depicted specific capacities of 801 and 758 mAh/g at 0.5 C during the 100th cycle, respectively. These performances were still much better than those measured for SnO_2/rGO samples with different $I_{\text{SnO}_2:\text{rGO}}$ values. Figure 4.19b showed the charge-discharge voltage profiles of the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrodes with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11 : 1 : 13$ for the first three cycles at a current rate of 0.5 C, which was similar to that of other $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrodes with different $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}}$ values, e.g. $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 2.82 : 1 : 5.27$ and $1.32 : 1 : 1.68$. The potential plateaus observed in the discharge curves were consistent with the CV results. The insertion process gave a first discharge capacity of 1509 mAh/g and a subsequent charge capacity of 941 mAh/g, showing a Coulombic efficiency of 62.4%. During the second cycle, the discharge capacity decreased to 976 mAh/g with a corresponding charge capacity of 896 mAh/g, leading to a much higher Coulombic efficiency of 91.8 %.

Figure 4.20 Cycling performance of the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11 : 1 : 13$ at various C rates. Here, 1C is equal to 790 mA h/g.

The cycling responses of the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrodes with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11:1:13$ were also evaluated at different C rates as shown in Figure 4.20. The sample showed a high capacity of 1000 mAh/g at 0.2 C, which changed to 900 and 770 mAh/g at 1 and 2 C, respectively. It could also depict a capacity as high as 540 mAh/g even at 5 C (3950 mA/g) rate. These performances at high C rates, especially at 5 C, were better than those reported for either SnO_2 - or Fe_2O_3 -based anode materials.^{18,49,84,95,155}

In order to make comparison, Fe_2O_3 NPs/rGO was prepared by similar synthetic conditions. The field emission scanning electron microscopy (FESEM) image (Figure 4.21a) reveals the morphology of samples formed by reacting FeCl_2 , ammonia with graphene oxides (GO) in the one-step solvothermal process as described in the experimental section. It clearly shows that the NPs are anchored uniformly on the surface of thin sheets. The reduction of GO is examined by Raman spectroscopy (Figure 4.21b) and electrical conductivity

measurements. Figure 1b shows the increase in the intensity ratio of D band (located at 1362 cm^{-1}) and G band (located at 1601 cm^{-1}), e.g. I_D/I_G , which is consistent with previous reports on GO reduction.^{27, 28} Meanwhile, the four-point-probe measurements show that the GO films on glass is insulating and the as-prepared samples depict a high electrical conductivity of $\sim 250\text{ S/m}$.

Figure 4.21 (a) FESEM image of $\text{Fe}_2\text{O}_3/\text{rGO}$ hybrid; (b) Raman spectra of the graphene oxides and $\text{Fe}_2\text{O}_3/\text{rGO}$ hybrids; (c) Low magnification and (d) high magnification TEM image of the $\text{Fe}_2\text{O}_3/\text{rGO}$ hybrid; the arrows in d indicates the small Fe_2O_3 nanocrystals formed on the rGO sheets; (e) SAED pattern of Fe_2O_3 NPs and (f) HRTEM image of the $\text{Fe}_2\text{O}_3/\text{rGO}$ hybrid; the blue circuits highlight individual grains on the rGO surface.

The transmission electron microscopy (TEM) image (Figure 4.21c) shows that these particles are 50-80 nm in size, while the high magnification TEM image (Figure 4.21d) indicates that there are also smaller nanocrystals with size of 4-7 nm (highlighted with arrows) attached uniformly on the reduced graphene oxide (rGO). The selected area electron diffraction (SAED) pattern (Figure 4.21e) of the large particles reveals ring patterns corresponding to hematite Fe_2O_3 with

rhombohedra crystal structure (JCPDS89-2810, lattice: Rhom-centered, $a=5.04$ and $c=13.75$), while the high resolution TEM observation (Figure 4.21f) of the smaller crystals confirmed the same crystal structure. Further examination using high resolution TEM indicates the 50-80 nm Fe_2O_3 NPs are polycrystalline with grain size in range of 3-5 nm. Here, the presence of the rGO/GO sheets in the solution may act as the heterogeneous nucleation seeds to facilitate formation of such small Fe_2O_3 crystal grains, which has not been demonstrated in other process.

Figure 4.22 (a) XRD patterns of $\text{Fe}_2\text{O}_3/\text{rGO}$ samples. The broad hump at 25° is from the glass substrate. (b) Thermogravimetry analyses (TGA) of $\text{Fe}_2\text{O}_3/\text{rGO}$ samples measured from 23 to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$ in air.

Figure 4.22a shows the x-ray diffraction (XRD) pattern of the as-prepared MO/rGO nanohybrids, which confirm the formation of either rhombohedral Fe_2O_3 that is consistent with the HRTEM and SAED results. No impurity phase is detected in both types of samples. A broad hump at 2θ of about 25° in XRD patterns is attributed to the glass substrate and it overlaps with the (012) peak of hematite Fe_2O_3 for the $\text{Fe}_2\text{O}_3/\text{rGO}$ sample. We have estimated the weight ratio between Fe_2O_3 and rGO, e.g. $I_{\text{MO}} : I_{\text{rGO}}$, by thermal gravimetric analysis (TGA) in

air (see Figure 4.22b). Assuming the final residues are only Fe_2O_3 after heating the samples to above $500\text{ }^\circ\text{C}$ in air, we calculated the weight ratio to be $I_{\text{Fe}_2\text{O}_3} : r_{\text{GO}} = 5.9$ for $\text{Fe}_2\text{O}_3/\text{rGO}$. Here, in Figure 4.33b, the weight loss at the temperature below $100\text{ }^\circ\text{C}$ is attributed to the evaporation of moisture.

Li-ion storage capabilities of $\text{Fe}_2\text{O}_3/\text{rGO}$ samples as anode materials were studied and a series of electrochemical measurements were carried out based on the half cell configuration^{21, 22} and using the nanohybrids as the anodes. Figure 4.23a depicts the representative CVs of $\text{Fe}_2\text{O}_3/\text{rGO}$ at a scan rate of 0.5 mV/s for the first, second, and third cycles. For the first cycle curve, there are three peaks at 1.74 , 1.38 and 0.73 V , respectively, which corresponds to the following three lithiation steps.^{5, 29}

Figure 4.23b shows the charge-discharge voltage profiles of the $\text{Fe}_2\text{O}_3/\text{rGO}$ nanohybrid electrode for the first two cycles and the ninetieth cycle at a current rate of 302 mA/g (0.3 C , where 1 C is defined as 1007 mA/g). The potential plateaus observed in the discharge curves are consistent with the CV results. The insertion process gave a first discharge capacity of 1334 mA h/g and a subsequent charge capacity of 823 mA h/g , resulting in an irreversible capacity loss of 38% . During the second cycle, the discharge capacity decreased to 837 mA h/g with a corresponding charge capacity of 764 mA h/g , leading to a much higher Coulombic efficiency of 91.3% . Moreover, the discharge and charge capacities of the hybrid improved to 881 and 856 mA h/g , respectively, in the 90^{th} cycle, which indicates a possible activation process in the electrode material.³⁰ The lower capacities measured during the initial few cycles are possibly due to the trapping of the Li ions inside the Fe_2O_3 crystal framework,

which are released gradually upon cycling and the capacity increases.³⁰ The Coulombic efficiency increased accordingly to 97.2%.

Figure 4.23 (a) Representative CV curves of the $\text{Fe}_2\text{O}_3/\text{rGO}$ hybrid electrode at a scan rate of 0.5 mV/s for the first, second, and third cycles; (b) Charge-Discharge voltage profiles of the $\text{Fe}_2\text{O}_3/\text{rGO}$ electrode for the first, second and ninetieth cycles at a current density of 302 mA/g (0.3 C); (c) Cycling performance of the $\text{Fe}_2\text{O}_3/\text{rGO}$ electrode at current densities of 0.3 C and 2C within a voltage window of 0.01-3.0 V; (d) Specific capacities of the $\text{Fe}_2\text{O}_3/\text{rGO}$ hybrid electrode for different charge/discharge cycles at various C rates. Here, 1C is equal to 1007 mA/g.

The discharge-charge cycling performance of the as-prepared $\text{Fe}_2\text{O}_3/\text{rGO}$ nanohybrids was evaluated between 0.01 and 3.0 V at 0.3 C (Figure 4.23c). A high discharge capacity of 837 mA h/g was delivered in the second cycle, which is ~83.1% of the theoretical value of Fe_2O_3 (1007 mA h/g). The small grains in Fe_2O_3 NPs and the small Fe_2O_3 nanocrystals, as seen in the HRTEM results,

allow the efficient diffusion of Li ions,³¹ which helps to realize the high specific capacities. Although the capacity decreased slightly during the first 17 cycles to 718 mA h/g, it started to show an upward trend after the 18th cycle, which is mainly attributed to the activation process.³⁰ The specific capacity of the Fe₂O₃/rGO anodes reached 881 mA h/g in the 90th cycle, revealing their excellent cyclability. The Fe₂O₃/rGO anode electrodes also exhibit excellent reversible capacity and cyclability even at 2 C (2014 mA /g) rate (Figure 4.23c) to deliver a discharge capacity as high as 641 mA h/g in the second cycle. The capacity slowly decreased to 470 mA h/g during the first 40 cycles and then increased to 541 mA h/g in the 100th cycles. The cycling responses of the Fe₂O₃/rGO nanohybrids at different C rates were evaluated as shown in Figure 4.34d. The sample showed a capacity as high as 653 mA h/g with a current density of 0.5 C, which changed to 595 and 456 mA h/g at 1 and 5 C, respectively, though it decreased to 215 mA h/g at 10 C. Here, Fe₂O₃/rGO nanohybrids show better performances of capacity and stability compared with reported value,^{2, 5, 32-34} especially at high C rate (e.g. 2C). For example, Fe₂O₃ nanospheres can deliver a reasonable discharge capacity as high as 800 mAh/g in the second cycle, but it quickly fades to 414 mAh/g after 60 cycles at 100 mA/g.⁵ We also prepared the Fe₂O₃ nanoparticles with 100 nm but it delivers a very low capacity, for example, 466 mAh/g at the second cycle and 84 mAh/g after 100 cycles (Figure 4.24).

Figure 4.24 FESEM image of the pure Fe_2O_3 nanoparticles and cycling performance of the Fe_2O_3 electrode at current densities of 0.2 C within a voltage window of 0.01-3.0 V.

The higher reversible capacity and cyclability presented above for the $\text{Fe}_2\text{O}_3/\text{rGO}$ hybrids are promising, which benefit from the unique structure of the NPs/ rGO hybrids. Normally, the pulverization process takes place due to the large volume swing generated during the Li ions insertion and extraction process that leads to the disintegration of anodes and hence a loss of electrical contacts.^{35, 36} Here, the rGO sheets in the hybrid samples serve as a highly conductive frame work to maintain the electrical contact from the MO NPs to the current collectors, and improve the cycling stability owing to their extremely high electrical conductivity and large surface area.³⁷

Here, the excellent Li storage properties of the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrodes at high C rates are proposed to be due to the following factors. In general, Li storage performance requires (1) fast and effective Li ion diffusion path in the electrodes; and (2) reliable electrical contact between individual active material components (e.g. each SnO_2 particle) and the current collectors; in order to achieve high specific capacitance and stable cycling performance at high current densities. The rGO sheets in the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ composite nanostructures could serve as the conductive scaffolds¹⁰ to maintain the reliable electrical

contacts between $\text{SnO}_2/\text{Fe}_2\text{O}_3$ with the current collectors. On the other hand, the amorphous Fe_2O_3 may prevent SnO_2 NPs on the rGO sheets from agglomerating during the charge-discharge process to maintain a large specific surface area for Li ion intercalation.

Figure 4.25 TEM images of (a) SnO_2/rGO electrode $I_{\text{SnO}_2:\text{rGO}} = 0.96 : 1$ and (b) $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrode with $I_{\text{SnO}_2:\text{Fe}_2\text{O}_3:\text{rGO}} = 11 : 1 : 13$ after 100 charge discharge cycles at a current density of 0.5 C. Here, the coin cells were opened in the glove box and the sample was then washed by N-methyl-2-pyrrolidinone (NMP) and further dried under room conditions. The resultant samples were dispersed in ethanol and dropped on copper grid for TEM characterization.

As indicated by the above EDS results (see Figure 4.24), the amorphous Fe_2O_3 and SnO_2 were homogeneously mixed with each other on the rGO surface. Amorphous Fe_2O_3 may favor the formation of barriers to prevent the agglomeration of SnO_2 NPs during the lithiation process as illustrated in Scheme 1. Otherwise, the agglomeration of SnO_2 NPs may hinder the effective diffusion of Li ion and resulted in decreased reversible capacities, which were observed in the SnO_2/rGO samples. Our HRTEM measurements showed that the SnO_2 in the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ remained as 5-8 nm particles (see Figure 4.25b) after the 100 charge-discharge cycles while obvious agglomeration of the SnO_2 was

observed in SnO_2/rGO electrodes after 100 charge-discharge cycles (see Figure 4.25a)

Scheme 1 Schematic diagram illustrates the possible mechanism for preventing the agglomeration of SnO_2 nanoparticles (NPs) in the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ composite during the discharging process. The Li intercalation of Fe_2O_3 takes place at a higher voltage (e.g. ~ 0.8 V) than that of SnO_2 (e.g. 0.2 V). Therefore, during the discharge process, the Fe_2O_3 NPs might effectively limit the SnO_2 NPs from being in contact with each other and prevent their agglomeration.

In this section, the effects of synergetic interactions between different phases and ratio of different phases on their Li storage performances were studied. The results revealed the Li storage performance of $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrodes was much better than those reported for SnO_2 - or Fe_2O_3 -based anode materials.^{18,48,49,84,95} Synergistic effects of $\text{SnO}_2\text{-Fe}_2\text{O}_3\text{-rGO}$ were found to achieve high capacity and long stability at high current density, where capacity mainly comes from SnO_2 and rGO maintains the electrical contact between metal oxides with the current collector. Here, the amorphous Fe_2O_3 NPs was not expected to contribute much to the total specific capacity of the $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ electrode, they can help to effectively prevent the agglomeration of SnO_2 NPs on the rGO sheets confirmed by our HRTEM observation.

As a result, these rGO-based metal oxides composites with rational design are potentially used as alternative anode materials. In addition, such a synergetic approach can be extended to other material systems and lead to promising routes to develop advanced electrode materials for rechargeable Li-ion batteries. However, more effects, such as phase, grain size, and surface area on their electrochemical performance are required to further understand.

4.4 Preparation of rGO based-Co₃O₄ nanowalls and CoO nanowalls/nanoparticles with controlled phase, grain size and porosity for LIB

1. Introduction

Many promising applications, e.g. photovoltaic devices,²⁴⁹ field effect transistors,^{250,251} thermoelectric modules^{208,214,252,253} and electrodes for supercapacitors^{254,255} or Li-ion batteries are dependent on the structure, shape, composition and size of nanomaterials.²⁵⁶ For applications as electrodes of Li ion battery, high specific surface area, high electrical conductivity, and an effective Li ion diffusion process are important to develop LIB with high energy density and high power density. The detailed study on the factors that could affect the electrochemical performance is pursued to understand the effects of all the parameters, such as their shapes, crystals size, phase and surface area

Herein, in order to study the effects of shape, grain size, phase and surface area of metal oxides on rGO, CoO nanoparticles and Co oxides ultrathin nanowall arrays attached on rGO sheets were prepared by a facile chemical approach to produce. Here, the Co oxides/rGO hybrids were derived from α -Co(OH)₂/rGO precursors produced from a hydrothermal process. Through controlled annealing process, e.g. under different gas environments and different temperatures, we could adjust the phase, grain size of the Co oxides and even the total surface area of the Co oxides/rGO hybrids.

2. Results and Discussion

Figure 4.26 (a-c) FESEM and TEM images of cobalt precursor/rGO samples obtained with graphene oxide, the arrow in c indicates the reduced graphene oxide nanosheet; (d) XRD pattern of cobalt precursor/rGO hybrids, the asterisks indicate the phase of cobalt hydroxide; (e) Raman spectra of the graphene oxides and cobalt precursors/rGO.

The morphology of the as-prepared samples formed by reacting $\text{Co}(\text{NO}_3)_2$ with graphene oxides (GOs) through the solvothermal process as described above were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (see Figure 4.26). The images revealed that the hybrids consisted of highly dense nanowall arrays attached onto two dimensional nanosheets. The thicknesses of the nanowalls were 3-5 nm. The x-ray diffraction (XRD) pattern of the sample (see Figure 4.26d) indicated that the nanowalls were $\alpha\text{-Co}(\text{OH})_2$. The reduction of the GOs to reduced graphene oxide (rGO) was confirmed by Raman spectroscopy (see Figure 4.26e) and electrical conductivity measurements. The Raman spectroscopy results showed the increase in the intensity ratio of D band (located at 1350 cm^{-1}) to G band

(located at 1580 cm^{-1}), e.g. I_D/I_G , from 0.9 to 1.2 upon the reduction of GOs through the solvothermal process, which is consistent with previous reports.²³³

Figure 4.27 FESEM images and XRD pattern of products obtained without GO; * indicates the peak from sample holder and overlap with [400] peak of Co_3O_4 .

Meanwhile, the four-point-probe measurements showed that the GO films on glass were insulating and the as-prepared nanohybrids depicted a high electrical conductivity of 200 S/m. Here, it was found that the phase and morphology of the Co compound were dependent on the presence of GOs. Without the addition of GOs during the solvothermal process, the resulting precipitates were agglomerated Co_3O_4 nanoparticles with an average diameter of 100 nm (see Figure 4.27).

Figure 4.28 FESEM and TEM images of $\text{Co}_3\text{O}_4/\text{rGO}$ obtained at different annealing temperature in air: (a and d) 250 °C for 30 minutes; (b and e) 350 °C for 30 minutes; (c and f) 450 °C for 30 minutes; red circles indicates pores.

The $\alpha\text{-Co}(\text{OH})_2$ attached rGO samples were annealed to convert them into Co oxides/rGO hybrids. It was found that the phases, grain sizes and surface area were highly dependent on the annealing temperatures and gas environments. For example, annealing the $\alpha\text{-Co}(\text{OH})_2/\text{rGO}$ samples in air at different temperatures did not significantly change the morphology of the nanowalls (see Figure 4.28a-c). However, it was noted that there were pores generated in the annealed nanowalls, especially for samples annealed at higher temperatures. The pore sizes in the annealed nanowalls were larger for samples annealed at higher temperatures as illustrated by the TEM images (see Figure 4.28d-f).

The pore size increased from 3-5 nm for samples annealed at 250 °C to 10-20 nm for samples annealed at 450 °C. The phase of the nanowalls was face-centered-cubic (fcc) Co_3O_4 (JCPDS78-1970) as confirmed by the SAED patterns and HRTEM image (see Figure 4.29).

Figure 4.29 Selected area diffraction pattern (SAED) and HRTEM image of $\text{Co}_3\text{O}_4/\text{rGO}$ -350

Furthermore, nitrogen adsorption/desorption isotherms for these porous $\text{Co}_3\text{O}_4/\text{rGO}$ hybrids showed type H3 hysteresis loops (see Figure 4.30), which are commonly observed for plate-like particles with slit-shaped pores.²⁵⁴ The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method and were determined to be 172.8, 133.6, and 72.3 m^2/g for $\text{Co}_3\text{O}_4/\text{rGO}$ samples after annealing at 250 °C, 350 °C and 450 °C (named as $\text{Co}_3\text{O}_4/\text{rGO}$ -250, $\text{Co}_3\text{O}_4/\text{rGO}$ -350, and $\text{Co}_3\text{O}_4/\text{rGO}$ -450), respectively.

Figure 4.30 Nitrogen adsorption and desorption isotherms measured at 77 K for (a) $\text{Co}_3\text{O}_4/\text{rGO-250}$, (b) $\text{Co}_3\text{O}_4/\text{rGO-350}$, and (c) $\text{Co}_3\text{O}_4/\text{rGO-450}$.

Figure 4.31 shows the XRD patterns of the $\text{Co}_3\text{O}_4/\text{rGO}$ samples. The XRD results of the as-prepared nanohybrids confirmed the formation of the face-centered-cubic (fcc) Co_3O_4 phase (JCPDS78-1970), which were consistent with the HRTEM and SAED results. No impurity phase was detected. By analyzing the peak width of the XRD patterns using Scherrer's equation, the crystallites of $\text{Co}_3\text{O}_4/\text{rGO-250}$, $\text{Co}_3\text{O}_4/\text{rGO-350}$, and $\text{Co}_3\text{O}_4/\text{rGO-450}$ were estimated to be 4.2, 6.3 and 9.7 nm, respectively, which were consistent with the TEM and HRTEM observations (see Figure 4.28). The broad hump at 2θ of about 25° in the XRD patterns was attributed to the glass sample holder.

Figure 4.31 XRD patterns of Co₃O₄/rGO obtained by thermal pyrolysis of the precursors at 250 °C, 350 °C and 450 °C for 30 minutes in Air.

The phase of the as-prepared hybrid samples was found to be able to be controlled by changing the annealing gas environment from air to Ar. FESEM and TEM images revealed that the products showed nanowall shape with porous structures after annealing in Ar at different temperatures (see Figure 4.32). The SAED and HRTEM analysis (see Figure 4.33) revealed that the nanowalls were polycrystalline fcc CoO phase (JCPDS71-1178).

Figure 4.32 FESEM and TEM images of CoO/rGO obtained at different annealing temperature in Ar: (a and d) 250 °C for 30 minutes; (b and e) 350 °C for 30 minutes and (c and f) 450 °C for 30 minutes; red circles indicates pores.

Weight ratio between CoO nanowall (obtained at 350 °C) and rGO, e.g. $I_{\text{CoO}} : r_{\text{GO}}$, was estimated by thermal gravimetric analysis (TGA) in air (see Figure 4.33c). Here, assuming the final residues are only Co_3O_4 after heating the samples to above 800 °C in air, we calculated the weight ratio to be $I_{\text{CoO}} : r_{\text{GO}} = 20.7$ for CoO nanowall/rGO nanohybrids.

Figure 4.33 (a) Selected area diffraction patterns (SAED); (b) HRTEM image of CoO/rGO-350; (c) Thermogravimetry analyses (TGA) of CoO nanowalls/rGO samples obtained at 350 °C measured from 23 to 800 °C at a heating rate of 10 °C/min in air, $I_{\text{CoO}} : I_{\text{rGO}} = 20.7$

The nitrogen adsorption/desorption isotherms (see Figure 4.34) for these porous CoO/rGO hybrids were also tested and the specific surface areas were determined by BET method to be 84.1, 103.3, and 61.5 m²/g for samples obtained at 250 °C, 350 °C and 450 °C (named as CoO/rGO-250, CoO/rGO-350 and CoO/rGO-450), respectively.

Figure 4.34 Nitrogen adsorption and desorption isotherms measured at 77 K for the (a) CoO/rGO-250, (b) CoO/rGO-350, and (c) CoO/rGO-450.

The corresponding XRD patterns of these samples (see Figure 4.35) indicated no detectable impurity phase except for the fcc CoO phase (JCPDS71-1178). The crystal sizes of CoO were estimated from the peak width using Scherrer's equation to be 3.3, 5.1 and 9.1 nm for CoO/rGO-250, CoO/rGO-350, and CoO/rGO-450, respectively.

Figure 4.35 XRD patterns of CoO/rGO obtained by thermal pyrolysis of the precursor at 250 °C, 350 °C and 450 °C for 30 minutes in Ar.

These two types of porous Co oxide nanowall hybrids were tested as anodes for Li-ion batteries and a series of electrochemical measurements were carried out based on the half cell configuration.^{59,258} The cyclic voltammetry (CV) of Co₃O₄/rGO electrodes at a scan rate of 0.5 mV/s for the first, second, and third cycles were carried out (see Figure 4.36).

Figure 4.36 Representative CV curves of $\text{Co}_3\text{O}_4/\text{rGO}$ hybrids electrodes were carried out at a scan rate of 0.5 mV/s for the first, second, and third cycles; Charge-Discharge voltage profiles of $\text{Co}_3\text{O}_4/\text{rGO}$ hybrids electrodes for the first and second cycles at a current density of 180 mA/g (0.2 C)

All $\text{Co}_3\text{O}_4/\text{rGO}$ electrodes depicted similar CV profiles. During the first cycle, two cathodic peaks were observed at 1.30 and 0.69 V corresponding to the electrochemical lithiation processes of Co_3O_4 .¹⁰⁴ During the second cycle, the main reduction peak was shifted to 1.15 V, which involved the conversion

reaction: $\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \leftrightarrow 3\text{Co} + 4\text{Li}_2\text{O}$.¹⁰⁹ The charge/discharge voltage profiles of $\text{Co}_3\text{O}_4/\text{rGO}$ hybrids at a current density of 180 mA/g (0.2 C where 1C is defined as 891 mA/g) were also examined (see Figure 4.36). It was observed that there were two voltage plateaus at 0.75 and 1.12 V for the first discharge step, corresponding to reactions between Li^+ with Co_3O_4 .²⁶² There was no obvious voltage plateau observed for reduced graphene oxide.²⁶³ The first discharge and charge capacities were 1236 mAh/g and 707 mAh/g, which gave a low Coulombic efficiency of 57.2%. The electrode depicted discharge and charge capacities of 884 mAh/g and 693 mAh/g during the second cycle, which resulted in a higher Coulombic efficiency of 78.4%.

The discharge/charge cycling performance of porous Co_3O_4 nanowalls/rGO hybrids were evaluated (see Figure 4.37) up to 100 cycles in the voltage range of 0.0 - 3.0 V and at a current rate of 180 mA/g (0.2C). The $\text{Co}_3\text{O}_4/\text{rGO}$ -250 electrode showed a poor cycling stability. Its discharge capacity increased during the first 10 cycles due to an activation process and then decreased to 320 mAh/g after 100 cycles. The $\text{Co}_3\text{O}_4/\text{rGO}$ -350 electrode showed much improved charge/discharge capacities and cycling stabilities. It depicted a discharge capacity of 884 mAh/g during the second cycle, which slightly reduced and maintained at 673 mAh/g during the 100th cycle. Such performance was better than those reported for Co_3O_4 at 180 mA/g.^{74,104,264-266}

Figure 4.37 Cycling performance of $\text{Co}_3\text{O}_4/\text{rGO}$ electrodes at current densities of 180 mA/g (0.2 C) within a voltage window of 0.01-3.0 V; Here, 1C is equal to 891 mA/g; (b) Cycling performance of CoO/rGO electrodes at current densities of 150 mA/g (0.2 C) within a voltage window of 0.01-3.0 V; Here, 1C is equal to 716 mA/g.

The $\text{Co}_3\text{O}_4/\text{rGO}$ -450 sample showed a discharge capacity of 802 mAh/g during the second cycle, which decreased to 582 mAh/g during the 100th cycle. The lower discharge capacity of $\text{Co}_3\text{O}_4/\text{rGO}$ -450 as compared to that of $\text{Co}_3\text{O}_4/\text{rGO}$ -350 is possibly due to the reduced specific surface area as a result of the collapsing of the pores upon annealing at high temperatures.

Figure 4.38 Representative CV curves of CoO/rGO hybrids electrodes were carried out at a scan rate of 0.5 mV/s for the first, second, and third cycles; Charge-Discharge voltage profiles of CoO/rGO hybrids electrodes for the first and second cycles at a current density of 150 mA/g (0.2 C)

A similar series of electrochemical measurements were also carried out for the CoO/rGO hybrids. The CVs of the CoO/rGO electrodes were also obtained at a scan rate of 0.5 mV/s for the first, second, and third cycles (see Figure 4.38). For

the first cycle curve, there were three peaks at 1.42, 0.86 and 0.42 V. The charge-discharge voltage profiles of the CoO/rGO electrodes (see Figure 4.38) were evaluated for the first two cycles at a current rate of 150 mA/g (0.2 C, where 1C is defined as 716 mA/g). For example, the insertion process in CoO/rGO-350 led to a discharge specific capacity of 1200 mAh/g with a low Coulombic efficiency of 70.6% for the first cycle while the discharge capacity decreased to 863 mAh/g with a corresponding charge capacity of 803 mAh/g, leading to a much higher Coulombic efficiency of 93.1%. The long characteristic plateau around 0.73 V observed in the first discharge curves was associated with the conversion reaction: $\text{CoO} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{O} + \text{Co}$, which implied a theoretical capacity of 716 mA h/g.²⁶²

Figure 4.37b shows the charge/discharge cycling performance between 0.01 and 3.0 V at 0.2 C (150 mA/g) for the CoO/rGO samples. The CoO/rGO-250 electrode delivered a discharge capacity of 914 mA h/g during the second cycle. However, the discharge capacity gradually decreased to 380 mA h/g after 100 cycles. Both CoO/rGO-350 and CoO/rGO-450 electrodes showed good capacity retention upon cycling. It was found that CoO/rGO-350 sample depicted higher discharge capacities, which increased gradually during the first 20 cycles to 998 mA h/g and decreased slightly to 732 mA h/g during the 100th cycle. The CoO/rGO-450 sample delivered a high capacity of 890 during the second cycle. However, the capacity faded gradually to 663 mA h/g during the 100th cycle.

Electrochemical impedance spectroscopy was used to understand the relevance of morphology and surface area of the synthesized CoO/rGO and Co₃O₄/rGO with the electrochemical performance in terms of the total internal electrochemical impedances of a cell. The characteristic impedance curves

(Nyquist plots) for the CoO/rGO and Co₃O₄/rGO samples annealed at different temperatures are shown in Figure 4.39.

Figure 4.39 Nyquist plots of Co₃O₄/rGO and CoO/rGO electrodes obtained by applying a sine wave with amplitude of 10.0 mV over the frequency range 10 kHz–0.1 Hz.

In impedance spectroscopy, high frequency activity is attributed to charge transfer phenomenon whereas low frequency region of the spectrum is ascribed to the mass transfer process.^{235,236} The Nyquist plots for the samples annealed at different temperatures for the two hybrid systems were similar except for the diameters of the semicircles, and thereby the associated impedance values. This means that the diameter of the semicircle is strongly dependent on the synthesis temperature, surface area and grain/grain interfaces, which may have a direct impact on the Li storage performance.²³⁷⁻²⁴² In order to quantify these respective values, a theoretical model consisting of resistance, capacitance, Warburg impedance and intercalation impedance was used to fit the experimental data (see Figure 4.40 and Table 1).^{235,236}

Figure 4.40 Equivalent circuit used for fitting the impedance spectra in Figure 6. R_e = electrolyte impedance; sf = surface film; ct = charge-transfer resistance, gb = grain boundary; W = warburg impedance; C_i = intercalation capacitance

Table1: Impedance parameters obtained by fitting the impedance spectra of the Co oxides/rGO hybrids (vs. Li) in open circuit voltage condition to the equivalent circuit shown in Figure 4.51

	CoO/rGO			Co ₃ O ₄ /rGO		
	Impedance Value					
Temperature	250	350	450	250	350	450
Re (±1) Ω	8	6	7	5	7	6
R (±5) Ω	167	76	82	186	88	177
CPE (±5)MF	33	19	29	58	23	40

The surface film and inter grain/grain boundary resistance are important factors that determine the electrochemical performance of a given sample. The thickness of surface film over active electrode affects the performance of a given electrode, since very thick layer may prevent the effective charge transfer and diffusion process from/to the electrolyte/electrode. Also, the number of grains and thereby grain boundaries give rise to the high charge transfer impedance and thereby a continuous capacity fading upon a long term cycling.^{238,239} The impedance curves obtained for the CoO/rGO and Co₃O₄/rGO samples were

identical. However, a variation in the diameter of the semicircles with annealing temperatures was observed. This was attributed to the differences in the surface area and grain size/grain boundaries interfaces in the various samples. From the analysis of the data obtained for the hybrid composites (see Figure 4.40 and table 1), it was noted that several factors (surface area, grain-size, inter-particles/grains interfaces) were competing with each other, which might affect the Li ion storage performance. For example, the 250°C annealed samples (CoO/rGO-250 or Co₃O₄/rGO-250) showed larger semicircles, which was attributed to their higher surface resistance or inter-particle impedance within the electrode. The diameter of the semicircles reduced significantly for the samples annealed at 450°C (CoO/rGO-450 or Co₃O₄/rGO-450), which indicated that the surface film and inter-grain boundary were smaller. Higher annealing temperature led to larger grain size, which corresponded to longer diffusion length and degraded Li ion storage performance. The sample annealed at 350°C was found to be appropriate in terms of the internal impedance of the cell, with the smallest semicircle indicating the lowest surface film resistance and optimized grain/grain-grain interface to achieve optimum Li ion storage performance.

In order to study morphologies effects on their electrochemical performances, CoO NPs/rGO was prepared for comparison. The field emission scanning electron microscopy (FESEM) image (Figure 41a) reveals the morphology of samples formed by reacting Co(CH₃COO)₂·2H₂O with GO in the one-step solvothermal process as described in the experimental section 3.3.

Figure 4.41 (a) FESEM image of the CoO/rGO hybrid; (b) Raman spectra of graphene oxide and CoO/rGO hybrids; (c) Low magnification and (d) high magnification TEM image of the CoO/rGO hybrid; (e) SAED pattern of CoO NPs and (f) HRTEM image of the CoO/rGO hybrid; the blue circuits highlight individual grains on the rGO surface.

The Raman spectrum confirms that the GO is reduced (Figure 4.41b), and the sample shows an electrical conductivity of ~ 200 S/m measured by four-point-probe measurement. TEM images (Figures 4.41c and d) reveal that there are also small nanocrystals with size in the range of 4-7 nm on the rGO. The SAED measurement (Figure 4.41e) and HRTEM observation (Figure 4.41f) show that both NPs and nanocrystals are face-centered-cubic (fcc) CoO (JCPDS71-1178), where the NPs are also polycrystalline with grain size of 3-5 nm.

Figure 4.42 (a) XRD patterns of $\text{Fe}_2\text{O}_3/\text{rGO}$ and CoO/rGO samples. The broad hump at 25° is from the glass substrate. (b) Thermogravimetry analyses (TGA) of $\text{Fe}_2\text{O}_3/\text{rGO}$ and CoO/rGO samples measured from 23 to 500°C at a heating rate of $10^\circ\text{C}/\text{min}$ in air.

Figure 4.42a shows the x-ray diffraction (XRD) pattern of the as-prepared MO/rGO nanohybrids, which confirm the formation of fcc CoO phases that is consistent with the HRTEM and SAED results. No impurity phase is detected in both types of samples. A broad hump at 2θ of about 25° in XRD patterns is attributed to the glass substrate. We have estimated the weight ratio between CoO and rGO , e.g. $I_{\text{CoO}} : I_{\text{rGO}}$, by thermal gravimetric analysis (TGA) in air (see Figure 4.42b). Assuming the final residues are only Co_3O_4 after heating the samples to above 500°C in air, we calculated the weight ratio to be $I_{\text{CoO}} : I_{\text{rGO}} = 4.3$ for CoO/rGO nanohybrids. Here, in Figure 4.42b, the weight loss at the temperature below 100°C is attributed to the evaporation of moisture.

Figure 4.43 (a) Representative CV curves of CoO/rGO hybrid electrodes at a scan rate of 0.5 mV/s for the first, second, and third cycles; (b) Charge-Discharge voltage profiles of CoO/rGO electrodes for the first, second and third cycles at a current density of 150 mA/g (0.2 C); (c) Cycling performance of CoO/rGO electrodes at current densities of 150 mA/g (0.2 C) within a voltage window of 0.05-3.0 V; Here, 1C is equal to 716 mA/g.

Electrochemical tests were carried out for the CoO/rGO nanohybrids. The CV curves for the CoO/ rGO hybrids at a scan rate of 0.5 mV/s for the first, second, and third cycles are shown in Figure 4.43a. There are two peaks in the first cycle CV curve at 1.25 and 0.72 V, respectively, which corresponding to the conversions reaction between CoO and Li ($\text{CoO} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{O} + \text{Co}$).³⁸ The charge/discharge voltage profiles (Figure 4.43b) at a current density of 150 mA/g (0.2 C) are consistent with the CV results. The sample delivered a first discharge capacity of 1342 mA h/g but with a large irreversible loss, e.g. Coulombic efficiency of only 57%, which is related to reactions of the electrolyte

solution and the formation of a solid electrolyte interface layer.³⁹ Despite the large irreversible loss, a very high charge capacity of 900 mA h/g was still attained during the first cycle. An increased Coulombic efficiency of 93.9 % was achieved in the second cycle with a discharge capacity of 931 mA h/g and a charge capacity of 874 mA h/g. The Coulombic efficiency was further increased to 96.3% in the third charge-discharge cycle, indicating a good reversibility.

The discharge capacity at 0.2 C-rate dropped from 931 mA h/g in the 2nd cycle to 600 mA h/g in the 90th cycle (Figure 4.43c). This value, however, is still much higher than that of the theoretical capacity of commercially used graphite anodes, e.g. 372 mA h/g and compared with reported value.^{6, 40, 41} For example, the CoO/C hybrids deliver 506 mAh/g in the second cycle and then gradually decrease to 345 mAh/g even at a constant current density of 30mA/g.⁶ However, the CoO NP/rGO nanohybrids show less stable capacity retention as compared to the CoO nanowall/rGO samples, which are attributed to that low mass loading of CoO NPs on rGO (Figure 4.33c and 4.42b). In addition, the CoO nanowall arrays on rGO favor the accommodation of volume change generated during the charge/discharge process.

In this section, the effects of shape, composition, grain size and surface area of Co oxides/rGO hybrids have been studied. The results revealed that these Co oxides/rGO nanohybrids showed structural-process-dependent performances as anode materials for Li-ion batteries. Higher annealing temperature led to larger grain size, which corresponded to longer diffusion length and degraded Li ion storage performance. Higher surface area allowed more Li ions to intercalate with active metal oxides and led to better electrochemical performance. In addition, the electrochemical performance of CoO nanowall arrays on rGO is

better than that of CoO NPs/rGO because of high mass loading of CoO nanowall and effective accommodation of volume swing.

4.5 Preparation of rGO based-ferrocene nanoclusters with controlled shape for LIB

1. Introduction

Improvements were reported by hybridizing graphene with metal oxides nanoparticles (NPs).^{55,113,120,141,155} However, the lithiation process of many metal oxides involves both the alloying and conversion processes, and hence involves structural change in the active materials which will affect the fast Li diffusion in the electrodes as well as high-C-rate performance.^{16,23,49,54,91,93} Combination of graphene and redox-active organic molecules may be a promising approach as organic molecules stay as amorphous clusters and the lithiation process does not require constant changes of any crystal structures, which provides the opportunity of achieving good high-C-rate Li storage properties. Nevertheless, there are few reports on the combination of redox-active organic molecular with graphene to achieve enhanced Li storage performance. It is worthwhile noting that the usage of organic redox-active materials is also considered to expand the availability of the resources of electrode materials and alleviate the environmental concerns to certain extent.^{271,272}

The redox-active organic molecules, such as 2,2,6,6-tetramethylpiperidinyloxy^{273,274} and galvinoxyl,²⁷⁵ have been demonstrated as cathodes and anodes for LIBs with attractive performance. However, there is a serious drawback that the organic materials may easily dissolve into the aprotic electrolytes commonly used in LIBs. It was demonstrated that anchoring the organic molecules onto certain inorganic structures, e.g. SiO₂ nanoparticles,²⁷⁶ could effectively prevent their dissolution and increase the cycling stability. For practical consideration, SiO₂ is not a redox-active material and will not contribute much to the total

capacity of the electrodes. Thus, using rGO sheets as the light weight and flexible platform to anchor the redox-active organic molecules may lead to promising Li storage strategies. In this section, combination ferrocene nanoclusters with rGO sheets were prepared via a facile, environment-friendly approach. The effects of ferrocene shape and synergetic interaction of ferrocene and rGo have been studied. Such systems also show promising potential in flexible batteries applications.

2. Results and Discussion

The morphology of the as-prepared samples through the solvothermal route with a precursor weight ratio, $R_{\text{ferrocene:GO}}$, of GO : ferrocene = 1:1 was characterized by TEM (see Figure 4.44a and b). The TEM images reveal that graphene nanosheets are decorated uniformly with small nanoclusters. The HRTEM images show that these nanoclusters are 3-5 nm in size and not crystalline as the measurements could not reveal defined lattice fringes (see Figure 4.44b). The insert in Figure 4.44b is the selected area electron diffraction (SAED) pattern of the samples, which only shows the point pattern corresponding to the rGO sheets. The X-ray diffraction (XRD) pattern (see Figure 4.45a) reveals no datable impurity phase in the nanohybrids. The reduction of GO to rGO was confirmed by the Raman spectra (see Figure 4.44c) as the intensity ratio of D band (located at 1362 cm^{-1}) and G band (located at 1601 cm^{-1}), e.g. I_D/I_G , increases from 0.90 to 1.33 after the solvothermal process, which agreed well with previous reports on GO reduction.^{155,277}

Figure 4.44 (a-b) TEM images, Insert of is SAED; (c) Raman spectra, (d) MALD-TOF-MS of the resultant samples with $R_{\text{ferrocene:GO}}=1:1$.

The matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALD-TOF-MS) of as-prepared nanohybrids is shown in Figure 4.44d. For comparison purpose, pure ferrocene powders were also measured. The dominant peaks observed in spectra of both ferrocene and nanohybrids at m/z 186.8, 184.8, and 182 are attributed to the fragmented species of $[M-H]^-$ or $[M-H]^{2-}$ with the isotropic multiplet of H, where the M is ferrocene. This confirms that the nanoclusters on the reduced graphene oxide are ferrocene nanoclusters.

Figure 4.45 X-ray diffraction pattern (XRD) of the as-prepared samples with (a) $R_{\text{ferrocene:GO}}=1:1$ and (b) $R_{\text{ferrocene:GO}}=1:2$.

Increasing the precursor weight ratio $R_{\text{ferrocene:GO}}$ to 1:2 led to the formation of nanorods on rGO sheets although there were still observable nanoparticles of 3-5 nm. The diameter of the nanorods is ~ 15 nm and the length is ~ 100 nm (Figure 4.46). Free standing ferrocene nanorods were also observed. Normally, the micelle shapes of organic molecules in solvent are dependent on its concentration. The formation of nanorods under high concentration is attributed to π - π stacking of the ferrocene molecules. The ferrocene nanorods are observed to transform to porous structure after electron beam irradiation as a result of thermal evaporation (Figure 4.46c), and the XRD results (see Figure 4.46b) indicated that these nanorods were amorphous since there was no other detectable peak except for the peak from rGO.

Figure 4.46 SEM image of the ferrocene/rGO samples prepared with $R_{\text{ferrocene:GO}}=2:1$; (b-c) TEM images of the same sample (b) before and (c) after electron beam irradiation for 10 seconds; (d) SEM image of the ferrocene/rGO samples prepared with $R_{\text{ferrocene:GO}}=2:1$ to show that there are free-standing ferrocene nanorods not attached to the rGO sheets.

The mass loading of the ferrocene nanoparticles and nanorods on the rGO sheets (defined as the weight ratio of ferrocene and rGO in the as-prepared samples, $I_{\text{ferrocene:rGO}}$) were determined by TGA (see Figure 4.47). The TGA results indicated that $I_{\text{ferrocene:rGO}}$ changed from 0.64 to 1.17 when $R_{\text{ferrocene:GO}}$ was changed from 1:1 to 1:2.

Figure 4.47 Thermogravimetry analyses (TGA) of the samples prepared with (a) pure ferrocene without HNO_3 acid treatment; (b) pure ferrocene after HNO_3 acid treatment; (c) ferrocene/rGO sample with $R_{\text{ferrocene:GO}} = 1:1$ after HNO_3 acid treatment, and (d) ferrocene/rGO sample $R_{\text{ferrocene:GO}} = 2:1$ after HNO_3 acid treatment. Here, TGA was measured from 25 to 700 °C under a heating rate of 10 °C/min in air, where the weight loss before 100 °C was attributed to the loss of water, the residual is treated as Fe_2O_3 .

Note: The residual powder after the TGA process is verified to be Fe_2O_3 . The TGA on pure ferrocene after HNO_3 treatment is used at the controlled experiment to verify that the Fe in the initial ferrocene sample is 43 wt%. Based on the weight of the residual Fe_2O_3 and the weight of the initial ferrocene/rGO samples, the weight percentage of ferrocene in ferrocene/rGO obtained with $R_{\text{ferrocene:GO}} = 1:1$ is around 39 wt% while the weight percentage of ferrocene in ferrocene/rGO obtained with $R_{\text{ferrocene:GO}} = 2:1$ is around 54 wt%.

Based on the above results, the formation mechanism of ferrocene/rGO nanohybrids is illustrated in the Scheme (see Figure 4.48). By mixing ferrocene with graphene oxide in ethanol solvent, ferrocene molecules can be decorated

on the surface of graphene oxide nanosheets through π -conjugated bonds. The ferrocene molecules on the surface of graphene oxide nanosheets serve as seeding sites for further heterogeneous nucleation for the growth of ferrocene nanoclusters through π -conjugated bonds. The ferrocene nanoclusters are expected to passivate the rGO sheets and prevent their agglomeration. The π -ring in each ferrocene molecule serves as redox active site for reacting with Li ions.

Figure 4.48 Scheme illustrates the proposed mechanism on grafting of ferrocene nanoclusters onto rGO and the proposed redox reaction.

To study the Li-ion storage performance of these ferrocene/rGO nanohybrids, a series of electrochemical measurements were carried out based on the half cell configuration.¹⁵⁵ The cyclic voltammetry (CV) curves of pure rGO and ferrocene/rGO electrodes (see Figure 4.49) were obtained at a scanning rate of 0.5 mV/s over the voltage range of 0.05-3.0 V. The first cathodic scan of the pure rGO shows a peak at 1.35 V, which may be ascribed to the formation of solid electrolyte interface (SEI) layers on the surface of active materials.²⁷⁰ The peak at 0.25 V is mainly associated with the insertion of Li into rGO. The first-

cycle CVs of ferrocene/rGO show two peaks at 1.2 V and 0.4 V, which are consistent with the formation of SEI layers and lithiated process of rGO. By comparing the CV profiles of pure rGO and ferrocene/rGO electrodes, two reversible peaks at 1.61V and 0.61 V in the 2nd and 3rd cycles were observed, which are attributed to the reversible lithiation reactions of ferrocene.

Figure 4.49 Representative CV profiles of (a) pure rGO electrode and (b) ferrocene/rGO electrode with $I_{\text{ferrocene:GO}} = 0.64$ at a scan rate of 0.5 mV/s for the first three cycles.

The cycling performance of pure rGO and ferrocene/rGO hybrids with $I_{\text{ferrocene:rGO}} = 0.64$ were evaluated (see Figure 4.50) in the voltage range of 0.05 - 3.0 V at current densities of 0.5 A/g and 2 A/g.

Figure 4.50 Cycling performance of pure rGO electrodes at a current density of 0.5 A/g and ferrocene/rGO electrode with $I_{\text{ferrocene:GO}}=0.64$ at current densities of 0.5 A/g and 2 A/g, respectively

The pure rGO electrode showed poor cycling stabilities and low capacities. Its discharge capacity quickly decreased to 190 mAh/g during the 30th cycle at a current density of 0.5 A/g. The ferrocene/rGO electrode showed much improved Li storage properties. The nanohybrid electrode with $I_{\text{ferrocene:rGO}} = 0.64$ depicted a discharge capacity of 515 mAh/g during the 30th cycle at a current density of 0.5 A/g and then gradually increased to 765 mAh/g during the 200th cycle, which was attributed to an activation process.¹⁵⁵ The Nyquist plots for the cell before and after cycling testing were similar except for the diameters of the semicircles, and thereby the associated impedance values (Figure 4.51). In impedance spectroscopy, high frequency activity is attributed to charge transfer phenomenon whereas low frequency region of the spectrum is ascribed to the mass transfer process. This indicates the impedance in ferrocene/rGO was reduced after cycling processes.

Figure 4.51 Nyquist plots of ferrocene/rGO with $I_{\text{ferrocene:GO}}=0.64$ electrodes before and after cycling testing obtained by applying a sine wave with amplitude of 10.0 mV over the frequency range 10 kHz–0.1 Hz.

This hybrid electrode also delivered a discharge capacity as high as 696 mAh/g during the 2nd cycle at a current density of 2 A/g and maintained it during the 400th cycle. However, increasing $I_{\text{ferrocene:rGO}}$ from 0.64 to 1.17 led to a slight drop in the discharge reversible capacities.

Figure 4.52 Cycling performance of the ferrocene/rGO with $I_{\text{ferrocene:GO}}=1.17$ at different current densities within a voltage window of 0.05-3.0 V.

For example, it delivered a discharge capacity of 453 mAh/g during the 2nd cycle at a current density of 0.5 A/g, which decreased to 470 mAh/g during the 200th cycle (see Figure 4.52). At higher current densities of 2 A/g, the ferrocene/rGO electrode with $I_{\text{ferrocene:rGO}} = 1.17$ depicted lower specific capacities of 301 and 286 mA h/g, respectively, during the 200th cycle. The higher mass loading of ferrocene on rGO sheets may cause them to agglomerate during the charge-discharge cycling process, which degrades their Li storage properties. In addition, the size of the ferrocene nanorods is much larger than its nanoparticles (3-5 nm in size). This also leads to low capacity.

Figure 4.53 specific capacities of the ferrocene/rGO electrode with $I_{\text{ferrocene:GO}} = 0.64$ at various current densities.

The cycling responses of the ferrocene/rGO electrode with $I_{\text{ferrocene:rGO}} = 0.64$ were also evaluated at various current densities as shown in Figure 4.53. The nanohybrid electrode showed a high capacity of 415 mAh/g at a current density of 3 A/g. It depicted capacities as high as 315 and 236 mAh/g even at high current densities of 5 A/g and 10 A/g, respectively. The specific capacity could

recover and sustain at 600 mAh/g when the current density was changed back to 0.5 A/g. Such excellent Li storage performance at high current densities for the ferrocene/rGO hybrid electrodes is better than those reported for graphene based electrodes.^{267-269,278-280} As mentioned earlier, for the rGO/metal oxide electrodes reported in the literature, the lithiation process includes insertion, alloying and conversion reactions, which leads to the collapse of crystal structures of the active materials. This may result in the slow kinetics of ion intercalation and migration in these materials and lead to unsatisfying performance at high current densities.^{25,90,117,273} Here, ferrocene nanoclusters were anchored on rGO and served as electrochemically active hosts. During charge-discharge cycling process, ferrocene can accommodate Li ions without structural collapse that gives rise to promising Li storage properties at very high current densities.

In this section, ferrocene/rGO nanohybrids were prepared via a scalable solvothermal route. Here, the ferrocene molecules were anchored onto rGO nanosheets through π -conjugated bonds and further aggregated into nanoclusters, e.g. nanoparticles or nanorods. The effects of ferrocene shape and synergetic interaction of ferrocene and rGO have been studied. The results indicate that excellent lithium storage properties especially at high current densities were achieved through synergetic effect of ferrocene and rGO. Ferrocene offer high specific capacity, while rGO serves as effective matrix to support ferrocene. In addition, small size of organic nanoparticle favors the insertion/extraction reactions between Li ion and active materials. This approach provides a promising choose for the development of other advanced rGO-based organic electrode materials for LIB.

Chapter 5 Conclusion

In this thesis, rational design of the advanced electrode combined active metal compound with highly conductive reduced graphene oxide has been developed. The detailed study on the factors that could affect the electrochemical performance has been studied to understand the effects of all the parameters.

To identify the ideal carbon supports for active nanoparticles, SnO₂ NPs hybridizing with different carbonaceous materials, e.g. amorphous carbon (AC), carbon nanotubes (CNT) and reduced graphene oxide (rGO) were prepared using a facile method. The matrix effects on their electrochemical performance have been studied and mechanism behind has been proposed. Among these carbon-based materials, rGO was found to offer the best effects on the improvement of electrochemical performance of SnO₂. In addition, results also showed that (1) smaller particle size, (2) maintaining electrical contact of nanoelectrodes with electron collector and (3) rational mass loading of SnO₂ on rGO sheets were the three keys important factors to achieve good electrochemical performance. However, heavy mass loading of SnO₂ on rGO sheets had led to significant agglomeration.

Consequently, a new environmental-friendly approach has been explored to prepare varieties of rGO-based metal oxides composites. Binary and ternary phased rGO-based metal oxides nanostructures have been prepared, e.g. CoO/rGO, Co₃O₄/rGO, SnO₂/rGO and SnO₂-Fe₂O₃/rGO. Among these nanostructures, studies manifested that high capacities, high rates capabilities and long cyclability of SnO₂-Fe₂O₃/rGO were attributed to the synergetic

interactions among these three phases. Small SnO_2 NPs favored the high capacities and large rate capabilities, amorphous Fe_2O_3 NPs prevented SnO_2 NPs from agglomeration, where rGO offered intimate electrical contact between individual active material components (e.g. each SnO_2 particle) and the current collectors. Furthermore, the weight ratio of these three components within this nanostructure can be fine-tailored to achieve higher capacity and longer cyclability at high current density.

Other than that, the effects of grain size, structure, surface area, and phases of metal oxides on electrochemical performance of metal oxides/rGO nanostructures were widely investigated. Cobalt oxides nanowall arrays on rGO nanosheets were fabricated. We found that metal oxide/rGO nanoelectrodes showed structure-performance relationship, where the smaller grain size and higher surface area arrays can lead to higher capacity and better cycling stability.

Besides metal oxides/rGO nanostructures, this versatile method is extended to prepare organic molecular decorated on rGO sheets under similar synthetic conditions. This will help to expand the availability of the resources of electrode materials and alleviate the environmental concerns. Such system also has promising applications in flexible Li-ion batteries. The electrochemical performance of new rGO-based nanoelectrode consisting of organic redox-active material, ferrocene, and rGO nanohybrids has been explored. Studies demonstrated that ferrocene can well accommodate Li ions without structural collapse that offers high capacities and large charge/discharge rates.

These novel strategies can be extended to obtain varieties of rGO-based nanomaterials for use in energy storage and conversion.

Chapter 6: Future Work

Based on our studies, it can be concluded that hybridizing of rGO with metal oxides and organic molecules (e.g. ferrocene) can largely improve their electrochemical performance. For example, a highly reversible capacity of 530 mAh/g was achieved at 5C (4A/g) for ternary phased $\text{SnO}_2\text{-Fe}_2\text{O}_3/\text{rGO}$ and a capacity of 235 mAh/g was delivered at 10 A/g for ferrocene/rGO hybrids. These hybrids are potentially used as alternative anode materials to replace graphite. Furthermore, the detailed study on the factors that could affect the electrochemical performance has been done to understand the effects of all the parameters. In addition, rational design of the advanced electrode materials has been explored help fundamental understanding of individual parameter. However, there are still improvements, e.g. relative low capacity of cobalt oxides at high C rates required to study.

Therefore, rGO-based metal oxides hybrids with controlled size, shape, composition and structure will be studied as one of the main targets. Plenty of reports show that metal oxides exposed special facets can lead to fast lithium insertion/deinsertion processes in batteries.^{22,254,255} Thus, metal oxides with tunable shape, e.g. nanoparticles, nanosphere, nanowires attached on rGO will be adopted to study effects of shape and crystal structure on their electrochemical performance. In addition, rGO-encapsulated metal oxides also demonstrate good Li ion storage performances,^{90,113} while most of our rGO-based metal oxides hybrids are consisted of metal oxides-encapsulated rGO. Thus, rGO-encapsulated metal oxides will be prepared to study the effects of rGO on transfer the Li ions and electrons during the charge/discharge processes.

Such as, rGO-encapsulated porous metal oxides nanosphere, porous structured metal oxides with high surface area potentially favorite the lithiation reactions and accommodate volume swing.^{195,256} However, the electrical conductivity of porous metal oxides is low. Thus, combination of graphene and porous metal oxides may also be a promising to study effects of surface area on achieving good high-C-rate Li storage properties.

Based on our studies, ferrocene nanoclusters were anchored on rGO and served as electrochemically active hosts. During charge-discharge cycling process, ferrocene can accommodate Li ions without structural collapse that gives rise to promising Li storage properties at very high current densities. Thus, more rGO-based organic hybrids will be prepared wot study the effects of type of active molecule, length of active molecule chain, etc. on their electrochemical performances. Furthermore, hybridization of two different active organic molecules with rGO will be of interest to study effects of interactions among them.

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