Achieving high Li storage properties in copper oxide based hybrid anodes

Somaye Saadat

2013

Somaye Saadat. (2013). Achieving high Li storage properties in copper oxide based hybrid anodes. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54841>

<https://doi.org/10.32657/10356/54841>

NANYANG
TECHNOLOGICAL
UNIVERSITY

Achieving High Li Storage Properties in Copper Oxide Based Hybrid Anodes

Somaye Saadat

School of Materials Science and Engineering

2013

Achieving High Li Storage Properties in Copper Oxide Based Hybrid Anodes

Somaye Saadat

Somaye Saadat

School of Materials Science and Engineering

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

2013

Acknowledgements

My deepest gratitude goes to my supervisor Asst. Prof. Alex Yan Qingyu, not only for his guidance through this research, but also for all his help and care. I have always cherished his accessibility and guidance.

I would also like to thank Prof. Ma Jan, who is no longer among us. He was my first instructor in NTU and gave me great advices and motivated me every time with his smile and encouraging words. I would also like to thank my co-supervisor Dr. Tay Bee Yen from Singapore Institute of Manufacturing Technology for her care, guidance and advices and Assoc. Prof. Hng Huey Hoon for her helpful instructions.

I am also grateful to School of Materials Science and Engineering and SIMTech to have given me this opportunity. I would like to thank all the members of MSE staff, especially technicians of electron microscopy & X-ray diffraction lab, the organic and inorganic synthesis labs, the computer lab, the central chemical and consumable stores.

My special appreciation to all my fellow group members. I'm especially thankful to Zhu Jixin, Dao Hao, Ziyang, Weiling, Tay Yee Yan and Teh Pei Fen. Finally, I want to thank my husband Saeed, for all his heart-warming support, instructions and encouragement, without which I would have never advanced in my PhD study. His encouragement and love has always lifted my spirit when I have failed repeatedly and his advice and helpful hints has helped me succeed. I will love and love him forever. At the end I like to thank my mother and father. Although I'm far apart from them, I have always felt their care and support. Their love and encouraging words are the lithium ion batteries with eternally excellent energy density and power density which powers me to believe in myself live and love beautifully and work hard to reach my goals.

Abstract

With an ever increasing demand for efficient energy storage devices and while many micrometer sized bulk materials have failed to meet the high demands, fabrication of various complex nanostructures with controlled size, shape and composition have attracted increasing attention. However, due to the limiting intrinsic properties, not a single material could be developed which could meet all the necessary requirements, e.g., high energy density, good cycling stability; especially at high cycling rates and good rate capability. At this point, application of hybrid electrodes was proposed.

In the present work, a rational design and development of nanostructured copper oxide based hybrid anodes in two categories of conversion and alloying-conversion hybrids is presented. The focus is to develop facile, green, template-free fabrication of free-standing hybrid anodes. Hybrids with explicit electrochemical properties are developed by using copper hydroxide as scaffold for growth. The aim of hybrid development is to benefit from multi-functionality or expose novel enhanced electrochemical properties and lead to hybrid anodes with high energy density, good cycling stability and rate capability with practical applications.

Copper oxide is an important transition metal oxide with high theoretical capacity, high safety, inexpensive and environmentally abundant nature. Well aligned arrays of CuO nanoneedles is fabricated by anodization. CuO nanoneedle arrays demonstrated excellent performance in high current densities. At 1C rate the electrode delivered an excellent discharge capacity of 559 mAh/g, with 99.2% Coulombic efficiency after 200 cycles, while demonstrating perfect rate capabilities when tested to up to 50 C. Based on the above observation, copper oxide was selected as scaffold for fabrication of coaxial hybrids.

A facile, two-step electrochemical method was used to fabricate free-standing Sb/Cu₂Sb/Cu alloying hybrid electrodes grown directly on copper substrate. The hybrid is fabricated by electrodeposition of Sb on Cu(OH)₂ nanoneedle arrays and is composed of numerous Sb nanoplate surrounding Cu₂Sb/Cu core-shell nanoneedle arrays. The initial purpose was to fabricate Sb-CuO core-shell nanowire hybrids. However, electrodeposition of Sb on Cu(OH)₂ scaffold resulted in reduction of the copper hydroxide and formation of Cu₂Sb/Cu core-shell. Compared to pure Sb nanoplates, the Sb/Cu₂Sb/Cu hybrids demonstrated lower initial capacity, while demonstrating improved cycling stability and enhanced rate capability to up to 20 C. In this hybrid, the free-standing Cu core provides 1D electronic pathway and structural spacer. While, the mesoporous Cu₂Sb nanocrystals with direct contact to the copper core and strong structural relationship with the lithiated phase; Li₂CuSb, provides a more stable electrochemical performance and enhanced rate capability.

Next, electrochemical anodization and CVD growth was combined to develop a safe fabrication route for growth of free-standing Ge-Cu₂O alloying-conversion hybrid with high theoretical capacity. To demonstrate the effectiveness of hybrid application Ge-Cu₂O core-shell nanowire arrays were compared with Ge nanoparticles; grown directly on copper substrate. Ge-Cu₂O hybrid demonstrated superior electrochemical properties at 0.5C and 1C rate and perfect rate capability when tested to up to 15C, while Ge nanoparticles demonstrated fast fading electrochemical properties. In-situ generation of GeO₂ was observed during the cycling process of Ge-Cu₂O, which can be explained based on the different electroactive response of hybrid's building block towards Li⁺; with Cu₂O undergoing conversion reaction and Ge undergoing alloying reaction, with the capability to react electrochemically with Li₂O. It is suggested that the excellent electrochemical performance of Ge-Cu₂O hybrid comes from their smart selection and unique hierarchical architecture. The Ge shell with high theoretical capacity, large surface area and short diffusion distance for Li⁺ lithiation\delithiation lead to delivery of large specific capacities. While, the one-dimensional Cu₂O nanoneedle arrays with direct contact to the current collector serve both as structural spacer to buffer the strain during lithiation/delithiation and act as a good electron pathway to improve electronic conductivity.

Finally, two-step electrochemical fabrication was applied to fabricate coaxial Fe₃O₄-CuO conversion hybrids grown directly on copper substrate. The electrodes are made of electrochemically coated mesoporous Fe₃O₄ nanocrystals, grown on free-standing CuO nanoneedle arrays. Two types of core-shell and hierarchical 3D network Fe₃O₄-CuO hybrids were fabricated by variation of electrodeposition conditions. Both Fe₃O₄-CuO hybrids were electrochemically tested at 1C rate and compared with pure Fe₃O₄ nanoflakes. It was observed that both Fe₃O₄-CuO hybrids have superior electrochemical performance at 1C rate compared to Fe₃O₄ nanoflakes. The hybrids were also tested for their rate capability; exposing excellent properties, while being tested to up to 15 C rates. It's believed that the high capacity, perfect stability and ultrafast charging/discharging capability of the coaxial Fe₃O₄-CuO hybrids comes from the intelligent integration of two compatible components to free-standing mesoporous architectures. In these hybrids free-standing ultra-fast CuO nanoneedle arrays core provide 1D electronic pathway, structural spacer and superior rate capabilities, while the mesoporous Fe₃O₄ nanocrystals with high specific capacity provide active sites for lithium interaction and lead to high specific capacities at high cycling rates while maintaining excellent stability.

The discussed findings highlights the many possibilities and advantages of template-free deposition routes and demonstrates the large opportunities of hybrid anodes to develop the next generation LIBs with superior electrochemical properties.

Table of Contents

Acknowledgements.....	I
Abstract.....	II
1 Literature review.....	1
1.1 Energy Storage Challenge.....	1
1.2 Advanced Materials for Lithium ion Battery Applications.....	5
1.2.1 Nanostructured electrodes.....	5
1.2.2 Anode Materials for Lithium Ion Battery Applications.....	8
1.2.3 Hybrid electrodes for lithium ion battery applications	16
1.3 Electrochemical Deposition	25
1.3.1 Principles of electrochemical deposition	25
1.3.2 Features of electrochemical synthesis.....	27
2 Thesis Design	29
2.1 Hypothesis.....	29
2.1.1 Nanowire based hybrids.....	29
2.1.2 Copper oxide nanoneedles as scaffold for hybrid growth	31
2.1.3 Selection of secondary phase decorating the CuO needles.....	33
2.2 Scope	34
3 Fabrication of CuO nanoneedle arrays as scaffold for growth of lithium ion battery hybrids.....	37
3.1 Overview	37
3.2 Experimental Details.....	39
3.2.1 Electrochemical fabrication of CuO nanoneedle arrays	39
3.2.2 Materials characterization.....	39
3.2.3 Electrochemical measurements.....	40
3.3 Electrochemical fabrication of CuO nanoneedle arrays.....	40

3.4	Electrochemical evaluation of CuO nanoneedle arrays	42
3.5	Conclusion.....	45
4	Fabrication attempt of Sb-CuO hybrid anodes for lithium ion batteries	47
4.1	Overview	47
4.2	Experimental Details	48
4.2.1	Electrochemical deposition of interconnected Sb nanoplates.....	48
4.2.2	Electrochemical fabrication attempt of free-standing Sb-CuO hybrids.....	49
4.2.3	Materials characterization	49
4.2.4	Electrochemical measurements.....	50
4.3	Electrochemical fabrication attempt of Sb-CuO hybrids	50
4.3.1	Electrodeposition of Sb nanoplates.....	50
4.3.2	Electrochemical fabrication attempt of free-standing Sb-CuO hybrid	52
4.4	Electrochemical evaluation of Sb/Cu ₂ Sb/Cu hybrids.....	56
4.4.1	Electrochemical properties of interconnected Sb nanoplates	56
4.4.2	Electrochemical properties of Sb/Cu ₂ Sb/Cu hybrid	58
4.5	Conclusion.....	61
5	Fabrication of Ge-Cu ₂ O hybrid anodes for lithium ion batteries	62
5.1	Overview	62
5.2	Experimental Details	63
5.2.1	Fabrication of free-standing Ge-Cu ₂ O hybrids	63
5.2.2	Materials characterization.....	64
5.2.3	Electrochemical measurements.....	64
5.3	Electrochemical fabrication of free-standing coaxial Ge-Cu ₂ O core-shell hybrid	64
5.4	Electrochemical evaluation of free-standing coaxial Ge-Cu ₂ O core-shell hybrid	68
5.5	Conclusion.....	76

6	Fabrication of Fe ₃ O ₄ -CuO hybrid anodes for lithium ion batteries.....	77
6.1	Overview	77
6.2	Experimental Details	78
6.2.1	Electrochemical deposition of interconnected Fe ₃ O ₄ nanoflakes	78
6.2.2	Electrochemical fabrication of free-standing Fe ₃ O ₄ -CuO hybrids	79
6.2.3	Materials characterization.....	79
6.2.4	Electrochemical measurements.....	80
6.3	Fabrication of Fe ₃ O ₄ -CuO hybrids.....	80
6.3.1	Electrodeposition of interconnected Fe ₃ O ₄ nanoflakes.....	80
6.3.2	Electrochemical fabrication of Fe ₃ O ₄ -CuO hybrids	82
6.4	Electrochemical evaluation of Fe ₃ O ₄ -CuO hybrid	84
6.4.1	Electrochemical properties of interconnected Fe ₃ O ₄ nanoflakes.....	84
6.4.2	Electrochemical properties of free-standing Fe ₃ O ₄ -CuO hybrids.....	88
6.5	Conclusion.....	93
7	Conclusion and future work	95
7.1	Conclusion.....	95
7.2	Future work	98
8	References:	101
	Publication List	110

1 Literature review

1.1 *Energy storage challenge*

The request for light weight and high energy density devices is growing fast with emergence of portable consumer electronics and electric vehicles. Fierce investigation of the three major conversion systems, which are fuel cell, batteries and supercapacitor is being conducted by many researchers worldwide. There are two main factors used to evaluate the conversion systems and do comparison between different energy devices, the energy density (Wh/kg or Wh/L) and power density (W/kg or W/L). These two parameters, respectively presents the amount of energy stored per unit weight/volume and how quickly it can be delivered by the electrochemical device. Currently, the electrochemical device with the highest power density are supercapacitor, however this is at the cost of low stored energy (see Figure 1.1).¹ Fuel cell is a device which can store the highest energy density, however application of this device suffers from the low efficiency (~50%) and high cost. In the meanwhile, batteries with high energy density, intermediate power rate properties are considered as a promising choice. Recently, there has been great interest in Li-ion batteries. With the fast advancement of mobile electronic devices, the market for Li-ion batteries has been growing rapidly and continuously over the years (Figure 1.2A). The domination of Li-ion battery for mobile devices is closely related with the improvement in cell capacity (Figure 1.2B). Other advantages of batteries is the low weight and more environmentally abundant nature of these devices.²

Currently, lithium ion cells are composed of carbonaceous material (graphite) as anode and a lithiated transition metal oxide (e.g. LiCoO_2) as cathode. In a lithium ion battery cell, upon charge the Li ions migrate to the electrolyte from cathode (deintercalation), and are attracted to the anode while the electrons transfer from cathode to the anode by application of an external electric field. The opposite process happens during discharge. A Li-ion cell is demonstrated in Figure 1.3. The chemical reactions happening on anode and cathode can be described as follows. The equations are in units of moles:²

Cathode: $\text{LiMO}_2 \rightleftharpoons \text{Li}_{1-x}\text{MO}_2 + x\text{Li}^+ + xe$

Anode: $\text{C} + x\text{Li}^+ + xe \rightleftharpoons \text{Li}_x\text{C}$

Total: $\text{LiMO}_2 + \text{C} \rightleftharpoons \text{Li}_x\text{C} + \text{Li}_{1-x}\text{MO}_2$

In this demonstration, the LiMO_2 is the lithiated transition metal oxide used as cathode and carbon presented as C represents anode.

Figure 1.1 Comparison of the different types of battery based on the gravimetric and volumetric energy density.³

Figure 1.2 A) Li-ion battery market in mobile electronic devices, B) Trend of capacity/energy density in cylindrical Li-ion batteries.⁴

The electrode materials known as intercalation material e.g. graphite, LiCoO_2 and some similar transition metal oxides usually have a tunneled or layered crystal structures which upon charge/discharge stays unchanged. While intercalation, the graphite anode expands only $\sim 1\%$ in plane, while the interlayer spacing increases by only 10% .⁵ The outstanding electrochemical stability, simple fabrication and low cost are the important factors which make graphite the number one choice for application in commercial lithium ion batteries for over a decade. However, this electrode suffers from the low energy density which is due to the limited vacancy sites for intake of Li ions in the intercalated graphite structures. To achieve devices with higher energy density it is essential that new materials especially anode material with high energy density and electrochemical stability are explored in details.

Figure 1.3 Schematic description of the charge-discharge process of a lithium-ion cell.⁶

Figure 1.4 The specific capacity of a number of electrochemically active metal elements.⁷

There are different types of electrode material. One category is the alloy metals⁸⁻¹⁰ which can reversibly undergo alloying reaction with lithium upon polarization to a potential of about 0.1 to 1.0 V versus Li/Li⁺. This can be presented by the following reaction:

The Li_xM alloys are lithiated structures with high lithium uptake. Therefore, these types of materials have high theoretical specific capacity and volumetric capacity. Theoretical capacity of several promising anode materials is compared to graphite in Figure 1.4.

This variety of alloying negative electrode which usually created crystalline phases with Li ion is also called the 'insertion' electrodes.¹¹ The lithium uptake of such structure is much larger compared to graphite. However, this large content of inserted lithium to structure results in huge volume expansions (see Figure 1.5). As an insertion electrode, uptakes Li ion and transforms from one crystalline phase into other huge strains is built up in the structure resulting in formation of cracks, loss of electrical contact due to detachment from the current collector and pulverization. Gradually this huge volume swings destroys the structure and the lithium ion battery fails.¹⁰

Numerous strategies has been suggested and explored in order to overcome the problems of novel electrode materials in the recent years. One interesting and applicable approach is to improve the electrochemical performance by application of an AB intermetallic phase instead of the single metal. This way, during the insertion/extraction of lithium during cycling one metal, e.g., B, undergoes the desire electrochemical reaction to form lithium alloy, Li_xB, while the other metal, A, keeps the integrity of the structure by remaining as an electrochemically inactive matrix. By application of a suitable inactive matrix in the active-inactive strategy the finely distributed particles are separated by the inactive matrix resulting in much more stable electrochemical properties.¹² Nanostructuring is another important and effective strategy which is studied extensively in the last decade. Reduction in size by nanostructuring are considered a

promising method to boost the electrochemical performance of lithium-ion batteries. Many superior properties such as enhanced capacities, rate capability and capacity retention have been reported for nanometer sized electrodes.¹³

Figure 1.5 Volumes (standardized for 1 mole Li storage capacity) of anode active materials before and after lithiation.¹⁰

Solid electrolyte interface (SEI) is a protective film formed on the surface of LIB electrodes during the first few cycles. SEI film has an important influence in determining battery performance such as, cycling stability, safety, irreversible capacity and also faradic efficiency. The SEI formation involves a reductive decomposition of electrolyte; consisting of solvents and salt. In general the reductive decomposition of solvents occurs in a potential range of 0.4-0.9 V vs. Li⁺/Li and permanently consumes Li⁺ and results in irreversible capacity. Many insoluble materials such as Li₂CO₃, Li₂O, LiF, ... are found in SEI film. Modification of electrode surface and application of electrolyte additives are some of the popular methods used to decrease the initial irreversible capacity.^{14, 15}

1.2 Advanced materials for lithium ion battery applications

1.2.1 Nanostructured electrodes

Nanomaterials can have crucial influence in enhancement of electrochemical properties of lithium-ion batteries. By nanostructuring of the active electrode material, the diffusion distance is dramatically reduced, making the insertion/extraction of lithium ions easier and quicker without

any deterioration to the structure. Other advantages of nanostructure e.g. nanoparticles, nanowires is the large surface area, short diffusion length of lithium ion and electrons and buffering effect which results in improved electrochemical stability. Enhanced properties such as high capacities, ultra-fast diffusion and improved cycling stability are among the many advantages of the novel Li ion battery architecture which benefit from nanometer size effects.¹³ Properties such as particle shape, size and texture strongly influence the delivered capacity and the structural stability during lithium interaction behavior during long term cycling. Therefore, by careful design of a suitable morphology, the electrochemical properties of the electrodes can be largely improved¹⁶ Application of suitable amorphous materials is another possible approach to reduce the strain build up in the structure and improve electrode cycle life. Beaulieu et al. have demonstrated that thin films of patterned amorphous Si and Sn which can withstand large volume swings of up to 200 % without crystallization and fracture¹⁷ Many types of nanostructures are designed and investigated for application as lithium ion battery anodes and cathodes. Here, we will briefly discuss the major categories of nanostructured systems.

Nanoparticles:

As discussed the volume swing of electrode materials upon alloying with lithium is in the order of several hundred percentage. However, by reduction of particle size large absolute volume changes and destructive strain build up can be prevented.^{10, 18, 19} Good cycling stability of up to 300 cycles has been reported for silicon nanoparticles by Sanyo. Despite the fact that nano-alloy particles can present much more stable cyclability compared to the equivalent bulk materials, however the good performance cannot be maintained for long. In overall, it can be concluded that solely reduction of the particle size is insufficient and further optimization of the structure is required to meet the demands for practical practice.¹⁸

Nanowires/nanotubes:

The concept of application of one-dimensional (1D) nanomaterials has been investigated extensively for application in supercapacitor and lithium ion batteries. This strategy has been

demonstrated with Co_3O_4 ,²⁰ SnO_2 ,²¹ and Si ,²² and many other electrode types and have demonstrated great improvements. The small nanowire diameter enables preferable accommodation of large volume swing without failure and the direct 1D electronic pathway allows effective electron transport. In case, the electrodes are grown directly on the current collector, each single wire is in direct contact with the current collector which allows enhanced electrical conductivity and individual contribution of each nanowire to capacity. In the meanwhile, the open space between the wires buffers the strain caused by the huge volume swing and allows efficient penetration of electrolyte in to the electrode material resulting in enhanced specific capacities. By application of nanotube instead of nanowires, the exposed surface area to the electrolyte is further increased while the relaxation of the structure from the built up stress is provided by the porosity of the active material.²² Guo et al. demonstrates fabrication of porous Co_3O_4 nanotubes with enhanced electrochemical properties, such as high delivered capacity (1200 mAh/g) and good cycling stability.²³

Mesoporous materials:

Application of highly mesoporous active materials which have outstanding accessible surface areas will decrease the transport distance for both electrons and lithium ions. Furthermore, electrode materials with hollow and porous nanostructures partially buffer the large volume change during cycling and provide long term electrochemical stability.^{18, 20} There is a report on Ge nanoparticles with 0D-3D porous assemblies. These structures demonstrated superior electrochemical properties with stable cycling stability. The reason for such outstanding performance is reported as thin wall thicknesses (<20 nm) as well as long-range ordering.²⁴

Self-assembled nano/micro materials:

Application of well-engineered architectures is another important strategy to overcome the shortcomings of novel nanostructure electrode materials. Higher level nanostructure constructed from nanometer-sized building blocks such as nanoparticles (0D), nanorods (1D), nano films (2D) has demonstrated promising results. Numerous hierarchical nanostructure fabricated from many

promising electrode materials promoted by the fast progress in synthetic strategies has been extensively investigated for lithium-ion batteries.¹⁶ Many facile solution-based fabrication methods have been reported. Production of a highly ordered V₂O₅ superstructures composed of interconnected nanoparticles which creates nanorod and these nanorods circle to produce hollow microspheres has been reported with outstanding performance, such as high delivered capacity and superior cycling stability.²⁵

1.2.2 Anode materials for lithium ion battery applications

Copper oxide:

Many important transition metal oxide (MO_x, M=Co, Fe, Cu, Ni, ...) used as lithium ion battery anodes go through conversion reaction. The conversion reaction mechanism is as follows:

According to this reaction the metal oxide are converted to metal and Li₂O in the first lithiation reaction and after the re-lithiation cycle they return reversibly to their original state. Because more than one electron is involved in the conversion reaction and the oxidation state is completely utilized these types of anode materials have high reversible capacity and energy density. However, most of the metal oxides in this category suffer from unstable formation of SEI formation resulting in low initial Coulombic efficiency and poor capacity retention.²⁶

Copper oxide with CuO and Cu₂O phase are considered as well known P- type semiconductors. Tarascon et al.²⁷ reports that the products formed during the discharge cycle is responsible for the obtained reversible capacity. During the charge cycle the CuO is reduced to Cu through Cu₂O phase. But, during the discharge process the Cu is re-oxidized to Cu₂O instead of CuO.²⁷ If the discharge process is reversible and the metallic Cu is turned completely to CuO a 674 MAh/g capacity will be achieved. Nevertheless, there are few reports available on electrochemical properties of copper oxide nanostructures used as LIB electrodes.²⁸ Results report that crystallinity and morphology are two important factors which determine the electrochemical performance. The existing literature studies demonstrate that capacity fading is the main problem of copper oxide electrodes used as anode material for LIBs. It was also observed that the

electrochemical performances of copper oxide electrodes largely depends on the nature of synthesis and material morphology.²⁸ An easy and low cost fabrication method has been reported in the literature. In this process mesoporous CuO nanosheets are directly grown of copper using an ammonia vapor phase corrosion method. This binder free electrode shows stable capacity of 640 mAh/g for 100 cycles at 1C rate and demonstrates excellent electrochemical performance at high rates (e.g. 10C). The unique structure with high surface to volume ratio and large space between is the proposed reason for such superior properties.²⁹

CuO nanorods fabricated by Lou et al. delivered a reversible capacity of 590 mAh/g at 1C after 100 cycles.³⁰ Zhang et al. also reported delivery of 583 mAh/g at 4C rate in cog-like CuO electrodes.³⁰ However, despite enhanced energy storage properties fabrication of such electrodes require application of surfactants, long and complicated procedures and special equipments. Therefore, development of a facile, green and cheap fabrication route with the possibility to be applied in large scale to meet the requirements of safe and green LIBs with high energy and power density is a challenge.²⁹

Electrochemical anodization is considered an efficient surface treatment method which has been successfully applied for fabrication of several nano-architectures on conductive metals^{31, 32} The fabricated film has been utilize in many different applications.^{33, 34} Production of copper oxide films by copper anodization has an advantage over other fabrication procedures, which is that the compositions and morphology of the final product can be varied by controlling of anodization parameters such as potential and time.³⁵

Recently, super-rate capabilities have been reported for nano-architecture copper oxide nanowire arrays electrodes. CuO pine needle like (PNL) arrays deliver the highest rate capacity of 545.9 and 492.2 mA h/g at 15 and 20C rates.³⁶ The super-rate properties is explained based on the unique PNL array structure, which provides free space for the migration of lithium ions and alleviate the large variation In volume.

There are also few reports on application of copper oxide in carbon based hybrids. In a report CuO/C nanowires is fabricated by carbonization of glucose absorbed on Cu nanowires on current

collector using heart treatment. This architecture has the electroactivity of carbon and the direct connection of transition metal oxide to the substrate. This synergic effect is the reason for the high initial capacity and Coulombic efficiency of 730 mAh/g and 83% respectively.³⁷

Application of CNT network is also an effective strategy to boost the electrochemical properties. Using a simple solution method CuO/CNT nano-microspheres are fabricated and compared to the pure CuO. It has been demonstrated that the addition of the highly conductive 3D network can largely improve the stability and rate capability of the electrode. The CNT network acts as both a high conductive network of current collector and an elastic buffer to reduce the huge strain caused by the volume changes during the charge/discharge process.³⁸

In another report three dimensional graphene networks is used to prepare CuO/graphene composite using a simple solution method. This composite exhibits excellent cycling performance compared to the pure CuO. At a current density of 65 mA/g, a stable capacity of 600 mAh/g is delivered for over 100 cycles. The specific capacity is maintained at 150 mAh/g, even with increase of current to 6400 mA/g. The carefully engineered composite with embedded CuO nanoflowers in a 3D conductive graphene network are reported responsible for the superior battery properties.³⁹

Antimony and antimony based compounds:

Antimony (Sb) undergoes alloying reaction with Lithium and transforms to Li_2Sb and Li_3Sb . Sb has a gravimetric capacity of 660 mAh/g and 1890 mAh/cm³ volumetric capacity. Sb electrodes suffer from high capacity decay due to the high volume change during lithiation and delithiation. To overcome this problem application of several Sb/C structure electrodes has been reported in the literature. Fabrication of a Sb-graphite hybrid electrode has been reported by Dailly et al.⁴⁰ The electrode demonstrated stable performance with charge capacity of 500 mAh/g. A Sb-C nanocomposite fabricated by HEMM also demonstrated superior electrochemical properties compared to Sb. Additionally, a Sb-C-graphite composite which was prepared by further HEMM of graphite with Sb-C nanocomposite was successfully fabricated. This hybrid electrode exposed an initial discharge capacity of 528 and maintained 86% of its capacity after 100 cycles.⁴⁰

However, low initial Coulombic efficiency with 33% capacity loss was the problem of this electrode which was explained based on the breakage of graphite during the HEMM process. Several other types of nanostructures and hybrids such as CNT and PAN (polyacrylonitrile) has been reported in the literature which demonstrate improvement in electrochemical properties.⁴¹

One of the effective strategies to improve electrochemical properties is application of intermetallic compounds (A_xB_y) with strong structural relationship to their lithiated products.^{42, 43} In these compound, both elements can be electroactive towards Li^+ , like $AlSb$ ⁴⁴ and $SnSb$,⁴⁵ or one can be inactive Cu_2Sb ,⁴⁶ $MnSb$, Mn_2Sb ⁴⁷ and Cu_6Sn_5 ⁴⁸. In these structures during the lithiation the metal A is extruded from the crystal structure and then during delithiation cycle is readmitted again. The MSb_y undergoes reaction with lithium based on insertion and alloying reaction which can be presented as follows:

Copper antimonide (Cu_2Sb) is a Sb based intermetallic compound which has been investigated as a possible candidate for lithium ion battery applications. Cu_2Sb fabricated by HEMM presented stable cyclability with a rechargeable capacity of 290 mAh/g. Strong structural relationship between Cu_2Sb and the lithiated phase which is Li_2CuSb is suggested to be the reason for such stable performance. Additionally, the divided copper which is extruded from the copper antimonide can provide good electronic conductivity during cycling and enable quick reaction kinetics.⁴⁶

Among the Sb based intermetallic compound, $SnSb$ can be considered the most studied electrode with promising electrochemical properties. The advantages of $SnSb$ are as follows:

- 1) Both constituents Sn and Sb undergo alloying reaction with lithium resulting in high theoretical capacity.
- 2) Ductile distributed tin phase can alleviate the volume expansion during cycling.

3) Reaction potentials of Sn and Sb are different; this will provide a buffering matrix and a good electrical connection while cycling by forming Li-based phases of Sb and Sn at different potentials during the charge and discharge cycles.

4) The possibility of reconstruction of initial electrode material after the charge cycle is an important issue and this reconstruction is possible in SnSb electrode.⁴¹

To achieve superior electrochemical properties various nanostructured composites/hybrids has been reported in the literature. A mechanochemical and electrochemically controlled SnSb/C which involves transformation of micron sized tin and antimony powders to uniformly distribute 10 nm and 2-3 nm SnSb nanocrystallites in a carbon matrix by mechanochemical and electrochemical means has been reported in the literature. This hybrid presents highly reversible capacity of 706 mAh/g with good initial Coulombic efficiency and only 19% capacity loss. The hybrid could deliver capacity higher than 550 mAh/g after 300 cycles.⁴⁹

Germanium :

Germanium (Ge) is an alloying anode with 1600 mAh/g theoretical capacity in its fully lithiated form ($\text{Li}_{4.4}\text{Ge}$) which is 44% of the theoretical capacity of Li-Si electrode. However, this electrode undergoes a huge volume expansion of 370% during lithiation. The advantage of Ge compared to Si is that it has 400 times higher diffusion rate in room temperature which makes this electrode an attractive candidate for high power rate LIB anodes. Carbon based Ge hybrids have demonstrated improvement in electrochemical stability.⁴¹

Two disparate voltage plateaus were observed in the electrochemical alloying cycle of Ge particles with lithium which represent the transformation of Ge to Li-Ge phases. A 3 step alloying reaction is proposed for Ge electrode which can be presented as follows:⁴¹

However, Baggetto and Notten argue that in the initial discharge cycle solely $\text{Li}_{15}\text{Ge}_4$ is formed. The Ge electrode experiences large capacity decay in its initial 10 cycles. Similar behaviors were

observed for Sn and Si electrodes.⁴¹ Application of various Ge thin films, nanostructures and hybrids with promising properties has been reported in literature.⁴¹ Embedded germanium nanoparticles in carbon matrix fabricated from pyrolysis of butyl-capped germanium has resulted in formation of an electrode with an initial capacity of 1067 mAh/g which can maintain 88% of its capacity for thirty cycles.⁵⁰ Ge nanowire arrays have been grown directly on current collector to achieve direct and individual electrical contact between the active material and current collector. Chemical vapor deposition (CVD) has been used to fabricate free-standing carbon free nanowire arrays. Superior electrochemical properties have been reported by Li et al. demonstrating impressive improvement compared to Ge electrodes containing carbon black and binders. The reason for such improvement is that the free-standing wires can relax and alleviate the stress build up during lithiation and expose stable cycling properties (see Figure 1.6). The Ge nanowires show good electrochemical performance for long cycles and remain intact without serious pulverization.⁵¹

Figure 1.6 Schematic drawing of (a) traditional battery electrode with amorphous carbon and a polymeric binder and (b) Nanowire array electrodes design consisting of nanowires directly grown on metallic substrate.⁵¹

Application of various Ge thin films, nanostructures and hybrids with promising properties has been reported in literature.⁴¹ Embedded germanium nanoparticles in carbon matrix fabricated from pyrolysis of butyl-capped germanium has resulted in formation of an electrode with an initial capacity of 1067 mAh/g which can maintain 88% of its capacity for thirty cycles.⁵⁰ Ge

nanowire arrays have been grown directly on current collector to achieve direct and individual electrical contact between the active material and current collector. Chemical vapor deposition (CVD) has been used to fabricate free-standing carbon free nanowire arrays. Superior electrochemical properties have been reported by Li et al. demonstrating impressive improvement compared to Ge electrodes containing carbon black and binders. The reason for such improvement is that the free-standing wires can relax and alleviate the stress build up during lithiation and expose stable cycling properties. The Ge nanowires show good electrochemical performance for long cycles and remain intact without serious pulverization.⁵¹

Fabrication of a branched $\text{Sn}_{78}\text{Ge}_{22}@$ carbon core-shell nanowires which was fabricated by thermal annealing of butyl-capped $\text{Sn}_{78}\text{Ge}_{22}$ nanoparticles at 600 °C was also reported in literature (see Figure 1.7). The authors report that the agglomeration of nanoparticles is inhibited by application of the special branched nanostructures and carbon layer. But instead $\text{Sn}_{78}\text{Ge}_{22}$ nanoparticles are fragmented to nanowires and nanoparticles. A high reversible capacity of 1107 mA h/g was obtained and 94% of the capacity was maintained for 45 cycles. The structure also demonstrated superior properties when tested at 8C rates with 93% capacity retention.⁵²

Figure 1.7 (a) Schematic diagram of branched $\text{Sn}_{78}\text{Ge}_{22}@$ carbon nanowire and TEM images of the $\text{Sn}_{78}\text{Ge}_{22}@$ carbon nanowires (b) before and (c) thermal annealing.⁵²

Iron oxide:

Iron oxide is an attractive conversion material; both hematite (Fe_2O_3) and magnetite (Fe_3O_4) are extensively studied as lithium ion battery anodes because of their environmental friendliness and low cost. The Li can be reversibly inserted in iron oxide in a wide range of 1.2–4.0 V vs Li/Li^+ . If the potential is decreased to 0.9V another two moles of Li can be inserted resulting in higher capacities, however the damage to the crystal is usually inevitable. By further reduction to 0.005V another 8.5 moles of Li can be inserted by turning Fe^{3+} to Fe^0 resulting in increase of theoretical capacity to 1007 mAh/g. The reactivity of Fe_2O_3 largely depends on morphology of the nanostructure.²⁶

As mentioned before Fe_3O_4 is also a promising anode material with 926 mAh/g theoretical capacity. Zhang et al. reported fabrication of carbon coated nanospindlers of Fe_3O_4 with 428 nm length and 106 nm diameters. It was confirmed that the carbon coating is thin and continuous. A high reversible capacity of 745 mAh/g was obtained. These carbon coated nanospindlers have much higher Coulombic efficiency and improved stability compared to pure Fe_3O_4 spheres. The uniform carbon coating which improved the electrical conductivity and holds the integrity of the active material was proposed responsible for the superior electrochemical properties.⁵³

In the recent years application of graphene based transition metal oxide as LIB electrodes has attracted a lot of attention. The graphene can be used as a buffer to help maintain the integrity of the structure and withstand the huge strain caused by the volume changes. The high electrical conductivity can improve the performance of the electrode. A magnetite/graphene were fabricated by heat treating the mechanically mixed graphene oxide and co-precipitated Fe_3O_4 nanoparticles. The monodispersed Fe_3O_4 nanoparticles imbedded in graphene demonstrated excellent rate capability, capacity and stability for over 1000 cycles. The robust graphene matrix and fine, monodispersed Fe_3O_4 nanoparticles are presented responsible for the excellent properties.⁵⁴

Application of porous three dimensional current collectors is another effective strategy to improve the electrochemical properties of oxide LIB electrodes. In a recent paper electrodeposition is used to fabricate a novel 3D porous Ni/ Fe_3O_4 film. The authors report a high

initial Coulombic efficiency of 86% and enhanced rate capability. The porous, binder free, electrode with high surface area and the direct contact between the active material and current collector and fast Li^+ diffusion are responsible for the superior battery properties.⁵⁵

1.2.3 Hybrid electrodes for lithium ion battery applications

There has been huge effort to develop the next generation lithium ion batteries which can meet the requirements of the emerging portable electronics and electric vehicles. Many different strategies has been suggested and examined in the last decade to overcome the limitations and develop the next generation Lithium ion batteries with enhanced properties in all aspects. However, finally it came to this point that limited by the intrinsic properties, e.g. low electrical conductivity, slow lithium ion diffusion, the single component nanostructures alone may not meet the high expectations.^{56, 57} Therefore, application of hybrid nanomaterials is being actively pursued in recent years.⁵⁸⁻⁶²

Carbon based hybrid electrodes:

Mesoporous electrodes have demonstrated enhanced electrochemical properties because of the so called 'ionic wiring'. However, the rate performance of these electrode materials is still limited. CNTs alone can be used as anode in lithium ion batteries with unique shape and a high capacity. This application is especially useful if Li ions can be intercalated into the CNT tube. However, previous reports have illustrated that based on the fabrication method and the applied treatment the reversible capacity of carbon nanotubes can vary. However in terms of application point of view the high irreversible capacity due to many reasons such as detrimental surface reactions with solution and formation of surface films of CNT limits its application. Many methods have been proposed in order to overcome the CNT problems; one of them is to use CNT as additive. Many studies report successful application of CNT composite for Li ion batteries, such as SnSb/CNT , CoSb_3/CNT and SnO_2/CNT .⁶³ Many metals and metal oxide with high electrochemical properties crack and de-attach from the current collector during charge and

discharge process causing fast capacity fade of the battery cell. The combining of active material with CNT can prevent agglomeration and improve the electrical conductivity of the electrode and improve the electrochemical properties. There are several reports on effectiveness of such network.^{19, 23, 64} In recently published paper manganese oxide was electrodeposited on a carbon nanotube (CNT) film substrate with a three-dimensional nanoporous structure. It was revealed that compared with the MnO₂ film electrode, the MnO₂/CNT electrode showed a much higher specific capacitance and better high-rate capability.⁶⁵ Also, it's reported that in a novel mesoporous nanotube composite which was fabricated by an in situ growth of mesoporous tin oxide on CNT superior electrochemical properties in terms of capacity and cycling stability can be seen in compared to mesoporous SnO₂ electrode(see Figure 1.8) . The synergetic effects of high surface area, porosity and good electrical conductivity are reported responsible for the improvement in the electrochemical properties.⁶³

Figure 1.8 Cyclic properties of (a) mesoporous SnO₂/MWCNT and (b) mesoporous SnO₂ tested at 33.3 mA/g current density. Inset demonstrates voltage-capacity profiles of 16th-20th charge/discharge cycles.⁶³

Graphite is currently the anode used in the commercially available LIBs. However the limited capacity of this material limits its application. Therefore, many studies have been conducted in order to replace graphite with other carbonaceous materials. Graphene is an attractive candidate with some unique features compared to graphite or CNT. The much higher surface area of

graphene can provide much more active sites for electrochemical reaction. Also the porous structure and high surface to volume ratio enables fast ion transport and high rate capability of graphene electrodes.⁶⁶ However, the graphene electrode suffers from serious agglomeration and re-stacking when removed from solution and dried. In order to overcome this problem and make use of the great advantages of such structure application of several graphene/metal oxides composite as lithium ion battery electrodes has been studied. Many different composite structures of graphene/metal oxide has been reported in literature, such as graphene/MnO⁶⁷, graphene/Fe₂O₃⁶⁸, graphene/Co₃O₄⁶⁹. In the graphene/ metal oxide structure, graphene as the conductive and porous 2D network enables the uniform dispersion of metal oxides and improves the electrical conductivity and ion transport, while the metal oxides suppress the re-stacking problem of graphene and increases the energy density.⁶⁶

Conductive polymer based hybrid electrodes:

Conducting polymers such as polyaniline (PANI), Poly(3,4-ethylenedioxythiophene) known as PEDOT, Polypyrrole (PPY) are known as promising electrode materials which can be coupled with metallic based electrodes with enhanced properties. Simplicity of synthesis, high ionic and electrical conductivity and the possibility to fabricate highly porous uniform films are the advantages of polymer based electrodes and hybrids. Integration of conducting polymer with metallic compound electrodes, e.g. metallic oxides results in superior electrochemical properties. Coated or mixed polymer can provide a flexible buffering blanket as well as improving the electrical conductivity of the hybrid electrode resulting in better cycling stability and often improved rate capabilities. Additionally, the conducting polymers demonstrate well-recognized reactions with lithium and can operate as good LIB electrode.⁷⁰

Figure 1.9 Fabrication process of ordered MnO_2 -PEDOT hybrid nanostructured array electrodes.⁷¹

The template-based electrochemical deposition is a well-known means for fabrication of ordered hybrid nanostructure arrays. In this method a thin layer of gold or silver are coated at the back side of anodized aluminum oxide (AAO) template and subsequently electrode material is grown inside the AAO channels by electrodeposition and finally the template is removed chemically to form a well aligned nanowire arrays on a conducting substrate. A coaxial MnO_2 -PEDOT nanowire arrays is grown by Lee et al. by a single step electrodeposition process (see Figure 1.9). The hybrid electrode possesses both good conductivity and electroactivity resulting in high specific capacities at high cycling rates as well as superior rate capabilities compared to pure MnO_2 nanowires and PEDOT nanowires.⁷¹

An interesting Silicon-polypyrrole hybrid which was fabricated by high-energy mechanical milling was also reported. In this hybrid, polypyrrole performs as buffering matrix which keeps the integrity during charge/discharge by holding the Si grains as they undergo reaction with Li. Introduction of polypyrrole results in improvement of initial Coulombic efficiency by reducing the SEI layer thickness. The hybrid with 50 wt% silicon fabricated by for 4 hours of milling exhibited good reversibility, Coulombic efficiency and cycling stability. Reasons suggested for such improvement are increase in conductivity due to the presence of PPY and a more stable electrode due to the presence of an integrating matrix. Based on the voltage profiles of Si-PPY(9:1) and pure Si electrodes it can be suggested that the reaction mechanisms in hybrid

electrodes is similar to Si which means the PPY is acting as an inert matrix and the capacity is a result of reaction of lithium with silicon crystals.⁷²

Hybrid electrodes with nanostructured current collectors:

Nanostructured current collectors are suitable scaffolds for fabrication of hybrid arrays and films. In order to achieve fast power source 4 resistance needs to be overcome; ion diffusion in the electrolyte and electrode, electrochemical reaction within the electrode and electron conductivity in current collector and active material. By application of 1D or 3D current collectors the mentioned resistance will be minimized. It should be explained that in hybrids with nanostructure current collector's nanosized units support a thin electroactive material resulting in short diffusion distance of Li^+ ion and electrons. Additionally, these hybrids have large surface area which enables loading a higher amount of active material while providing an open structure with buffering properties. The effective pathway for electron diffusion in the hybrid structure is another advantage of such hybrids. This leads to formation of a storage device with the so-called "capacitor like" rate capability and "battery like" capacity. Based on geometrical characteristic nanostructured current collectors can be categorized into 3 groups; 1D nanowire/nanotube arrays e.g., Cu pillars, 2D nanowall/nanoflake network e.g., Ni nanowalls, 3D continuous/quasi-continuous webs e.g., Ni nets.⁷⁰

Metallic nanowire arrays are common current collector in LIB applications. 1D metallic arrays have the advantage of higher initial capacity and rate capability. However, the 1D current collector have some issues. If the diameter of the wires is too small, it will collapse during the cycling. While, if it's too big it will occupy too much space and reduce the energy density of the hybrid electrode.⁷⁰ Template-free fabrication of Cu nanowire arrays by thermal reduction of CuO nanowires has been reported recently. The Cu-Si nanopillar electrodes with a thin alumina layer delivered 1560 mAh/g capacity at 1.4 A/g current density and remained electrochemically stable for up to 100 cycles.⁷³

Single crystal metal oxide nanowires have high electronic conductivity and in recent years application of some oxides such as ZnO, ITO and SnO₂ has been reported in literature.⁷⁰ For example it was reported that TiO₂ electrodes supported on ITO nanowires can deliver stable capacities for up to 1000 cycles without any serious capacity decay.⁷⁴

Figure 1.10 Schematics drawing of (a) production of 1D Ni/TiO₂ nanowire arrays and (b) production of 3D Ni/TiO₂ nanowire network. (c-d) SEM and (e-f) TEM images (g) areal capacity as a function of the electrode length and (h) cycling performance of the 3D Ni/TiO₂ nanowire network.⁷⁵

The difficulty to fabricate long 1D current collector without any agglomeration is another problem of 1D electrodes. Usually the wires have 2–3 μm length which limits the material loading (see Figure 1.10A). To overcome this problem, Wang et al. suggested application of a 3D Ni network. A 3D Ni/TiO₂ interconnected nanowire network is used as lithium ion battery electrode (see Figure 1.10). According to the SEM the Ni wires have up to 32 μm length and are interconnected to the surrounding wires by small bridges (see Figure 1.10B-G). The Ni/TiO₂ interconnected nanowire network compared to straight Ni/TiO₂ nanowire arrays has additional gain in capacity with increase in nanowire lengths (see Figure 1.10G). when the length is increased from 5 to 30 μm the areal capacity of the 3D hybrid electrode and 1D hybrid electrode increases 6.8 and 4.4 times respectively. When the wires have the same length the 3D network

delivers 2.4 times higher areal capacity compared to the 1D Ni-TiO₂ nanowire array electrode and 100 times higher than TiO₂ thin film (see Figure 1.10H).⁷⁵ This clearly demonstrates the importance and influence of current collector structures.

Metallic compound hybrid electrodes:

Although there has been many efforts to fabricate carbon based hybrid electrodes and hybrids which utilize nanostructured current collectors, there is few successful reports on fabrication and application of metallic compound hybrids especially for LIB application. Metallic compound hybrids have the advantage that usually all building blocks are electroactive materials. By smart selection of the components and careful engineering of the hybrid nanostructures, integration of the properties and achievement of an electrode with high energy density, long term stability and good rate capability would be possible. Such electrode would have the required criteria to find practical application in novel energy storage devices.

Hydrothermal, CVD and electrodeposition are the three fabrication methods which are commonly used to produce ordered hybrid nanostructures. The CVD and hydrothermal products have the advantage of higher crystallinity, while the electrodeposition has the advantage of simplicity. However, the electrodeposition fabricated routes of hybrids are usually template based which makes the process more complicated.⁷⁶

Only recently there has been some promising progress in this field. An interesting SnO₂-Fe₂O₃ hybrid was fabricated directly on current collector by CVD and hydrothermal process. In the hierarchical nanostructure Fe₂O₃ branches were grown on SnO₂ stem. The hybrid nanostructure exposed high initial Coulombic efficiency and superior reversibility compared to its individual components when tested as LIB electrode. This report is a good representative of successful integration of an alloying and conversion active material. The authors suggest that the transition metal iron improves the reversible electrochemical reaction of tin oxide with lithium.⁷⁷

Figure 1.11 Rate performance of MnO₂ @Co₃O₄ hybrid electrode synthesized by a hydrothermal method.⁷⁸

Co₃O₄ porous nanowires- MnO₂ ultrathin nanosheets are another ordered hybrid electrode which demonstrated promising properties. Carbon assisted hydrothermal approach was used to fabricate this hybrid. In the initial step Co₃O₄ nanowire arrays are grown on current collector and pre-coated with carbon and in the second step MnO₂ shell is grown on the nanowire arrays by interfacial reaction with KMnO₄. The interesting facts about this hybrid are the interesting architecture of the hybrid which is well aligned; open with direct connection to the current collector and that the components of the hybrid are both good pseudocapacitive materials which undergo reaction with the electrolyte. In this hybrid the cobalt oxide core provides 1D electron pathway, while the shell holds the hybrid integrity. As a result, the hybrid electrode exhibits excellent properties with areal capacitance 4-10 times higher than the Co₃O₄ nanowire arrays (see Figure 1.11).⁷⁸

Silicon is an important anode material with the highest theoretical capacity. However the huge volume change during charge/discharge process, low ionic and electronic conductivity has limited the application of this electrode. Recently application of coaxial Si-Ge nanotube hybrid was reported in literature. The nanotube hybrid was composed of Si with the higher theoretical capacity as the core and Ge with higher electrical conductivity as the shell. This results in formation of an electrode with both impressive mechanical stability and improved kinetics. The

fabricated electrode was tested as LIB battery and demonstrated excellent electrochemical properties with 85% capacity retention after 50 cycles. This hybrid compared to Si electrodes tested as 3C rates demonstrated 3 times higher capacity. The authors suggest that the reason for such improved properties is lower max. hoop strain in the hybrid nanotubes and reduction in activation energy barriers of lithium ion diffusion.⁵⁸

Figure 1.12 (A) Schematic drawing, (B) TEM and (C) Charge capacity and Coulombic efficiency of the Si/TiSi₂ hybrid electrode at 8400 mA/g rate between 0.150 and 3.00 V.⁷⁹

Zhou et al. also reported application of a heterostructure Si-TiSi₂ hybrid. For the fabrication of this hybrid Si nanoparticles were grown on highly conductive TiSi₂ mesh using CVD. The TiSi₂ matrix is a net of TiSi₂ nanowires which supply a 3D electronic pathway and good structural support (see Figure 1.12A-B). The Si and TiSi₂ have similar crystal structure; this makes the interfacing quite simple. When tested as LIB battery, the hybrid deliver a high capacity of 1000 mAh/g at a high charge rate of 8400 mA/g and retained 99% of its capacity when tested for 100 cycles (see Figure 1.12C).⁷⁹ The focus of the presented work is copper oxide based metallic hybrids. However, to our knowledge no copper oxide metallic hybrid is reported in the literature.

1.3 *Electrochemical deposition*

1.3.1 *Principles of electrochemical deposition*

Electrodeposition is based on the principles of electrochemistry. Electrochemistry is known as a chemistry branch which interrelates of chemical and electrical effects. A large part of electrochemistry deals with production of electrical energy by chemical reactions and chemical changes caused by the passage of an electrical current.

In order to determine the conditions required for the electrosynthesis of any material, we can begin by considering the stability of the target material in aqueous solution. A Pourbaix diagram indicates the *pH* and potential values at which chemical species are stable in aqueous solution. These *pH*/potential phase plots are thermodynamic calculations of the stability of the metal oxides, metal hydroxides, and metal ions in water.⁸⁰ A simplified version of the Pourbaix diagram for Zn^{2+} , Zn , and $\text{Zn}(\text{OH})_2$ at 1 atm and 25°C can be seen in Figure 1.13.

The standard potentials for electrochemical reactions shown on the ordinate axis in a *pH*-potential phase diagram (Pourbaix diagram) are measured relative to the potential difference between the working electrode, at which the reaction occurs, and a reference electrode. Potential is applied with an external power supply, and the *pH* is varied with the addition of acids (i.e. HCl) or bases (i.e. NaOH) as noted. The phase boundaries in a Pourbaix diagram indicate reduction/oxidation (redox) reactions that can occur during an electrochemical experiment. Such reactions can be written as a redox couple:

Figure 1.13 Diagram indicating the potentials and pH regions at which Zn^{2+} , Zn, and $\text{Zn}(\text{OH})_2$ are stable.

Where O is the oxidized species, R is the reduced species, and n is the number of electrons transferred per reaction. At potentials more negative than the standard reaction potential (E°), the reductive formation of O is more favored, while at potentials more positive than E° the oxidative formation of R is favored. A straightforward example is the reduction-oxidation of zinc metal (Zn°) and the zinc ion (Zn^{2+}), for which the standard potential is -0.962 V vs. Ag/AgCl.⁸¹

At potentials more negative than -0.962 V vs. Ag/AgCl, the formation of the reduced species (Zn°) is more favorable, while above this potential Zn^{2+} is more favorable. If a redox reaction occurs at a high enough rate that it can be considered to be in thermodynamic equilibrium as the potential is swept, it is considered a reversible reaction. Such a system can, in principle, be reduced and oxidized an infinite number of times without adverse effect (no loss of O or R). Zinc metal deposition is an example of a reversible reaction.

A cyclic voltammogram (CV) of the reversible zinc metal deposition can be seen in Figure 1.14. A CV is collected by sweeping an applied potential across the working electrode and reference electrode and recording the current response. Current peaks in a CV indicate movement of charge at or near the working electrode surface. The peak at more negative potentials is due to both Zn metal deposition and hydrogen evolution. The peak at more positive potentials corresponds to stripping of electrodeposited Zn metal.⁸¹

Figure 1.14 cyclic voltammogram illustrating a reversible reaction. ⁸¹

1.3.2 Features of electrochemical synthesis

By flow of an electric current between two or more electrodes which are separated by an electrolyte electrochemical synthesis is obtained. The synthesis takes place at the interface of electrode-electrolyte. We list below several features which distinguishing electrosynthesis from other synthetic means:

- (i) The electrochemical synthesis is taking place in a very high potential gradient of 105 V/cm within the electric double layer of the electrode. Under these conditions, some products can be obtained using electrochemistry which cannot be obtained by chemical synthesis methods.
- (ii) The deposited product is formed on a conductive electrode in the form of a coating/thin film in one single step. This is especially favorable in fabrication of electrodes for energy conversion/storage applications. The formed electrode is binder free with good adhesion and high conductivity. Further, growth of conformal coatings on substrates with any kind of shape is facilitated by the existence of the solid-liquid interface facilitates.
- (iii) This is a low-temperature technique which is limited by the boiling point of the electrolyte. This is especially favorable for fabrication of materials which are sensitive to heat such and experience problems such as compositional changes and decomposition in high temperature such as β -Zn₄Sb₃. However, if required, this can be raised by application of molten salt electrolytes.

(iv) By controlling the passed current kinetics can be controlled, while thermodynamics can be controlled by variation of applied cell potential with good thickness controllability and uniformity.

(v) An electrochemical synthesis is an oxidation or reduction reaction. This reaction can be moderately controlled and fine-tuned by controlling the electrodeposition parameters. Such control can rarely be afforded by chemical synthesis.

(vi) The film composition can be carefully controlled by varying the bath composition.

(vii) The experiments are simple and easy to perform and the instruments are inexpensive and readily available.

(viii) The application of electrochemical deposition allows growth of homogenous nanostructure with controllable features.⁸²⁻⁸⁴

However, there are some disadvantages. Poorly ordered products which make structural characterization difficult are a result of the ambient temperature fabrication. Often, the product comes with X-ray amorphous impurities. Finally, only on conducting electrodes the production can be carried out.⁸⁴

2 Thesis design

2.1 Hypothesis

2.1.1 Nanowire based hybrids

With an ever increasing demand for efficient energy storage devices and while many micrometer sized bulk materials have failed to meet such demands, fabrication of various novel materials with controlled size, shape and composition have attracted increasing attention.^{13, 42, 85-89} Nanostructured materials can give rise to new Li-storage mechanisms, allowing achievement of higher capacities than conventional intercalation mechanisms. Recent results demonstrate that Li^+ can be stored on the surface, interfaces, and in nanopores. Such storage does not create any mechanical damage in the electrode during charge/discharge, thus results in additional lithium storage.⁹⁰

The concept of application of one-dimensional (1D) nanomaterials has been investigated extensively for application in lithium ion batteries. This strategy has been demonstrated with Co_3O_4 ,²⁰ SnO_2 ,²¹ and Si ,²² and many other electrode types and have demonstrated great improvements. The small nanowire diameter enables preferable accommodation of large volume swing without failure and the direct 1D electronic pathway allows effective electron transport. In case, the electrodes are grown directly on the current collector, each single wire is in direct contact with the current collector which allows enhanced electrical conductivity and individual contribution of each nanowire to capacity. In the meanwhile, the open space between the wires buffers the strain caused by the huge volume swing and allows efficient penetration of electrolyte in to the electrode material resulting in enhanced specific capacities. Nevertheless, the nanowire structure also has the disadvantage of low material loading, which results in low specific energy densities.²² Many superior properties such as enhanced capacities, rate capability and capacity retention have been reported for nanowire electrodes.¹³ Superior electrochemical properties have also been reported by Li et al. for free-standing Ge nanowires; demonstrating impressive improvement compared to Ge electrodes containing carbon black and binders. The Ge nanowires show good electrochemical performance for long cycles and remain intact without serious

pulverization.⁵¹ During the lithiation/delithiation process, many different material properties, such as size, shape, porosity and texture influence the structural stability and determine the cycling stability. Therefore, by careful optimization of these parameters, the electrochemical performance of electrodes can be enhanced dramatically in comparison to the conventional bulk electrode.¹⁶ Therefore, deep understanding, careful design and engineering of influencing parameters are essential.

Nevertheless, although knowledge and understanding of electrodes and energy storage devices has grown and deepened, not a single material could be developed which could meet all the necessary requirements, e.g., high energy density, good cycling stability especially at high cycling rates and good rate capability. At this point application of hybrid electrodes was proposed.⁷⁰ There is no unique and vivid definition of hybrid electrodes in literature. However, in general hybrids are combination of chemically distinct materials with explicit properties, which can deliver desired properties due to multi-functionality or expose novel enhanced properties distinctive from their individuals due to the synergetic effects.

Hybrids with attractive properties can be fabricated by smart assembling and fine tuning of the composition, shape and architecture of the constituent building blocks.^{91, 92} Although there have been many efforts to fabricate carbon based hybrids and hybrids which use nanostructured current collectors, there is few successful reports on application of metallic compound hybrids with solely electroactive constituents, especially for LIB application.^{91, 92} In hybrid electrodes which utilizes nanostructured current collectors, such as Cu nanowire arrays or Ni mesh, only small material loading is possible and a large portion of the electrode does not contribute in energy storage, but adds to the electrode mass and size.⁷⁵ The metallic compound hybrids with solely electroactive materials have the advantage that all components undergo reaction with Li^+ , resulting in higher specific capacity. Only recently there has been some promising progress in this field. For example, an interesting $\text{SnO}_2\text{-Fe}_2\text{O}_3$ hybrid was fabricated directly on current collector. The hybrid nanostructure exposed high initial Coulombic efficiency and superior reversibility compared to its individual components when tested as LIB electrode. This report is a good representative of successful integration of an alloying and conversion active material. The

authors suggest that the transition metal iron improves the reversible electrochemical reaction of tin oxide with lithium.⁷⁷

Hydrothermal, CVD and electrodeposition are the three fabrication methods which are commonly used to produce ordered hybrid nanostructures. The CVD and hydrothermal products have the advantage of higher crystallinity, while the electrodeposition has the advantage of simplicity.⁷⁶ In general, most proposed production routes suggested in the literature are multi-step, complicated, high temperature and atmosphere controlled processes. They also usually require the application of hazardous materials such as toxic reducing agents (e.g. N_2H_4) and surfactant (e.g. CTAB). However, to find practical application, the proposed anode material and fabrication processes needs to be environmentally friendly, facile and cheap with the capability to be fabricated in large scale. Additionally, the general preparation process of nanostructured electrodes is to mix with a binder, e.g. poly(vinylidene difluoride), and paste on conductive current collectors. Usually, a conductive agent such as carbon black is required to improve the electrical conductivity of the electrode. These additives essentially adds extra mass to the electrodes and reduce the overall charge capacity. While, binder free mesoporous electrode and 1D free-standing nanowire/nanotube arrays generally fabricated by CVD and electrodeposition method have demonstrated promising properties. Direct deposition of electroactive materials on current collector by electrochemical methods is an attractive technique since it omits the need for any binding or pasting processes.⁹³⁻⁹⁶ However, nanostructures fabrication using electrodeposition usually need application of hard templates, e.g. anodized aluminum oxides to produce nanowire arrays^{97, 98}, or polystyrene sphere for fabrication of porous nanostructures which need to be removed afterwards.⁹⁹ This makes the process more difficult and long. Additionally, the probability of template remainder as impurities is high, which will affect the charge capacity. Therefore, development of template free fabrication methods is highly desirable.

2.1.2 Copper oxide nanoneedles as scaffold for hybrid growth

Copper oxide is an important oxide which is largely investigated in different applications such as catalysts,¹⁰⁰ gas sensors,¹⁰¹ photoconductive/photochemical cells, and other electronic devices.¹⁰²

They are cheap and nontoxic which makes them an attractive candidate for LIB electrodes. Recently, super-rate capabilities have been reported for nano-architecture copper oxide nanowire arrays electrodes. CuO pine needle like (PNL) arrays deliver the highest rate capacity of 545.9 and 492.2 mA h/g at 15 and 20C rates.³⁶ The super-rate properties is explained based on the unique PNL array structure, which provides free space for the migration of lithium ions and alleviate the large variation In volume. In this nanostructure the residual copper nanoparticles of the incomplete conversion reaction with lithium behaves as a good electron pathway and improves the electronic conductivity of the anode material, resulting in outstanding cycling stability and rate capability.

Electrochemical anodization is considered an efficient surface treatment method which has been successfully applied for fabrication of several nano-architectures on conductive metals^{31, 32} The fabricated film has been utilize in many different applications.^{33, 34} Production of copper oxide films by copper anodization has an advantage over other fabrication procedures, which is that the compositions and morphology of the final product can be varied by controlling of anodization parameters such as potential and time.³⁵

In the presented thesis development of free-standing, coaxial, core-shell hybrids with copper oxide as core are pursued. The novelty of the presented work is that, in CuO based hybrid systems, the CuO nanowire arrays provides similar advantages to nanostructured metallic current collector. The free-standing coaxial hybrid with ordered copper oxide array architecture as the core have the privilege of effective electronic transport due to the direct connection to the substrate, fast ion transport due to the existence of space between; which allow easy penetration of the electrolyte and solely electroactive building blocks.⁶² Furthermore, the open space between the well aligned ordered nanostructure accommodates the volume expansion during lithiation/delithiation and improves cycling stability.⁶⁰ Additionally, this hybrid system has the advantage that all components can undergo electrochemical reaction with lithium and contribute to capacity.

2.1.3 Selection of secondary phase decorating the CuO needles

As discussed, copper oxide was selected as the appropriate scaffold for growth of coaxial metallic compound hybrids. In the next stage, by smart selection of the material decorating the CuO scaffold and careful engineering of the hybrid nanostructures, integration of the properties and achievement of an electrode with high energy density, long term stability and good rate capability would be possible.

Antimony (Sb) is a promising anode material with high electrical conductivity which undergoes alloying reaction upon interaction with lithium during the charge/discharge process. This electrode has been widely investigated as anode due to its high theoretical capacity and better safety compared to the commercially available graphite anode. However, Sb experiences huge volume changes and stress build up upon charge/discharge, which can lead to rapid capacity decay.^{9, 103, 104} It can be anticipated that by fabrication of free-standing Sb-CuO hybrids, by direct growth of highly conductive Sb on several micron length Cu(OH)₂ nanoneedle arrays allows higher material loading and electronic conductivity, as well as better structural support during charge/discharge cycles resulting in improved electrochemical properties.

Germanium (Ge) is an important alloying anode with high theoretical capacity (1600 mAh/g) in its fully lithiated form (Li_{4.4}Ge) and very high diffusion rate. However, as explained this electrode suffers from huge volume change which causes fast capacity decay. Although application of free-standing 1D Ge nanowires grown by CVD method have proven to be an effective strategy to improve electrochemical problems, the unsafe GeH₄ gas used for the material CVD growth and the short wire length which is usually less than 1 μm length limits its practical application.⁵¹ In Ge hybrid electrode with high theoretical capacity, direct CVD growth of Ge on Cu(OH)₂ nanoneedles using Ge powder as source enables a safer and more practical growth procedure. The template based growth of Ge on several micron length copper oxide nanoneedles also allows higher material loading and better structural support during charge/discharge cycles. The contact is also improved, enhancing electrical conductivity. Ge shell affords high Li⁺ intake, as well as high diffusion rate. Additionally, the short diffusion

distances for both Lithium ion and electron transport and the open interspaces between the core-shell nanowires allows quick infiltration of electrolyte into the structure, partially accommodating the volume expansion during lithiation and alleviating material loss. As a result, the kinetic performance of the electrode is improved and the lithiation/delithiation is performed much more effectively.^{23, 105}

Iron oxide is an important conversion material; which is extensively studied as LIB anodes because of their environmentally friendliness and low cost. Fe_3O_4 electrode has a high theoretical capacity, but suffers from poor cycling stability (especially at high rates) and poor rate capability. In Fe_3O_4 -CuO hybrid the smart selection of two compatible components with promising properties and their intelligent integration to unique hierarchical architectures can result in a hybrid electrode with all attractive characteristics; such as, low cost and abundant nature, high material loading, 3D architecture with open porosity, high energy and power density. In this hybrid the free-standing ultra-fast CuO nanoneedle arrays as core provides 1D electronic pathway, structural spacer and superior rate capabilities.¹⁰⁶ On the other hand, Fe_3O_4 nanocrystals with high theoretical capacity grown directly on CuO nanoneedles enable achievement of high specific capacities. Additionally, binder-free ordered array architectures have the advantage of effective electrical transport due to the direct connection to the substrate and fast ion transport due to the existence of voids that allow the easy penetration of the electrolyte.⁶²

2.2 *Scope*

There has been huge effort to develop the next generation lithium ion batteries which can meet the requirements of the emerging portable electronics and electric vehicles. However, finally it came to this point that limited by the intrinsic properties, e.g. low electrical conductivity, slow lithium ion diffusion, the single component nanostructure electrodes alone may not meet the high expectations.^{56, 57} Therefore, application of hybrid nanomaterials is being actively pursued in recent years.

Based on the above reports and primary investigation, copper oxide was selected as the suitable scaffold and core for growth of coaxial metallic compound hybrids. In order to evaluate the capability of copper oxide as scaffold and core in metallic compound hybrids, free-standing copper oxide nanoneedles arrays will be developed and electrochemically investigated in chapter three. By smart selection of the components and careful engineering of the hybrid nanostructures, integration of the properties and achievement of an electrode with high energy density, long term stability and good rate capability would be possible.

Antimony is a promising alloying anode material with high theoretical properties (660 mAh/g) and high conductivity, but low cycling stability. It can be anticipated that in Sb-CuO hybrid, the high conductivity of Sb improves the electronic conduction and rate capability of the hybrid, while the highly stable CuO core improves the cycling stability. Initially in chapter four, binder-free Sb nanostructures will be developed and electrochemically investigated. Then, Sb-CuO hybrid will be fabricated using $\text{Cu}(\text{OH})_2$ nanoneedle arrays as scaffold for deposition of Sb nanocrystals. Finally, the electrochemical properties of the developed anodes will be compared and influence of application of $\text{Cu}(\text{OH})_2$ as scaffold will be investigated.

Next, Germanium (Ge) with very high theoretical capacity (1600 mAh/g) and 400 times higher diffusion rate than Si; as the material with the highest theoretical capacity was selected as the suitable candidate to integrate with copper oxide to form coaxial Ge- Cu_2O hybrid. By application of a combination of electrochemical and CVD growth method, free-standing, core-shell Ge- Cu_2O hybrids will be developed (chapter five). In this section, the influence of interface and the synergetic effects between the core and shell of a hybrid with alloying and conversion building blocks will be thoroughly explored. To highlight the importance of electrode architecture and application of core-shell hybrid the electrochemical properties are further compared to Ge nanoparticles electrode.

Fe_3O_4 is another attractive conversion material with 1007 mAh/g theoretical capacity, low cost and environmentally friendly nature, which is considered as an important candidate for practical application. In chapter six, two types of free-standing Fe_3O_4 -CuO conversion hybrids with

coaxial and 3D interconnect nanostructure will be developed by a two-step template free electrochemical technique.⁹³⁻⁹⁶ The electrochemical properties of the two hybrids will be investigated and compared with their individual components at high cycling rates. The influence of hybrid architecture and the synergetic effects of the electrochemical properties will also be examined in details.

3 Fabrication of CuO nanoneedle arrays as scaffold for growth of lithium ion battery hybrids

3.1 Overview

CuO is an attractive candidate for the substitution of graphite as the conventional anode currently used in most lithium ion batteries. The low cost, environmental abundant nature, better safety compared to graphite and superior theoretical capacity (670 mAh g⁻¹) are the advantages of CuO anode. However, the copper anode suffers from huge and uneven volume change, e.g. ~ 174% during lithiation/delithiation. This results in low cycling capacity and large capacity decay. Nanostructuring is an important method to improve the electrochemical properties of LIB electrodes. Application of free-standing 1D nanoarrays electrodes, which is composed of one-dimensional nanoarrays directly grown on conductive substrates, has proven to be an effective approach. In this architecture, the free-standing 1D nanostructure can act both as active material and conductive scaffold.²⁹ This 1D nanostructured electrode possess distinct properties, such as improved electronic transport path, due to the direct connection of individual nanoarrays to the substrate, fast Li⁺ migration across the interface and sufficient free space between the individual nanoarrays which alleviates the large volume change during lithiation-delithiation cycles.³⁶

Fabrication of different nanostructured CuO and its application as LIB has been reported in the literature. CuO thin films were fabricated by using a spray pyrolysis method. Copper acetate was utilized as precursor, while stainless steel was used as substrate. According to AFM images, the average particle size ranged from 30 to 160 nm. The CuO $\rightleftharpoons$ Cu₂O $\rightleftharpoons$ Cu peaks was observed in the discharge STEP curves. At 0.2 C, the electrode exhibited capacity values of over 625 Ah kg⁻¹ for more than 100 cycles. This capacity, which involves a CuO $\rightleftharpoons$ Cu reversible electrochemical reaction was reported 50% higher than that of bulk CuO. The good adhesion of the active material to current collector and the nanometer size of the particles is considered the key factors for the enhanced electrochemical activity.¹⁰⁷ Uniform Cu₂O nanocubes were synthesized by a polyol process. By controlled oxidation of Cu₂O nanocubes, CuO hollow cubes, hollow spheres, and urchin-like particles were produced using a sequential dissolution-precipitation process.

Among the different morphologies the CuO urchin-like particles demonstrated the best electrochemical performance as LIBs. At a current density of 150 mA/g (0.23 C), the urchin-like particles maintained a charge capacity of over 560 mAh/g for up to 50 cycles, whereas under the same conditions the hollow cubes and spheres declined gradually to 79 and 91 mAh/g, respectively. The superior performance of urchin-like particles may be attributed to the structural robustness of the thick branches and the stability of the large single-crystalline domains. The authors believe that although the hollow structures are initially active, but during the reduction-oxidation reaction and the large strain build up, the hollow structures become unstable and fails. The rate performance of these nanostructures was not investigated in this work.¹⁰⁸ In another interesting work, using a simple solution-immersion method and heat treatment, CuO nanofibers with network-like architectures were produced directly on copper substrate. A stable reversible capacity of 560 mAh g⁻¹ was delivered after the second cycle at a current density of 0.2 mA cm⁻², and the CuO electrode kept its capacity at 520 mAh g⁻¹ after cycling for 50 cycles, exposing good cycling stability. The resulted CuO film also exhibited good rate capability, delivering 450 mAh g⁻¹ at 1C, and 300 mAh g⁻¹ at 3C. This result indicates that the CuO electrode exhibits good rate performance in lithium ion batteries. The authors suggest that binder free nature of the fabricated electrode and the direct connection of active materials to current collector is the main reason for the enhanced electrochemical behavior.¹⁰⁹ Another interesting morphology of CuO is flower-like architectures, which was obtained by simple immersion of copper foils in an aqueous solution of NaOH/SDS, followed by heat treatment. At a current density of 0.15 mA/cm², a stable reversible capacity of about 600 mAh g⁻¹ can be achieved in the second cycle, which decays gradually to 550 mAh/g after 50 cycles. The rate capability of this structure was also quite impressive, delivering a stable capacity of 341 mAh g⁻¹ even at 4C rate. The authors believe that the good electrochemical performance mainly originates from the short diffusion path, the large contact area and direct growth of the flower-like nanostructures on current collector.¹¹⁰ Recently, super-rate capabilities have been reported for nanoarchitected copper oxide nanowire arrays electrodes. CuO pine needle like (PNL) arrays deliver the highest rate capacity of 545.9 and 492.2 mAh/g at 15 and 20C rates.³⁶ The super-rate properties is

explained based on the unique PNL array structure, which provides free space for the migration of lithium ions and alleviate the large variation in volume.

In the presented thesis, development of free-standing, coaxial, core-shell hybrids with superior electrochemical properties as LIB anodes is pursued. In this chapter free-standing copper oxide nanoneedles will be developed and electrochemically investigated, in order to evaluate their capability for application as scaffold and core in metallic compound hybrids.

3.2 Experimental details

3.2.1 Electrochemical fabrication of CuO nanoneedle arrays

All reagents used were purchased from SIGMA Aldrich and used as received, without any further purification. Millipore water was used in all experiments. Cu(OH)₂ nanoneedle arrays were fabricated on copper substrate by a fast and simple electrochemical anodization of battery grade copper foil. Prior to the experiment the copper foil was washed carefully in acetone, ethanol diluted HCl solution and deionized water to remove any impurities and oxides. A one compartment three electrode cell with copper foil, stainless steel sheet and Ag/AgCl reference electrode was used as the working, counter and reference electrode. The electrolyte was a 1 M NaOH solution which was deaerated by argon gas for 30 minutes prior to experiment. The anodization was carried out at constant current density of 1.5 mA/cm² for 700 second in room temperature to fabricate pale blue Cu(OH)₂ films. The thin films were then rinsed with water and dried in oven. To test the electrochemical properties, Cu(OH)₂ films were annealed at 120°C for 2 h and then maintained at 200°C for 2 h to prepare free-standing CuO electrodes.

3.2.2 Materials characterization

The as-prepared CuO and Cu(OH)₂ thin films on Cu substrates were directly used for SEM and XRD measurements. The thin film morphology was examined using a field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The elemental compositions of the samples

were characterized with energy-dispersive X-ray spectroscopy (EDX) which is attached to the SEM instrument. Crystallographic data of the specimen was collected using a thin film Shimadzu Shimadzu 6000 X-ray diffractometer and a powder X-ray diffractometer (Bruker, Cu KR radiation with $\lambda = 1.5406 \text{ \AA}$). The determination of the phase was done using the Match software. For TEM characterization, the samples were scratched from the substrate and added to ethanol. After ultrasonication for 2-10 mins, the solution was drop cast onto carbon coated 200 mesh Cu grids. HRTEM and EDX were obtained by using a JEOL 2010 system operating at 200kV.

3.2.3 *Electrochemical measurements*

The coin cells were assembled inside an Ar-filled glove box with oxygen and moisture content less than 1.00 ppm. Coin cells were fabricated using CuO nanoneedle arrays. The free-standing electrodes were used directly as working electrode without addition of any binder. The lithium foils were used as counter/reference electrodes and the electrolyte was a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). For the electrochemical measurement coin battery cells were installed and galvanostatically tested using a NEWARE battery tester (vs. Li/Li⁺).

3.3 *Electrochemical fabrication of CuO nanoneedle arrays*

Figure 3.1A-B displays the scanning electron microscopy (SEM) images of nanoneedle arrays of copper hydroxide on Cu foil, anodized at constant current density of 1.5 mA/cm² for 700 seconds. The x-ray diffraction (XRD) pattern (see Figure 3.1F) demonstrates the formation of Cu(OH)₂ with orthorhombic phase (ICDS No. 68459). It can be observed in the SEM images that the Cu(OH)₂ nanoneedles are free-standing and have grown densely and uniformly on the copper substrate. The nanoneedles have over 6 μm length and diameter in the range of 50-100 nm. The detailed microstructure of the anodized Cu(OH)₂ nanoneedles is demonstrated in TEM and HRTEM images shown in Figure 3.1C-E. As can be seen the anodized Cu(OH)₂ nanoneedles are highly mesoporous with fine 1-2 nm pores spreading through the Cu(OH)₂ nanoneedles (see Figure 3.1C-D). The high resolution TEM image displays the (002) plane of orthorhombic

$\text{Cu}(\text{OH})_2$ with 0.26 nm interfringe spacing (ICDS No. 68459) (see Figure 3.1E). The selected area electron diffraction (SAED) pattern can be also indexed to orthorhombic $\text{Cu}(\text{OH})_2$ crystal structure which is consistent with the XRD results (see inset in Figure 3.1E). The nanoneedles have single crystalline nature and grow in the [100] direction. The growth of $\text{Cu}(\text{OH})_2$ nanoneedle arrays on the Cu substrate corresponds to a simple anodization process as follows:

Figure 3.1 (A-B) SEM, (C-D) TEM, (E) HRTEM, SAED pattern and (F) XRD pattern of $\text{Cu}(\text{OH})_2$ nanoneedle arrays fabricated by anodization of high purity Cu foil at 1.5 mA/cm^2 for 700 second.

After heat treatment of copper hydroxide at 120°C and 200°C for 2 hours each, the $\text{Cu}(\text{OH})_2$ is transformed to pure monoclinic CuO phase (ICSD No. 31059) (see Figure 3.2A). Based on our observation and recent report on growth mechanism of such $\text{Cu}(\text{OH})_2$ nanoneedle arrays, at the start of anodization process some copper hydroxide micro-rods grow which act as nucleates for further growth of $\text{Cu}(\text{OH})_2$ crystals. With increase in anodization time the micro-rods crack and start to grow in the preferred [100] orientation until finally the complete nanoneedle arrays are formed on copper substrate.³⁶ The interesting fact about this structure is that based on TEM study performed on different $\text{Cu}(\text{OH})_2$ thin films, it was observed that some of the $\text{Cu}(\text{OH})_2$

nanoneedles have a Cu core which can be clearly seen in TEM images of several copper oxide nanoneedles (see Figure 3.2B-D). This is probably because the process of oxidation of the copper is incomplete, resulting in a structure with copper core and Cu(OH)₂ shell.

Figure 3.2 (A) XRD of Cu(OH)₂ nanoneedle arrays fabricated by anodization of high purity Cu foil at 1.5 mA/cm² for 700 second, (B-D) TEM Of Cu/Cu(OH)₂ core-shell fabricated by incomplete anodization of high purity Cu foil at 1.5 mA/cm² for 700 second

3.4 Electrochemical evaluation of CuO nanoneedle arrays

In order to evaluate the Li-ion storage capabilities of the CuO nanoneedle structures a series of electrochemical studies were performed based on the half-cell configuration. Here, the CuO nanoneedle structure grown on copper substrate was directly used as the anodes without addition of any binder. Figure 3.3A displays the cyclic voltammograms (CVs) of the first to third cycles of CuO nanoneedle arrays fabricated by anodization of copper foil in a 1M NaOH solution at 1.5 mA/cm² for 700 s. The observed redox peaks in the charge and discharge cycles were in agreement with previous reports on CuO.^{29, 111} The corresponding reaction can be presented as follows¹¹¹:

In the cathodic cycle the three peaks correspond to the reduction of CuO to an intermediate phase of copper oxide presented as $Cu_{1-x}^{II}Cu_x^I O_{1-x/2}$, and then to Cu_2O and finally to Cu and Li_2O . Additionally, the two wide peaks in the anodic scan of CuO correspond to the formation of Cu_2O and CuO respectively. As can be observed in the Figure 3.3A; the position of anodic peaks in the subsequent cycles is almost unchanged, while the cathodic peaks are shifted to higher potentials. Figure 3.3B illustrates the charge/discharge voltage profiles of the CuO nanoneedle arrays electrode tested at 674 mA/g (1C). In the charge and discharge curves the the potential plateaus were consistent with the CV results in both first and subsequent cycles. The insertion process in the first cycle gave a discharge capacity of 835 mA h/g and a subsequent charge capacity of 553 mA h/g, this results gives an initial Coulombic efficiency of 66%. This is not surprising, since a huge initial irreversibility capacity loss is reported for many conversion anodes including CuO.^{29, 105, 112} This irreversible capacity loss may be assigned to formation of solid electrolyte formation (SEI) and electrolyte decomposition.^{107, 113} In the second cycle, the discharge capacity reaches 561 mA h/g with a corresponding charge capacity of 547 mA h/g, leading to a high Columbic efficiency of 97.5%. The sample exposed perfect cycling stability and remained reversibly stable for 200 cycles without showing any capacity fade; delivering an excellent discharge and charge capacity of 559 and 554 mAh/g respectively with Coulombic efficiency of 99.2% at the 200th cycle (see Figure 3.3C).

The rate capability of fabricated CuO nanoneedle arrays was further examined by performing discharge-charge rate capability of CuO nanoneedles from 134.8 mA/g (0.2C) to as high as 33700 mA/g (50C) (see Figure 3.3D). At 0.2C there is again a high irreversible capacity of 870 mAh/g in the initial cycle but from the second cycle a stable capacity of 575 mAh/g could be achieved. With increase in rate to 0.5C, 1C, 2C, 5C and 10C still highly reversible capacities of respectively 555, 547, 496, 417 and 325 mAh/g with more than 99% Coulombic efficiencies

could be obtained. This demonstrates the high stability of CuO nanoneedle arrays in high rate cycling rates. Even with increase in rate to 15C, 20C and 50C corresponding to huge currents of 10110, 13480 and 33700 mA/g discharge capacities of respectively 239, 161 and 133 mAh/g could be delivered. With reduction of charge/discharge rate to 0.2C the structure remained stable and a very stable capacity of 600 mAh/g was obtained in the second cycle.

Figure 3.3 (A) Cyclic voltammograms (CVs) of the first to third cycles, (B) Charge/discharge voltage profiles at a current of 674 mA/g (1C), (C) Charge/discharge cycling performance at a current of 674 mA/g (1C), (D) Plot of the discharge and charge capacity vs. cycle number at various C rates between 0.05-3.0 V (vs Li/Li⁺) of CuO nanoneedle arrays fabricated by anodization of copper at 1.5 mA/cm² for 700 between 0.05-3.00 V (vs Li/Li⁺).

In order to further examine the stability of CuO nanoneedle arrays structure, lithium ion battery cells cycled at 1C rate for 100 cycles were opened in glove box and studies using SEM (see Figure 3.4). It can be observed that CuO have retained their nanoneedle morphology and although some agglomeration can be observed, breakage and deformation is not visible and CuO nanoneedles free-stand individually on the substrate. However, the diameters of nanoneedles have increased to about 200 nm which is a result of reaction with lithium.¹²⁶

Figure 3.4 (A-B) SEM images of CuO nanoneedle arrays after Charge/discharge at current of 674 mA/g (1C) between 0.05-3.00 V (vs Li/Li⁺) for 100 cycles.

electron microscopy paper investigated the reactivity of CuO particles with lithium ions. This paper reports the continuous existence and thickening of SEI layer while cycling which could be the reason responsible for the good reversibility and high Coulombic efficiency after the first cycle.¹¹⁴ The direct growth of CuO nanoneedles on the Cu substrates improves the contact and enhances electrical conductivity, while the free space between helps buffer the strain caused by the huge volume swing. Also, the mesoporous nature of single CuO nanoneedles enhances surface to volume ratio and reduces the diffusion distance.^{23, 105} The core-shell Cu/CuO nanoneedle fabricated by incomplete anodization of copper substrate also provides a good electronic pathway for fast electron transport and superior rate capabilities. Additionally, the residual copper nanoparticles of the incomplete conversion reaction with lithium behaves as a good electron pathway and improves the electronic conductivity of the anode material, resulting in outstanding cycling stability and rate capability.¹⁰⁶

3.5 Conclusion

Copper oxide is an important transition metal oxide with high theoretical capacity, high safety, inexpensive and environmentally abundant nature. Herein, uniform, well aligned arrays of CuO nanoneedles were fabricated on copper substrate by a simple anodization process. CuO nanoneedle arrays demonstrated excellent performance in high current densities delivering an excellent discharge capacity of 559 mAh/g with Coulombic efficiency of 99.2% at 1 C rate after

200 cycles. The electrode also demonstrated perfect rate capabilities when tested to up to 50 C. The residual copper nanoparticles of the incomplete conversion reaction with lithium behaves as a good electron pathway and improves the electronic conductivity of the anode material, resulting in outstanding cycling stability and rate capability. Based on the above observation, copper oxide was selected as a suitable scaffold for fabrication of coaxial hybrid anodes.

4 Fabrication attempt of Sb-CuO hybrid anodes for lithium ion batteries

4.1 Overview

Antimony is a promising anode material which undergoes alloying reaction upon interaction with lithium during the charge/discharge process. This electrodes has been widely investigad as anode due to its high theoretical capacity and better safety compared to the commercially available graphite anode. However, as explained in the literature review, Sb experiences huge volume changes and stress build up upon charge/discharge, which can lead to rapid capacity decay.^{9, 103, 104} To overcome this problem different strategies such as nanostructuring¹³⁹ and application of buffering matrix by using Sb based intermetallic compounds has been actively pursued, e.g. Co-Sb^{103, 115, 116}, Mn-Sb.⁴⁷

Hybrids with superior electrochemical performance fabricated by smart assembling of building blocks has been reported in the literature.^{91, 92} Coaxial free-standing hybrid with ordered array architecture have the advantage of effective electronic transport due to the direct connection to the substrate and fast ion transport due to the existence of void between which allow easy penetration of the electrolyte.⁶² Furthermore, the open space between the well aligned ordered nanostructure accommodates the volume expansion during lithiation/delithiation and improves cycling stability.⁶⁰ Usually multi step fabrication procedures are used to fabricate the ordered hybrid electrodes and the growth of the second components is usually aided by interfacial reactions.

In this section of the thesis, Cu(OH)₂ nanoneedle arrays discussed in chapter 4 will be used as scaffold to grow Sb-CuO hybrids. CuO is an important transition metal oxide with quite high theoretical capacity (674 mAh/g). It was observed in chapter 4 that well aligned arrays of CuO can expose have high rate capability and demonstrate excellent performance in high current densities. It is believed that the residual copper nanoparticles of the incomplete conversion reaction with lithium behaves as a good electron pathway and improves the electronic

conductivity of the anode material, resulting in outstanding cycling stability and rate capability.¹⁰⁶ In Sb-CuO hybrid, direct growth of Sb on several micron length CuO nanoneedles allows higher material loading and better structural support during charge/discharge cycles. Additionally, application of simple electrochemical techniques in open atmosphere and room temperature conditions provides a simple, cheap and practical growth procedure.

4.2 Experimental details

4.2.1 Electrochemical deposition of interconnected Sb nanoplates

The electrodeposition of antimony was carried out in a three-electrode cell using a Ch 1200A potentiostat/galvanostat instrument. A Teflon cell composed of three parts were designed and fabricated. The copper foil is placed on top of the bottom flat disc and the middle part which is cup shape contained with a circle hole at bottom is placed on top. The top part which is another flat disk with holes for the three electrodes is placed on top and all three pieces are screwed together. O-rings are used to seal the gaps and prevent electrolyte leakage. Just before deposition the electrolyte is poured inside through one of the top holes and the electrodes are put in place. The schematic drawing of the cell is illustrated in Figure 4.1. A platinum mesh with $1.5 \times 1.5 \text{ cm}^2$ in size was used as a counter-electrode and an Ag/AgCl electrode was used as the reference electrode. The distance between working and counter electrodes was fixed at 2.0 cm. The working electrodes were chosen from high-purity metallic foils (99.99%). Prior to electrodeposition, the copper substrate were cut into $1 \times 1 \text{ cm}^2$ pieces and was rinsed with acetone and distilled water to remove impurities. The mass of each substrate was measured accurately before and after deposition for capacity calculation.

To deposit antimony a solutions which contained 0.42 M potassium antimony tartrate trihydrate ($\text{K}_2(\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2) \cdot 3\text{H}_2\text{O}$) and 0.265 M tartaric acid was used. Pulse galvanostatic electrodeposition with 6.8 mA current and 0.05 seconds on and off time for a total time of 300 seconds was applied to directly deposit Sb on copper substrate.

Figure 4.1 Schematic drawing of the Teflon cell designed and fabricated in house.

4.2.2 *Electrochemical fabrication attempt of free-standing Sb-CuO hybrids*

A two step electrochemical process was used to prepare the Sb-CuO hybrid. First, the $\text{Cu}(\text{OH})_2$ films were prepared using anodization process discussed in 3.2. In the second stage $\text{Cu}(\text{OH})_2$ nanoneedle arrays were used as working electrode. To deposit antimony a solutions which contained 0.42M potassium antimony tartrate trihydrate ($\text{K}_2(\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2) \cdot 3\text{H}_2\text{O}$) and 0.265M tartaric acid was used. Pulse galvanostatic electrodeposition with 6.8 mA current and 0.05 seconds on and off time for a total time of 100 seconds was applied to directly deposit Sb on copper substrate. Finally, fabricated samples were annealed at 120°C for 2 h and then maintained at 180°C for 2 h to prepare free-standing Sb-CuO hybrid electrodes.

4.2.3 *Materials characterization*

The as-prepared thin films on metallic substrates supported with glass were directly used for SEM and XRD measurements. The Sb based morphology was examined using a field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The elemental compositions of the samples were characterized with energy-dispersive X-ray spectroscopy (EDX) which is attached to the SEM instrument. Crystallographic data of the specimen was collected using a thin film Shimadzu Shimadzu 6000 X-ray diffractometer and a powder X-ray diffractometer (Bruker, Cu

KR radiation with $\lambda = 1.5406 \text{ \AA}$). The determination of the phase was done using the Match software. For TEM characterization, the Sb based samples were scratched from the substrate and added to ethanol. After ultrasonication for 2-10 mins, the solution was drop cast onto carbon coated 200 mesh Cu grids. HRTEM and EDX were obtained by using a JEOL 2010 system operating at 200kV.

4.2.4 Electrochemical measurements

Assemble of the coin-type battery cells were performed in an Ar-filled glove box with moisture and oxygen lower than 1.00 ppm. The working electrode was Sb, and Sb/Cu₂Sb/Cu electrodes. Li foil was used both as the counter and reference electrodes while 1M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) was used as the electrolyte.

In order to distinguish the redox reactions, cyclic voltammograms (CVs) was performed on coin cells at a scanning rate of 0.5 mV/s using the potentiostat/galvanostat Ch 1200A instrument. The scanning was performed for two complete cycles. All of the coin cells were tested using a NEWWARE battery tester galvanostatically between 0.0 V and 2.0 V (vs. Li/Li⁺) at a current density of 100 mA/g.

4.3 Electrochemical fabrication attempt of Sb-CuO hybrids

4.3.1 Electrodeposition of Sb nanoplates

Figure 4.2A-B displays the scanning electron microscopy (SEM) images of 1-1.5 μm antimony nanoplate bundles on Cu foil. Each bundle is made of numerous antimony plates stacked together while growing perpendicular to the substrate. Each plate is about 150-250 nm in diameter with 20-40 nm thickness. The x-ray diffraction (XRD) pattern (see Figure 4.2C) of the as-prepared Sb thin films confirms the formation of rhombohedral Sb phase (ICSD No.55402). The detailed microstructure of the Sb nanoplates is demonstrated in TEM and HRTEM images shown in Figure 4.2D-F. As can be seen the Sb nanoplates bundles are composed of several plates stacked

together from the sides (see Figure 4.2D). Each plate is highly mesoporous with fine 1-2 nm pores (see Figure 4.2E). The high resolution TEM image displays that Sb plates have polycrystalline nature with grain size in the range of 5-10 nm. It was also observed that exposed lattices have an interfringe spacing of 0.23 nm, corresponding to the $(\bar{1}14)$ plane of rhombohedral Sb phase (ICSD No.55402) (see Figure 4.2F). This indicates that the crystals grow mainly in the $[\bar{1}14]$ direction.

The electrodeposition reactions which involves electrodeposition of antimony and a simultaneous release of tartrate can then be demonstrated as follows¹¹⁷:

Figure 4.2 (A-B) SEM, (C) XRD pattern (D-E) TEM and (F) HRTEM pattern and Sb nanoplates fabricated by galvanostatic pulse electrodeposition by application of -6.8 mA current for 300 s with 0.05s on and off time.

Figure 4.3 SEM images of Sb nanoparticles fabricated by galvanostatic electrodeposition by application of -6.8 mA for 300 s.

Such preferred growth direction has been reported repeatedly in the literature for materials with hexagonal or rhombohedral crystal structures. It is also believed that the application of pulsed current is another reason for the preferred growth direction of Sb crystals, since the application of constant current of -6.8 mA resulted in formation of nanoparticles with 50-80 nm diameters (see Figure 4.3). By application of pulse a 0.05 s relaxation time is provided for the Sb^{3+} ions to recover and the crystal to grow in its preferred orientation, making the preferred growth orientation more obvious. This observation is also in good agreement with the literature.¹¹⁸

4.3.2 Electrochemical fabrication attempt of free-standing Sb-CuO hybrid

Fabrication of Sb-based hybrid was performed in two steps. In the initial step $\text{Cu}(\text{OH})_2$ nanoneedle arrays were fabricated by anodization of copper foil as discussed. Then in the second step, $\text{Cu}(\text{OH})_2$ thin film was utilized as substrate and pulsed galvanostatic electrochemical process discussed in chapter 5 was used to grow Sb. Finally, the fabricated hybrid was heat treated at 120°C and 200°C for 2 hours each.

Figure 4.4 SEM of Sb-Cu₂Sb hybrid anode fabricated by galvanostatic pulse electrodeposition of -6.8 mA current with 0.05s on and off time for (A-B) 200 s, (C-D) 300 s.

Figure 4.4A-B displays the scanning electron microscopy (SEM) images of Sb based hybrid fabricated by pulse electrodeposition for 200 seconds. It can be observed that the film is composed of numerous Sb nanoplates surrounding the nanoneedles. Sb plates are stacked together while growing around the wires. Each plate has about 150-250 nm diameter with 20-40 nm thickness. With increase in the total deposition time (see Figure 4.4C-D) the amount of Sb nanoplates increase and the Sb thickness increases reaching close to the tip of nanoneedles. At first it was assumed that the wires are CuO, but according to the x-ray diffraction (XRD) pattern (see Figure 4.5) it was proven otherwise. According to the XRD study the formation of rhombohedral Sb phase (ICSD No.55402) was confirmed, but there was no peaks belonging to any type of copper oxide. The additional peaks could be matched perfectly with tetragonal Cu₂Sb phase (ICSD No.42323).

Figure 4.5 XRD of Sb based hybrid anode fabricated by galvanostatic pulse electrodeposition of Sb at -6.8 mA current with 0.05s on and off- time for 200 s on free-standing Cu(OH)₂ nanoneedle arrays.

Formation of Cu₂Sb and absence of copper oxide can be explained as follows. As explained in the previous section application of a reductive pulse current results in electrodeposition of antimony based on the following reactions¹¹⁷:

However, simultaneous to Sb reduction, application of the reductive current can result in reduction of copper hydroxide and formation of Cu based on the following reactions:

By application of heat treat treatment at 120°C for 2 h and then at 180°C for 2 h copper and antimony are diffused together and Cu₂Sb is formed.

Figure 4.6 TEM and HRTEM of (A) Sb-Cu₂Sb/Cu hybrid (B-C) Sb of Sb-Cu₂Sb/Cu hybrid, (D-F) Cu₂Sb/Cu of Sb-Cu₂Sb/Cu hybrid, fabricated by galvanostatic pulse electrodeposition of Sb on Cu(OH)₂ nanoneedle arrays at -6.8 mA current with 0.05s on and off time for 200 s.

Based on the TEM observation shown in Figure 4.6A both Sb plates and core-shell nanostructures were observed. The Sb nanoplates were in a large size range between 30-150 nm (see Figure 4.6A-B) and with polycrystalline nature and highly mesoporous structure. The pore distribution was un-uniform with small round shape pores in the size range of 1-2.5 nm in the middle and stretched pores with a wide size range of 3-14 nm at the sides. The Sb nanocrystallites size also had a wide range of 5-15 nm. The exposed lattices of Sb had an interfringe spacing of 0.23 nm, corresponding to the ($\bar{1}14$) plane of rhombohedral Sb phase (ICSD No.55402) (see Figure 4.6C). The wires observed in the TEM study all had core-shell structure with 50-100 nm core and 30-70 nm shell (see Figure 4.6D-E). Based on the discussion regarding the growth of Cu₂Sb, it was assumed that the core-shell nanowires had a Sb-Cu₂Sb composition. Similar pore distribution to Sb plates was observed in the Cu₂Sb shell with round pores close to the interface and stretched pores closer to the edge with length as high as 8 nm (see Figure 4.6D). HRTEM studies indicate that shell is also polycrystalline with 2-5 nm nanocrystallites (see Figure 4.6C-F). The exposed lattices had an interfringe spacing of 0.2 nm

and 0.25 nm respectively corresponding to the (112) and (111) plane of tetragonal Cu₂Sb phase (ICSD No.42323) (see Figure 4.6F).

4.4 *Electrochemical evaluation of Sb/Cu₂Sb/Cu hybrids*

4.4.1 *Electrochemical properties of interconnected Sb nanoplates*

Electrochemical studies were performed based on the half-cell configuration. Here, the Sb nanoplates grown on copper substrate were directly used as the anodes without addition of any binder. Figure 4.7A displays the cyclic voltammograms (CVs) of the first and second cycles of Sb nanoplates. The observed redox peaks in the charge and discharge cycles were in agreement with previous reports on Sb.^{119, 120} The corresponding reaction can be presented as follows:

According to the above reactions when the voltage is reduced, the Sb nanocrystals first undergo a reaction with 2 Li⁺ ions and then intakes another Li⁺ ion. During discharging, at around 1.1V the Li₃Sb phase is disappeared due to the extractions of the 3 Li⁺ ions and Sb phase is reformed.

Figure 4.7B illustrates the charge/discharge voltage profiles of the Sb nanoplates tested at 133 mA/g (0.2C). In the charge and discharge curves the potential plateaus were consistent with the CV results in both first and second cycles. The alloying process in the first cycle gave a discharge capacity of 827 mA h/g and a subsequent charge capacity of 631 mA h/g, resulting in an initial Coulombic efficiency of 76%. As observed the initial capacity is higher than the theoretical value of 660 mAh/g. However such behavior is repeatedly reported for Sb and other alloying materials in the literature and can be explained based on the SEI formation in the initial cycle.^{119, 121} The initial irreversible capacity loss of 24% can also be assigned to the formation of solid electrolyte formation (SEI) and electrolyte decomposition.^{107, 113} In the second cycle, the discharge capacity reaches 658 mA h/g with a corresponding charge capacity of 619 mA h/g, leading to a high Columbic efficiency of 94%. The sample exposed good cycling stability and

remained reversibly stable until the 9th cycle, beyond which the capacity dropped abruptly until the 20th cycle, which it delivered 141 and 123 mAh/g discharge and charge capacity respectively with low Coulombic efficiency of 87% (see Figure 4.7C). Thereafter, the capacity decay continued gradually while retrieving its Coulombic efficiency, to finally reach 34 mAh/g discharge capacity with 98.5% Coulombic efficiency in the 70th cycle. The rapid decay in capacity in the initial cycles is also reported in other works in literature.^{119, 120} The reason for such rapid capacity drop in the initial cycles can be explained base on the huge volume change during the lithiation process which leads to stress build up and crack formation in the structure which will result in pulverization and loss of active material.¹²¹ Although nanostructuring of the material helps achieve high initial capacity and stabilize the capacity in the initial cycles, but this capacity cannot be maintained and further improvement of the structure is required to overcome the huge stress build up.⁴²

The rate capability of fabricated Sb nanoplates was also examined by performing discharge-charge rate capability from 132.8 mA/g (0.2C) to 3300 mA/g (5C) (see Figure 4.7D). At 0.2C there is again a high irreversible initial discharge capacity of 877 mAh/g with 27% irreversible capacity loss. In the second cycle although the capacity continued to fade but the Coulombic efficiency is increased to 96%. In overall the rate performance of Sb nanoplates can be considered very poor. With increase in cycle number and rate the delivered capacity continued to decay continuously. With increase in rate to 0.5C, 1C, 2C, 5C fading capacities of respectively 603, 429, 227 and 80 mAh/g with Coulombic efficiencies of higher than 94% could be obtained. With reduction of charge/discharge rate to 0.2C the capacity could not be recovered and only 202 mAh/g discharge capacity could be delivered which continued to fade in the subsequent cycles. The reason for such poor electrochemical properties especially at high cycling rate can be related to the intrinsic properties of Sb and the huge volume swing imposed on the structure during lithiation which results in pulverization of the electrode and fast capacity decay. Although the direct growth of Sb nanoplates on the cu substrates and binder free electrode fabrication improves the contact and enhances electrical conductivity, however the compactness of the nanostructure and lack of open space makes it hard for the strain to be relaxed during the cycling,

resulting in crack formation and material loss which will lead to poor cycling stability and rate capability.^{114 106} Crack formation and the breakage of active material is so severe that when the cell was opened after cycling to investigate the active material after lithiation, obvious cracks could be seen in the film and some of the active material were detached from the current collector. To improve the electrochemical properties of the Sb electrodes it is essential that other strategies are employed to overcome the discussed problems.

Figure 4.7 (A) Cyclic voltammograms (CVs) of the first and second cycles, (B) Charge/discharge voltage profiles at a current of (0.2C), (C) Charge/discharge cycling performance at a current of (0.2C), (D) Plot of the discharge and charge capacity vs. cycle number at various C rates of Sb nanoplates fabricated by galvanostatic pulse electrodeposition by application of -6.8 mA current for 300 s with 0.05s on and off time between 0.05-2.00 V (vs. Li/Li⁺).

4.4.2 Electrochemical properties of Sb/Cu₂Sb/Cu hybrid

Figure 4.8A depicts the discharge CV curve of Sb/Cu₂Sb/Cu during the 1st and 2nd cycles in the voltage range of 0.5-3.0 V vs. Li/Li⁺. The cycling was performed to up to 3.0 V in order to confirm the absence of copper oxide. It can be observed that the characteristic oxidation/reduction peaks of copper oxide discussed in chapter 4 are absent in the derived CV

derives. Nevertheless, oxidation/reduction peaks of Sb are clearly visible. The electrochemical reactions of Sb and Cu₂Sb can be suggested as follows:

There is strong structural relationship between Cu₂Sb and the lithiated phase which is Li₂CuSb, which is suggested as the reason for the more stable performance of Cu₂Sb. Additionally, the divided copper which is extruded from the copper antimonide can provide good electronic conductivity during cycling and enable quick reaction kinetics.⁴⁶

The electrochemical properties of the Sb-based hybrid were tested at 0.2C (see Figure 4.8B-C). The 1st, 2nd, 100th charge–discharge profiles of Sb-based hybrid is compared to pure Sb nanoplates at 0.2C rate in the potential range of 0.05-2.0 V (vs Li/Li⁺). In the case of the Sb-based hybrid, the electrode delivers a discharge capacity of 748 mAh/g followed by 615 mAh/g charge capacity. The 20% irreversible capacity in the initial cycle can again be ascribed to the formation of SEI layers. Nevertheless, in the subsequent cycle 608 and 582 mAh/g discharge and charge capacity was respectively obtained, elevating the coulombic efficiency to 96%. The capacity then degrades gradually until it almost stabilizes in the 50th cycle with 219 mAh/g discharge capacity (see Figure 4.8C), beyond which the capacity decays very slowly to deliver 186 mAh/g discharge capacity with 99 % coulombic efficiency in the 100th cycle.

If the electrochemical properties of Sb hybrid are compared to pure Sb nanoplates, it can be observed that although the initial capacity of Sb hybrid has decreased compared to pure Sb, due to the reduction in theoretical capacity, the cycling stability has improved. Good battery performance of Sb/Cu₂Sb/Cu hybrids comes from their effective hierarchical architecture. The one-dimensional Cu core acts as a structural spacer and provides a good one dimensional electrical pathway, while the mesoporous Cu₂Sb crystals with high surface area undergoes electrochemical reaction. Sb nanoplates grown between the Cu₂Sb/Cu nanoneedle arrays fill the

free space between and increase the specific capacity. However, although the mesoporous Sb nanocrystals increase the delivered capacity, the compactness of the nanoplates structure and the huge volume swing of Sb during charge/discharge cycles, results in agglomeration and stress build up in the hybrid electrode, which can lead to material pulverization and capacity decay.

Figure 4.8 (A) Cyclic voltammograms (CVs) of the first and second cycles, (B) Charge/discharge voltage profiles at a current of (0.2C), (C) Charge/discharge cycling performance at a current of (0.2C), (D) Plot of the discharge and charge capacity vs. cycle number at various C rates of Sb nanoplates fabricated by galvanostatic pulse electrodeposition by application of -6.8 mA current for 300 s with 0.05s on and off time between 0.05-2.00 V (vs. Li/Li⁺).

To do a more detailed investigation regarding the rate capabilities of the fabricated hybrid, the Sb hybrids were examined from 0.2 C to 20 C for 6 cycles at each current rate (see Figure 4.8E). At 0.2C an initial discharge capacity of 791 mAh/g with 77% Coulombic efficiency was achieved which reduced to 610 mAh/g in the second discharge cycle and continued to decay to deliver 521 mAh/g in the 6th cycle. As expected Sb hybrids displayed irreversible capacity drop in the first cycle each time the rate was increased, beyond which it stabilized, delivering an almost reversibly stable capacity at each rate. Thereafter, capacity of 436, 338, 243, 195, 68 and 57

mAh/g was delivered at 0.5, 1, 2, 5, 10 and 20 C respectively. After applying such high rates to the electrode, when the rate was again decreased to 0.2C the Sb hybrid first gave an initial capacity of 383 mAh/g and then increased to deliver 419 mAh/g discharge capacity. However, the capacity was not stabilized and it continued to decay gradually. These results demonstrate high delivered capacity of Sb hybrid with improved cycling stability at high cycling rates compared to pure Sb nanoplates. Compared to Sb thin films the presented hybrid presents better electronic pathway and improved Li ion transport efficiency, resulting in enhanced rate capability.

4.5 Conclusion

Herein, we report a facile, template free, two-step electrochemical method to fabricate free-standing Sb/Cu₂Sb/Cu hybrid electrodes grown directly on copper substrate. Although the aim of this project was to fabricate Sb-CuO core-shell nanowires, electrochemically coating of Sb on Cu(OH)₂ nanoneedle arrays scaffold resulted in reduction of the copper hydroxide and formation of Cu₂Sb/Cu. The fabricated hybrid is composed of numerous Sb nanoplate surrounding Cu₂Sb/Cu core-shell nanoneedle arrays.

The Sb/Cu₂Sb/Cu hybrid electrodes were directly used as lithium-ion battery anodes, without use of any binder and compared with pure Sb nanoplates. Compared to pure Sb nanoplates, the Sb/Cu₂Sb/Cu hybrids demonstrated lower initial capacity, due to their lower theoretical capacity, while demonstrating improved cycling stability and enhanced rate capability to up to 20 C. The authors believe that this improvement is due to the effective integration of Sb nanoplates and Cu₂Sb/Cu core-shell nanowires to a unique hierarchical architecture. In this structure the free-standing Cu core provides 1D electronic pathway and structural spacer. While, the mesoporous Cu₂Sb nanocrystals with direct contact to the copper core and strong structural relationship with the lithiated phase Li₂CuSb, provides a more stable electrochemical performance and enhanced rate capability. This structure allows buffering of huge volume swings at high cycling rates and reduction of Li⁺ ions diffusion length.

5 Fabrication of Ge-Cu₂O hybrid anodes for lithium ion batteries

5.1 Overview

Germanium is an alloying anode with high theoretical capacity (1600 mAh/g) in its fully lithiated form (Li_{4.4}Ge). The advantage of Ge compared to Si is that it has 400 times higher diffusion rate in room temperature, which makes this electrode an attractive candidate for high power rate LIB anodes. However, this electrode undergoes huge volume expansion of 370% while lithiation.

Application of various Ge thin films, nanostructures and hybrids has been reported in literature with promising properties.⁴¹ Ge nanowire arrays have been grown directly on current collector to achieve direct and individual electrical contact between the active material and current collector. Chemical vapor deposition (CVD) has been used to fabricate free-standing carbon free nanowire arrays. Superior electrochemical properties have been reported by Li et al. demonstrating impressive improvement compared to Ge electrodes containing carbon black and binders. The reason for such improvement is that the free-standing wires can relax and alleviate the stress build up during lithiation and expose stable cycling properties. The Ge nanowires show good electrochemical performance for long cycles and remain intact without serious pulverization.⁵¹

Although application of free-standing 1D Ge nanowires grown by CVD method have proven to be an effective strategy to improve electrochemical problems, the unsafe problematic GeH₄ gas used for CVD growth of Ge nanowires and the short wire length, which is usually less than 1 μm length limits its practical application.⁵¹ In Ge-Cu₂O hybrid, direct CVD growth of Ge on Cu₂O nanoneedles using Ge powder as source provides safer and more practical growth procedure. Additionally, the template based growth of Ge on several micron length copper oxide nanoneedles arrays allows higher material loading and better structural support during charge/discharge cycles.

5.2 Experimental Details

5.2.1 Fabrication of free-standing Ge-Cu₂O hybrids

A two-step process was used to prepare the Ge-Cu₂O hybrids. First, the Cu(OH)₂ films were prepared using anodization process discussed previously (section 3.2). Second, the Ge-Cu₂O core-shell nanostructures were grown using a custom-made vapor transport setup which includes a horizontal tube furnace (Lingberg Blue M) that is connected with a flow meter and vacuum pump (see Figure 5.1). Germanium (Alfa Aesar, 99.999%) and activated carbon (Alfa Aesar) powder were mixed in a molar ratio of 1:2 and placed into a one end closed quartz tube (~12mm diameter). The quartz tube is then placed in the middle of the tube furnace. The Cu(OH)₂ nanowires substrate is then placed 18 cm downstream from the source materials. Before the deposition, the quartz tube was evacuated to $\sim 10^{-2}$ mbar and flowed with forming gas (5% H₂/Ar) at a flow rate of 200 sccm. For Ge deposition, the furnace is heated to 1273 K for 1h at a heating rate of 20 K min⁻¹. During the deposition, the ambient pressure is ~ 1.7 mbar. The furnace is then cooled to room temperature and the grown Ge-Cu₂O thin films were removed from the furnace without further treatment. For comparison purposes Ge was directly grown on copper substrates using the same CVD growth procedure.

Figure 5.1 Schematic drawing of the CVD set up.

5.2.2 *Materials characterization*

The as-prepared Ge-Cu₂O thin films on metallic substrates were directly used for SEM and XRD measurements. The sample morphology was examined using a field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The elemental compositions of the samples were characterized with energy-dispersive X-ray spectroscopy (EDX) which is attached to the SEM instrument. Crystallographic data of the specimen was collected using a thin film Shimadzu Shimadzu 6000 X-ray diffractometer and a powder X-ray diffractometer (Bruker, Cu KR radiation with $\lambda = 1.5406 \text{ \AA}$). The determination of the phase was done using the Match software. For TEM characterization, the Ge-Cu₂O were scratched from the substrate and added to ethanol. After ultrasonication for 2-10 mins, the solution was drop cast onto carbon coated 200 mesh Cu grids. HRTEM and EDX were obtained by using a JEOL 2010 system operating at 200kV.

5.2.3 *Electrochemical measurements*

The coin cells were assembled inside an Ar-filled glove box with oxygen and moisture content less than 1.00 ppm. Two sets of coin cells were fabricated using the three types of fabricated anodes; Ge-Cu₂O and Ge. The free-standing electrodes were used directly as working electrode without addition of any binder. The lithium foils were used as counter/reference electrodes and the electrolyte was a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). For the electrochemical measurement coin battery cells were installed and galvanostically tested using a NEWARE battery tester (vs. Li/Li⁺).

5.3 *Electrochemical fabrication of free-standing coaxial Ge-Cu₂O core-shell hybrid*

Ge-Cu₂O hybrid electrodes were fabricated by chemical vapor deposition of Ge on Cu(OH)₂ nanowire arrays fabricated by anodization. The XRD results confirm the formation of pure cubic Ge (ICSD No. 53788) and cubic Cu₂O (ICSD No. 261853) (see Figure 5.2). This pattern demonstrates transformation of Cu(OH)₂ to Cu₂O during CVD growth of Ge without formation of any binary phases.

SEM Figure (see Figure 5.3A-B) displays Ge-Cu₂O core-shell nanowires arrays grown at a substrate distance (d_{sub}) of 18 cm from the center of the tube furnace with substrate temperature of $T_s \sim 556$ K, which is judged from the temperature profile of the furnace at 1273 K (see Figure 5.4). In substrate distance (d_{sub}) of 17 cm, with substrate temperature of $T_s \sim 631$ K, additional to the core-shell structure some Ge nanoparticles in the size range of 100-300 nm were also grown on Ge-Cu₂O nanowires (see Figure 5.3C-D). Based on the TEM study, Ge coating with 50-80 nm thickness were grown homogenously and uniformly on Cu₂O nanoneedles (see Figure 5.5A-B). HRTEM studied indicates that Ge shell is mesoporous with uniform pores in the range of 0.5-2 nm (see Figure 5.5B). The Ge coating has polycrystalline nature with nanocrystalys in the size range of 6-10nm (see Figure 5.5C) and interfringe spacing of 0.32 nm corresponding to (111) plane of cubic Ge phase (ICSD No. 53788) (see Figure 5.5D) which is in good agreement with the XRD results. Because of the core-shell morphology, grains representing Cu₂O were not observed. But the SAED (selected area diffraction pattern) display diffraction rings of both cubic Cu₂O (ICSD No. 261853) and cubic Ge (ICSD No. 53788) phase (see Figure 5.5D). This was also confirmed by performing energy dispersive line scanning which exhibited Cu₂O as core and Ge as shell (see Figure 5.5E).

Figure 5.2 XRD of Ge-Cu₂O Hybrid

Figure 5.3 SEM images of Ge-Cu₂O hybrid fabricated by CVD growth of Ge on Cu(OH)₂ nanoneedle arrays in substrate distance (d_{sub}) of (A-B) 18 cm, (C-D) 17 cm.

Figure 5.4 Temperature profile of the CVD furnace

Figure 5.5 (A-C) TEM, (D) HRTEM, (D) EDS linear scan of Ge-Cu₂O core-shell fabricated by CVD growth of Ge on Cu(OH)₂ nanoneedle arrays at substrate distance 18 cm using Germanium and activated carbon powder, (F) Ge-copper oxide hybrids fabricated by CVD growth of Ge on Cu(OH)₂ nanoneedle arrays at substrate distance 18 cm using GeO₂ and activated carbon powder.

GeO₂ was also used as source following the same growth procedure discussed above. Interestingly it was observed that the core-shell nanowire arrays grown using this source were covered with numerous fine nanowires with 0.5 μm length and 40-50 nm diameters. However, the adhesion of these electrodes was very poor and the fabricated thin film peeled off easily upon handling. Therefore, further examination of these electrodes was not performed (see Figure 5.5F).

For comparison purposes Ge nanoparticles were also grown directly on copper substrate using Ge powder as source. The same growth conditions applied for the growth of Ge on Cu(OH)₂ was applied. It can be observed in SEM images displayed in Figure 5.6A that growth Ge has nanoparticle morphology. The Ge nanoparticles have polycrystalline nature and compose of nanocrystalys in the size range of 6-15nm (see Figure 5.6B) and inter-fringe spacing of 0.32 nm corresponding to (111) plane of cubic Ge phase (ICSD No. 53788) (see Figure 5.6C). The

diffraction pattern presented as inset in Figure 5.6C and XRD of Ge thin film also demonstrates formation of cubic Ge phase (ICSD No. 53788) (see Figure 5.6D).

Figure 5.6 (A) SEM, (B) TEM, (C) HRTEM images and diffraction pattern and (D) XRD of Ge nanoparticles on copper substrate grown by CVD at substrate distance 18 cm.

5.4 *Electrochemical evaluation of free-standing coaxial Ge–Cu₂O core-shell hybrid*

Figure 5.7 depicts the initial three CV curves of core-shell Ge–Cu₂O hybrid nanowire arrays. The cathodic cycle lower than 1.5V correspond to the reduction of Cu₂O to Cu and Li₂O. The observed redox peaks in charge and discharge cycles were in agreement with previous reports on Cu₂O and the reaction can be proposed as following:

(1) Reduction of Cu₂O to Cu at plateau region <1.5V:

The Ge is an alloying electrode which undergoes reaction with lithium ions at potentials lower than 0.5V.¹²² The cyclic voltammetry of pure Ge nanoparticles grown on copper is demonstrated for reference (see Figure 5.8). The reaction can be presented as follows:

(2) Alloying reaction of Ge at plateau region of <0.5V:

In the initial anodic cycle the first reaction happening at potential $\sim 0.6V$ is the de-alloying reaction of Li_xGe .¹²² In the anodic sweep of pure Ge nanoparticles grown on copper substrate this peak is observed in the same position as a single anodic peak (see Figure 5.8). However, since Li_2O is present in the Ge- Cu_2O interface as a result of reductive reaction of Cu_2O with Li, based on electrochemical thermodynamics and literature Ge undergoes an oxidation reaction to form GeO_2 in the potential over 1 V.^{123, 124} The discussed reactions of Ge can be proposed as follows:

(1) De-alloying reaction of Ge at potential $\sim 0.6V$:

(2) Oxidation of Ge to GeO_2 at potential plateau $> 1.0V$:

When the potential is increased further to $2.5V$ the copper is oxidized to form Cu_2O based on the following reaction:

(3) Oxidation of Cu to form Cu_2O :

It is assumed that since some of the oxygen has been consumed by Ge to form GeO_2 , there is not sufficient oxygen for copper to completely oxidize back to Cu_2O and therefore there will be some copper remaining in the structure. This residual copper can provide an electronic pathway and improve the electronic conductivity of the electrode.

Figure 5.7 Cyclic voltammograms (CVs) of the first to third cycles of Cu₂O-Ge core-shell nanowire arrays between 0.05-3.00 V (vs Li/Li⁺).

In the second cathodic sweep there is a wide plateau between 1.3V and 2.2V which is proposed to be mostly related to formation of SEI layer and an amorphous Li_xGeO₂ phase.¹²⁵ Again reduction reaction of Cu₂O to copper will take place at potentials lower than 1.2V. Additionally, the GeO₂ reacts with Li⁺ through a conversion reaction to form Ge at potential around 0.7V.¹²⁴

These reactions at plateau region <1.2 V can be proposed as follows:

(1) Reduction of Cu₂O:

(2) Conversion reduction of GeO₂ to Ge:

When the potential is decreased further to lower than 0.5V alloying reaction of Ge with Li takes place similar to the initial cycle.

(3) Alloying reaction of Ge at plateau lower than 0.5V:

Figure 5.8 Cyclic voltammograms (CVs) of the first to third cycles of Ge nanoparticles between 0.05-1.5 V (vs Li/Li⁺).

In the second anodic sweep of Ge-Cu₂O, the peak positions are similar to the first cycle and the reaction can be considered as reversible. Again in the third cyclic voltammogram the peak positions are the same as second cycle, so it can be concluded that the materials and reactions are stabilized. To confirm the proposed mechanism XRD was performed on Ge-Cu₂O hybrids which had lithiated for 50 cycles. As can be observed in the XRD pattern shown in Figure 5.9 the Cu₂O peaks remain unchanged while the Ge peaks disappear. In the meanwhile, some new peaks have appeared which match the cubic GeO₂ phase (JCPDS 23-0999).^{89, 127} Peaks of Ge were also detected, illustrating that some Ge still remains unchanged inside the structure.^{51, 126} However, the formation of GeO₂ is confirmed, since obvious peaks could be recognized in the lithiated electrode. Based on the above observation, it can be concluded that in-situ generation of GeO₂ hybrid has taken place by lithiation-delithiation of Ge-Cu₂O hybrid electrode. This transformation is based on different types of electroactive response of hybrid's building block toward Li⁺; with Cu₂O undergoing conversion reaction and Ge undergoing alloying reaction with the capability to react electrochemically with Li₂O.

Figure 5.9 XRD pattern of Ge-Cu₂O hybrid lithiated at 0.5C for 50C between 0.05-3.00 V (vs Li/Li⁺).

The electrochemical properties of the Ge-Cu₂O core-shell were tested at 0.5C and 1C (see Figure 5.10A-B). Figure 5.10A compares the 1st, 2nd, 100th charge–discharge profiles of Ge-Cu₂O core-shell at 0.5C rate in the potential range of 0.05-3.0 V (vs Li/Li⁺). In the initial cycle the electrode delivers a discharge capacity of 1356 mAh/g followed by 1193 mAh/g charge capacity. This results in only 12.20% irreversible capacity which can be ascribed to the formation of SEI layers. In the subsequent cycle 1143 and 1107 mAh/g discharge and charge capacity was respectively obtained, elevating the Coulombic efficiency to 96.8%. The capacity then degrades very gradually until it reaches 732 mAh/g discharge capacity in the 100th cycle with 99.2% Coulombic efficiency (see Figure 5.10B). The electrochemical respond of Ge-Cu₂O was also evaluated at 1C rate. At this rate the core-shell Ge-CuO nanowire arrays delivered an initial discharge capacity of 1302 mAh/ followed by 1108 mAh/g charge capacity resulting in 15% capacity loss which is similarly subsided in the subsequent cycle by delivering 1098 and 1063 mAh/g discharge and charge capacity respectively and achieving 95% Coulombic efficiency. The capacity then degrades eventually to deliver 468 mAh/g discharge capacity in the 100th cycle with 98% Coulombic efficiency.

Figure 5.10 (A) Charge/discharge voltage profiles at (0.5C), (B) Charge/discharge cycling performance at 0.5C and 1C rate (C) Plot of the discharge and charge capacity vs. cycle number at various C rates of core-shell Ge-Cu₂O nanowire arrays hybrid between 0.05-3.00 V (vs Li/Li⁺).

To make a comparison and demonstrate the significance of Ge-Cu₂O nanowire arrays hybrid on electrochemical properties, Ge nanoparticles grown on copper substrate were also tested at 0.5C rate (see Figure 5.10B). In the Ge electrode the insertion process in the first cycle gave a discharge capacity of 1112 mA h/g and a subsequent charge capacity of 817 mA h/g, this results in an initial Coulombic efficiency of 78%. In the second cycle, the discharge capacity dropped to 915 mAh/g with corresponding charge capacity of 879 mA h/g, resulting in 96% Columbic efficiency. The Ge nanoparticles continued to fade abruptly and reached 164 mA h/g discharge capacity with 98.7 Coulombic efficiency by the 40th cycle. The capacity decay decreased from this point onwards. However, the sample delivered capacities lower than 100 mAh/g after 100 cycles. The large volume change of Ge electrodes, compact nanostructure and lack of open porosities of nanoparticles thin film can be considered the main reason for low initial capacity and fast fading electrochemical properties of Ge nanoparticles.

To further investigate the rate capabilities, Ge-Cu₂O electrodes were electrochemically examined from 0.2 C to 15 C for 6 cycles at each current rate (see Figure 5.10C). It was observed that the Ge-Cu₂O presented an initial discharge capacity of 1372 mAh/g and 88.4% Coulombic efficiency. In the second cycle discharge capacity of 1136 with 96.6% Coulombic efficiency was achieved. Thereafter, the capacity continued to drop gradually to finally reach discharge capacity of 820 mAh/g in the 6th cycle with 99% Coulombic efficiency. As expected, a sudden capacity drop was observed every time the capacity was increased. However, the structure was stabilized thereafter and a reversibly stable capacity was achieved at each rate. Stable capacity of 845, 694, 581, 380, 333 and 336 mAh/g were achieved at 0.5, 1, 2, 5, 10 and 15C. When the rate was again reduced to 0.2C discharge capacity of 1079 mAh/g with 95% Coulombic efficiency could be achieved in the second cycle and the Coulombic efficiency increased to over 98% Coulombic efficiency in the subsequent cycles.

In order to further examine the stability of Cu₂O-Ge core-shell hybrid structure, lithium ion battery cells cycled at 1C rate for 100 cycles were opened in glove box and studies using SEM (see Figure 5.11). It can be observed that Cu₂O-Ge hybrid have retained their nanowire morphology. However, the wires are no longer free-standing and individual. It seems like while cycling the wires are curled up together to form woven like islands. Nevertheless, the open structure is retained and no breakage and deformation of wires is visible. It needs to be noted that the diameters of nanoneedles have increased to about 400 nm, which is a result of undergoing reaction of Cu₂O-Ge with lithium during cycling.¹²⁶

Figure 5.11 SEM images of Ge-Cu₂O core-shell hybrid after Charge/discharge at (1C) between 0.05-3.00 V (vs Li/Li⁺) for 100 cycles.

The reason for such outstanding electrochemical properties can be related to the intrinsic properties of CuO and the unique nanostructure of CuO nanoneedle arrays

Excellent electrochemical performance of Ge-Cu₂O hybrid comes from their smart selection and unique hierarchical architecture (Figure 5.12). The one-dimensional Cu₂O nanoneedle arrays with direct contact to the current collector serve both as structural spacer to buffer the strain during lithiation/delithiation and act as a good electron pathway to improve electronic conductivity. In Ge-Cu₂O electrode direct growth of Cu₂O nanoneedles on Cu substrates improves contact and enhances electrical conductivity. Ge shell with uniform mesoporosity affords short diffusion distances for both Lithium ion and electron transport and open interspaces between the core-shell nanowires allow quick infiltration of electrolyte into the structure, partially accommodating the volume expansion during lithiation and alleviating material loss. As a result, the kinetic performance of the electrode is improved and the lithiation/delithiation is performed much more effectively. However, although in Ge thin film the nanoparticles are small with nanometer grain size, but the compact structure increases diffusion length of electrons and lithium ions and makes lower layer of Ge inaccessible to the electrolyte, resulting in low initial capacity. Additionally, large volume swings of Ge and lack of open space between results in agglomeration and pulverization of active material, leading to huge capacity decay.

Figure 5.12 Schematic drawing of (A) Cu(OH)₂ nanoneedle arrays fabricated by anodization of high purity Cu foil at 1.5 mA/cm² for 700 second, (B) coaxial Ge-Cu₂O core-shell arrays fabricated CVD of Ge on Cu(OH)₂ nanoneedle arrays.

5.5 Conclusion

Herein, we report a facile, template free two-step fabrication of free-standing Ge-Cu₂O core-shell nanowire arrays hybrids by combining electrochemical anodization of copper and Ge CVD growth. The electrodes are composed of free-standing Cu₂O nanoneedle arrays coated with mesoporous Ge. The electrochemical properties of Ge-Cu₂O hybrids were thoroughly studied and compared with Ge nanoparticles thin films grown directly on Cu foil. In-situ generation of GeO₂ was observed from the initial charge/discharge cycle of Ge-Cu₂O hybrid electrodes. The formation of GeO₂ was explained based on the different electroactive response of hybrid's building block towards Li⁺; with Cu₂O undergoing conversion reaction and Ge undergoing alloying reaction with the capability to react electrochemically with Li₂O. The Ge-Cu₂O hybrid demonstrated superior electrochemical properties at 0.5C and 1C rate and perfect rate capability when tested to up to 15C, while Ge nanoparticles demonstrated fast fading electrochemical properties. Excellent electrochemical performance of Ge-Cu₂O hybrid comes from their smart selection and unique hierarchical architecture. Direct growth of Cu₂O nanoneedles on Cu substrates improves contact and enhances electrical conductivity. While, mesoporous Ge shell with high theoretical capacity, large surface area and short diffusion distance lead to delivery of large specific capacities. The authors believe that constructive design and development of such hierarchical hybrids can open new opportunities in energy storage application and many other fields.

6 Fabrication of Fe₃O₄-CuO hybrid anodes for lithium ion batteries

6.1 Overview

Hybrids with superior electrochemical performance can be fabricated by smart assembling and fine tuning of the composition, shape and architecture of the constituent building blocks.^{91, 92} Coaxial free-standing hybrid with ordered array architecture have the advantage of effective electronic transport due to the direct connection to the substrate and fast ion transport due to the existence of void between which allow easy penetration of the electrolyte.⁶² Furthermore, the open space between the well aligned ordered nanostructure accommodates the volume expansion during lithiation/delithiation and improves cycling stability.⁶⁰

Reducing the size and mass of the lithium ion battery, while improving its storage capacity is another important factor. Fabrication of 2D and 3D thin film Li micro-batteries with high areal capacities is presented as an effective strategy.^{127, 128} The 3D hybrids such as core-axial nanowires or nanotube arrays have the tendency to increase the material loading in the vertical dimension while maintaining the open structure and short Li diffusion lengths.¹²⁹ Direct electrodeposition of active materials by electrochemical techniques is an encouraging method for fabrication of high areal capacity 3D hybrid electrodes.⁹³⁻⁹⁶ However, fabrication of such structures e.g. nanowires, nanotubes arrays is usually template assisted,^{97, 98} which makes the process more difficult, expensive and unpractical. Therefore, detailed investigation of template free fabrication processes is highly recommended.¹³⁰

Study of hybrids in the literature mainly focuses on carbon based hybrids and application of nanostructured current collectors, while there is little investigation related to coaxial metallic hybrids with both constituents with electroactive properties.^{91, 92} The coaxial metallic hybrids have the advantage that both components undergo reaction with Li⁺, resulting in higher specific capacity. CuO is a transition metal oxide with quite high theoretical capacity of (674 mAh/g), high safety, inexpensive and environmentally abundant nature. Recently it has been reported that

well aligned arrays of CuO have high rate capability and demonstrate excellent performance in high current densities.³⁶ The residual copper nanoparticles of the incomplete conversion reaction with lithium behaves as a good electron pathway and improves the electronic conductivity of the anode material, resulting in outstanding cycling stability and rate capability.¹⁰⁶ Fe₃O₄ is also considered as one of the most promising and practical anodes for high performance lithium ion batteries, for its high theoretical capacity (924 mAh/g) and half-metallic conductivity,¹³¹ and its practicality due to its low cost, abundant and environmentally friendliness.¹³² However, application of Fe₃O₄ in lithium-ion batteries is limited by its poor cycling performance especially in high cycling rates due to its huge volume swing and severe aggregation during Lithiation/delithiation.^{53, 131}

Herein, we report a simple, template free two-step electrochemical method to fabricate hierarchical heterogeneous Fe₃O₄-CuO electrodes grown directly on copper substrate. The electrode is composed of CuO nanoneedle arrays fabricated by a simple anodization process with ultra-fast lithium ion properties as core and electrochemically coated Fe₃O₄ nanocrystals as shell. In this report, first the electrochemical properties of single phase CuO and Fe₃O₄ nanostructures as the hybrid components will be thoroughly studied. Next, the properties of two types of core-shell and hierarchical 3D network of Fe₃O₄-CuO hybrids will be studied and discussed in details to demonstrate how application of hybrids can emerge multifunctional performance, as well as novel enhanced electrochemical properties due to the synergetic effects. To our knowledge such hybrids has not been reported in the literature.

6.2 Experimental details

6.2.1 Electrochemical deposition of interconnected Fe₃O₄ nanoflakes

An aqueous alkaline solution consisting of Fe₂(SO₄)₃·5H₂O (0.09M) stabilized with tri-ethanol-amine (TEA) (0.14M) was used to prepare the Fe₃O₄ thin films. A 2 M NaOH solution was used to adjust the Ph of the solution. Electrodeposition of Fe₃O₄ was performed in a three electrodes

system at temperature of 60°C under constant stirring. A copper foil cleaned with acetone, ethanol, diluted HCl solution and deionized water was used as the working electrode, while a Pt mesh electrode (CH instrument) and Ag/AgCl electrode was used as the counter and reference. To fabricate a uniform Fe₃O₄ deposit a constant potential of -1.2 V was applied for 60 seconds.

6.2.2 Electrochemical fabrication of free-standing Fe₃O₄-CuO hybrids

A two step electrochemical process was used to prepare the Fe₃O₄-CuO hybrids. First, the Cu(OH)₂ films were prepared using anodization process discussed in 3.2 In the second stage Cu(OH)₂ nanoneedle arrays were used as working electrode to deposit Fe₃O₄ nanostructures using the same solution explained in section 6.2.1. The deposition was again performed at 60°C under constant stirring. Constant potential of -1.1 to -1.2V was applied for 60 to 200 seconds. Finally, fabricated samples were annealed at 120°C for 2 h and then maintained at 200°C for 2 h to prepare free-standing Fe₃O₄-CuO hybrid electrodes.

6.2.3 Materials characterization

The as-prepared Fe₃O₄-CuO hybrid and Fe₃O₄ thin films on metallic substrates were directly used for SEM and XRD measurements. The sample morphology was examined using a field-emission scanning electron microscopy (FESEM; JEOL, JSM-7600F). The elemental compositions of the samples were characterized with energy-dispersive X-ray spectroscopy (EDX) which is attached to the SEM instrument. Crystallographic data of the specimen was collected using a thin film Shimadzu Shimadzu 6000 X-ray diffractometer and a powder X-ray diffractometer (Bruker, Cu KR radiation with $\lambda = 1.5406 \text{ \AA}$). The determination of the phase was done using the Match software. For TEM characterization, the samples were scratched from the substrate and added to ethanol. After ultrasonication for 2-10 mins, the solution was drop cast onto carbon coated 200 mesh Cu grids. HRTEM and EDX were obtained by using a JEOL 2010 system operating at 200kV.

6.2.4 Electrochemical measurements

The coin cells were assembled inside an Ar-filled glove box with oxygen and moisture content less than 1.00 ppm. Two sets of coin cells were fabricated using two types of fabricated anodes; Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-CuO}$ thin films. The free-standing electrodeposited electrodes were used directly as working electrode without addition of any binder. The lithium foils were used as counter/reference electrodes and the electrolyte was a solution of 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). For the electrochemical measurement coin battery cells were installed and galvanostically tested using a NEWARE battery tester between 0.005 and 3.00 V (vs. Li/Li^+).

6.3 Fabrication of $\text{Fe}_3\text{O}_4\text{-CuO}$ hybrids

6.3.1 Electrodeposition of interconnected Fe_3O_4 nanoflakes

Electrodeposition of various iron oxide morphologies using different electrolyte baths has been reported in the literature.^{133, 134} In several reports TEA has been used as an effective complexing agent for Fe^{2+} and Fe^{3+} to form a complex metal compound with liberation to water and prevent the formation of insoluble Fe^{3+} hydroxide.^{133, 134}

The XRD of the deposited Fe_3O_4 thin film also confirms the formation of magnetite Fe_3O_4 (ICSD No. 64829) (see Figure 6.1). SEM images of Iron oxide nanoflakes obtained by application of -1.2 V at 60°C for 60s (see Figure 6.2A-B) demonstrates formation of interconnected iron oxide nanoflakes with open porosities. The iron oxide deposits are continuous and uniform with small porosities in the range of 80-250 nm. The nanoflakes are very thin with 10-20 nm thickness and as can be seen in the TEM image the flakes appear translucent while spreading to the sides (see Figure 6.2C-D). It needs to be noted that each flake is highly mesoporous with fine porosities in the range of 0.5-2 nm (see Figure 6.2E). The high resolution TEM (HRTEM) observation (see Figure 6.2F) of the Fe_3O_4 nanoflakes indicates that the flakes are single crystal with interfringe spacing of 0.25 nm corresponding to the (113) plane of magnetite Fe_3O_4 (ICSD No. 64829).

Figure 6.1 (XRD) of Fe_3O_4 nanoflakes structure electrodeposited on Cu foil from a Fe^{3+} -TEA system at 60°C by application of -1.2 V for 60 s.

Figure 6.2 (A-B) SEM and (C-D) TEM images, (E-F) HRTEM images of interconnected Fe_3O_4 nanoflakes electrodeposited from Fe^{III} -TEA system by application of -1.2 V for 60 seconds at 60°C .

In overall the electrochemical deposition of Fe_3O_4 in Fe^{3+} - TEA can be presented as follows:

The process is composed of three stages, the electrochemical reduction of Fe^{3+} -TEA complex, dissociation of Fe^{2+} -TEA to form Fe^{2+} and finally the precipitation of Fe_3O_4 . Temperature has significant influence on the morphology of the electrodeposited Fe_3O_4 thin film in a Fe^{3+} -TEA complex system and such nanoflakes morphology cannot be obtained at lower temperatures. This can be explained based on the dependency of ion/complex activity and mobility on temperature. It's common that ligand dissociation increases with raise in solution temperature. At higher temperature the Fe^{2+} -TEA becomes more unstable, favoring the second reaction and rapidly forming numerous Fe^{2+} ions. These ions then undergo reaction with $\text{Fe}(\text{TEA})^{3+}$ to form Fe_3O_4 nanoflake deposits.¹³³

6.3.2 Electrochemical fabrication of Fe_3O_4 -CuO hybrids

Fabrication of hybrid Fe_3O_4 -CuO electrodes was performed in two steps. In the initial step $\text{Cu}(\text{OH})_2$ nanoneedle arrays were fabricated by anodization of copper foil at 1.5 mA/cm^2 for 700 s in a 1 M NaOH. Then in the second step, $\text{Cu}(\text{OH})_2$ thin film was utilized as substrate to grow Fe_3O_4 nanostructures using the solution applied to fabricate mesoporous Fe_3O_4 nanoflakes structure discussed in section 5.2.2. Two constant potentials of -1.1 and -1.2 V are applied for 100 s to produce two different heterogeneous structures. The fabricated hybrid structure is then heat treated at 120°C and 200°C for 2 hours each to transform the copper hydroxide to CuO and improve the electrical conductivity of the hybrid electrode. The XRD results confirms the co-existence of both magnetite Fe_3O_4 (ICSD No. 64829) and monoclinic CuO (ICSD No. 31059) for both core-shell CuO/ Fe_3O_4 and 3D hierarchical CuO/ Fe_3O_4 thin films (see Figure 6.3).

By application of -1.1 V a homogeneous coaxial core-shell CuO/ Fe_3O_4 nanostructure was formed in which CuO nanoneedles was coated homogeneously with Fe_3O_4 nanocubes (see Figure 6.4A-B). The Fe_3O_4 nanocubes with the size range of 20-50 nm cover the nanowires uniformly and completely from the root to the tip. According to the TEM observation the stacked nanocubes growing in random directions are highly mesoporous with uniform pores in the range of 0.5-2 nm (see Figure 6.4C-D). This is a great advantage when the sample is used as lithium ion battery electrodes. According to HRTEM study, Fe_3O_4 crystals in core-shell CuO/ Fe_3O_4 structure are

single crystals with interfringe spacing of 0.25 nm corresponding to (113) plane of magnetite Fe_3O_4 phase (ICSD No. 64829) (see Figure 6.4E). With increase in deposition time from 60 to 200 s the nanocubes size enlarges to 0.2-0.5 μm , while maintaining its cubic shape (see Figure 6.4F).

Figure 6.3 XRD of Fe_3O_4 -CuO hybrid fabricated by two step electrochemical fabrication method.

Figure 6.4 (A-B) SEM, (C-D) TEM, (E) HRTEM images of Fe_3O_4 -CuO core-shell hybrid fabricated by electrodeposition of Fe_3O_4 at -1.1 V on CuO nanoneedle arrays for 60s, (F) SEM of Fe_3O_4 -CuO core-shell hybrid fabricated by electrodeposition of Fe_3O_4 at -1.1 V on CuO nanoneedle arrays for 200s.

For the second set of samples while keeping all parameters constant the electrodeposition potential was increased to -1.2 V. As a result a 3D hierarchical CuO/Fe₃O₄ hybrid composed of CuO nanoneedle arrays as core covered completely with a thin layer of interconnected Fe₃O₄ nanoflakes was fabricated (see Figure 6.5A-B). According to the TEM observation the core-shell form of CuO/Fe₃O₄ is maintained, however due to close packing of CuO arrays and nanoflakes nature of Fe₃O₄ deposits in this electrodeposition condition porous hierarchical CuO/Fe₃O₄ 3D network is formed as a result (see Figure 6.5C). According to HRTEM study, Fe₃O₄ crystals are polycrystalline with 1-5 nm nanocrystallites. The exposed nanocrystals with interfiring spacing of 0.25 nm and 0.29 nm correspond to (113) and (022) plane of magnetite Fe₃O₄ phase (ICSD No. 64829) (see Figure 6.5D).

Figure 6.5 (A-B) SEM, (C) TEM, (HRTEM) images of Fe₃O₄-CuO hybrid network fabricated by electrodeposition of Fe₃O₄ at -1.2 V on CuO nanoneedle arrays.

6.4 *Electrochemical evaluation of Fe₃O₄-CuO hybrid*

6.4.1 *Electrochemical properties of interconnected Fe₃O₄ nanoflakes*

To evaluate the electrochemical performance of the Fe₃O₄ electrodes half-cell electrodes were installed and tested in a discharge/charge window of 0.05-3.0 V (vs. Li/Li⁺). The CV profile of interconnected Fe₃O₄ nanoflakes for the first two cycles is shown in Figure 6.6A. In the initial

cycle the cathodic peak observed in 0.8V could be attributed to the reduction of Fe^{3+} and Fe^{2+} to Fe^0 .¹³⁵ In the anodic cycle the two peaks appearing in the 1.6 and 1.8V correspond to the reversible oxidation of Fe^0 to Fe^{3+} and Fe^{2+} . As can be observed in the CV curve in the following cycles, the oxidation and reduction peaks are both slightly shifted. This phenomenon also reported by others is due to the polarization of Fe_3O_4 .¹³⁵ The overall lithiation-delithiation process of Fe_3O_4 can be presented as follows:

In terms of practical application it is important to investigate the electrochemical behavior in high currents. Therefore, the stability performance of electrodeposited Fe_3O_4 nanoflakes structure was tested in 924 mA/g (1C). The first, second and hundred charge/discharge curves of Fe_3O_4 nanoflakes in the potential window of 0.05–3.0 V (vs. Li/Li^+) at a rate of 1 C is shown in Figure 6.6B. The sample delivered an initial discharge capacity of 1180 mAh/g and a subsequent charge capacity of 860mAh h/g, resulting in an initial Coulombic efficiency of 72%. Due to the high irreversible capacity in the first cycle the initial coulombic efficiency is low, which is very common in nanostructured metal oxide electrodes with high surface/volume ratio.¹³⁶ After the first cycle the Coulombic efficiency improves significantly. In the second cycle, the discharge capacity drops even further to 852 mAh/g, but delivers 819 mAh/g charge capacity, leading to a high Coulombic efficiency of 96%. However, the capacity continues to decay gradually until discharge capacity of 260 mAh/g is obtained in the 100th cycle with a Coulombic efficiency of 98.6% (see Figure 6.6B). This result demonstrates that although the fabricated Fe_3O_4 nanoflakes with favorable honeycomb structure can initially deliver capacities close to the theoretical value, this capacity cannot be maintained at such high currents (924 mA/g) and the nanostructure continues to collapse leading to gradual capacity loss. It should be noted that the initial discharge

capacities of Fe_3O_4 electrode exceeds the theoretical capacity of Fe_3O_4 (924 mAh/g). This behavior was also observed for CuO electrodes and other reports of Fe_3O_4 electrodes.^{137, 138} As explained, such phenomenon is observed extensively in transition metal oxides.^{135, 136}

Figure 6.6 (A) Cyclic voltammograms (CVs) of the first three cycles, (B) Charge/discharge voltage profiles at a current of 924 mA/g (1C), (C) Charge/discharge cycling performance at a current of 924 mA/g (1C), (D) Plot of the discharge and charge capacity vs. cycle number at various C rates of interconnected Fe_3O_4 nanoflakes fabricated by electrodeposition between 0.05-3.00 V (vs Li/Li^+).

To further investigate the rate capabilities, the Fe_3O_4 nanoflakes electrodes were examined from 0.2 C to 15 C for 6 cycles at each current rate (see Figure 6.6D). The Fe_3O_4 nanoflakes structures delivered an initial discharge capacity of 1321 mAh/g with 70% Coulombic efficiency. However, from the second cycle onwards the capacity continued to drop to finally reach discharge capacity of 744 mAh/g in the 6th cycle with 95% Coulombic efficiency. An irreversibly capacity drop was observed in the initial cycle each time the rate was increased. At 0.5C an initial capacity of 662 with 95% Coulombic efficiency was delivered which decreased even further to 641 with 96% Coulombic efficiency in the second cycle. Fairly stable capacity of 401, 261, 122 mAh/g was achieved respectively at 1, 2, 5C. With increase of cycling rate to 10 and 15C the delivered

capacity dropped below 100 mAh/g; demonstrating poor rate capability. When the rate was again reduced to 0.2, discharge capacity of 541 mAh/g with 87% Coulombic efficiency was achieved in the second cycle, but the capacity did not stabilize and continued to deplete in the following cycles.

Figure 6.7 Charge/discharge cycling performance of interconnected Fe_3O_4 nanoflakes fabricated by electrodeposition between 0.05-3.00 V (vs Li/Li^+) at a current of 184 mA/g (0.2C).

The focus of this study is to fabricate nanostructures which can function effectively at high cycling rates. But, it still needs to be mentioned that the fabricated Fe_3O_4 nanoflakes structure exposed acceptable electrochemical performance at lower rates (0.2C) (see Figure 6.7). The Fe_3O_4 nanoflakes delivered a high initial discharge capacity of 1255 mAh/g. Upon initial charging to 3.00 from the fully discharged condition, only 70% charge capacity corresponding to 883 mAh/g could be extracted. However, after the first cycle similar to what was observed in 1C rate the Coulombic efficiency improved extensively to reach 90% Coulombic efficiency. The Fe_3O_4 sample demonstrated rapid capacity decay in their initial 33 cycles, however henceforth the structure was stabilized and the capacity gradually improved to reach 615 mAh/g with 99.6% Coulombic efficiency in the 100th cycle. This observation clearly demonstrates that Fe_3O_4 thin films with favorable hierarchically mesoporous structure and large surface area deliver high specific capacity and demonstrate fairly stable cycling performance at low current density, but fail to buffer the strain at higher cycling rates and lead to poor electrochemical properties. Since Fe_3O_4 undergoes a conversion reaction with three components Fe_3O_4 , Fe^0 , and Li_2O , the kinetics

plays an important role. Therefore, it is necessary to decrease the diffusion length, while maintain a good electronic pathway.¹³⁴

6.4.2 *Electrochemical properties of free-standing Fe₃O₄-CuO hybrids*

Figure 6.8A depicts the discharge CV curve of CuO/Fe₃O₄, CuO and Fe₃O₄ during the 1st and 2nd cycles. All the reduction and oxidation peaks of CuO and Fe₃O₄ discussed 6.4.1 and 3.4 sections can be observed in the CV curve of Fe₃O₄-CuO. It should be noted that the cathodic peaks of CuO and Fe₃O₄ in the range of 0.5-1.2 V (vs Li/Li⁺) overlap and project a wider plateau. The longer plateau of redox reactions in Fe₃O₄-CuO CV curve compared to CuO and Fe₃O₄ clearly demonstrates the superior performance of the hybrid compared to its single components. Since for many applications of lithium ion batteries e.g. power tools, fast discharge/charge rates are crucial, it is necessary to test the functionality of the hybrid at high rates. Therefore, the electrochemical properties of the CuO/Fe₃O₄ core-shell and 3D hierarchical Fe₃O₄-CuO network were tested at 1C (see Figure 6.8B-C). Figure 6.8B compares the 1st, 2nd, 100th charge-discharge profiles of the CuO/Fe₃O₄ core-shell and 3D hierarchical Fe₃O₄-CuO network at 1C rate in the potential range of 0.05-3.0 V (vs Li/Li⁺). In the case of the CuO/Fe₃O₄ core-shell, the electrode delivers a discharge capacity of 1207 mAh/g followed by 870 mAh/g charge capacity. The 30% irreversible capacity in the initial cycle can again be ascribed to the formation of SEI layers. Nevertheless, in the subsequent cycle 868 and 839 mAh/g discharge and charge capacity was respectively obtained, elevating the Coulombic efficiency to 96.6%. The capacity then degrades gradually until it reaches its minimum in the 25th cycle with 699 mAh/g discharge capacity (see Figure 6.8C), beyond which the capacity increases steadily to deliver 953 mAh/g discharge capacity with 98.7% Coulombic efficiency in the 100th cycle. The gradual increase in capacity of Fe₃O₄-CuO hybrids is probably due to effective contact of electrolyte and electrode and also increased thickness of SEI film.^{29, 114} Additionally, the synergetic effect of the CuO and Fe₃O₄ cannot be neglected. The wider plateau of redox reaction observed in the CV curve is an indication of such phenomenon. Additionally, the synergetic effects of CuO and Fe₃O₄ cannot be neglected. The 3D hierarchical Fe₃O₄-CuO network also demonstrates similar behavior at this

rate (1C). An initial capacity of 1225 mAh/g is obtained for 3D hierarchical Fe₃O₄-CuO network followed by 872 mAh/g charge capacity resulting in 29% capacity loss which is similarly greatly alleviated in the subsequent cycle by delivering 872 and 816 mAh/g discharge and charge capacity respectively and achieving 93.6% Coulombic efficiency. The capacity then degrades eventually to reach its lowest value of 567 mAh/g in the 33rd cycle. Thereafter, the capacity increases to achieve 751 mAh/g discharge capacity with 99% Coulombic efficiency after 100 cycles.

To do a more detailed investigation regarding the rate capabilities of the fabricated hybrids, the CuO/Fe₃O₄ core-shell and CuO/Fe₃O₄ 3D network were examined from 0.2 C to 15 C for 6 cycles at each current rate (see Figure 6.8D). Both structures displayed an irreversibly capacity drop in the first cycle each time the rate was increased, beyond which it stabilized, delivering a reversibly stable capacity at each rate. For core-shell Fe₃O₄-CuO an initial discharge capacity of 1269 mAh/g with 73% Coulombic efficiency was achieved which reduced to 870 mAh/g in the second discharge cycle. Thereafter, a stable capacity of 734, 630, 538, 416, 319 and 204 mAh/g was delivered at 0.5, 1, 2, 5, 10 and 15C respectively. After applying such high rates to the electrode, when the rate was again decreased to 0.2C the Fe₃O₄-CuO core-shell first gave an initial capacity of 383 mAh/g and then increased to reach a reversibly stable capacity of 860 mAh/g with 95% Coulombic efficiency which increased to over 98% in the subsequent cycles. In case of hierarchical Fe₃O₄-CuO 3D network the performance was also very impressive with an initial discharge capacity of 1283 mAh/g and 70% Coulombic efficiency, which as expected reduced to 875 in the second cycle. Thereafter, similar to Fe₃O₄-CuO core-shell stable capacity of 727, 628, 525, 368, 248 and 140 mAh/g were delivered at 0.5, 1, 2, 5, 10 and 15C respectively. Again, when the rate was decreased to 0.2C after application of such high currents to the structure, the Fe₃O₄-CuO 3D network first gave an initial capacity of 382 mAh/g and then increased to reach a reversibly stable capacity of 860 mAh/g with 95% Coulombic efficiency which gradually increased to reach higher than 98% in the following cycles.

Figure 6.8 (A) Cyclic voltammograms (CVs) of the first three cycles, (B) Charge/discharge voltage profiles at 1C cycle rate, (C) Charge/discharge cycling performance at 1C cycle rate, (D) Plot of the discharge and charge capacity vs. cycle number at various C rates of CuO-Fe₃O₄ heterostructures fabricated by two step electrochemical method between 0.05-3.00 V (vs Li/Li⁺).

Electrochemical impedance spectroscopy was applied to investigate the influence of CuO-Fe₃O₄ hybrid compared to their individual CuO and Fe₃O₄ counterparts in terms of the total internal electrochemical impedances of a cell. The characteristic impedance curves (Nyquist plots) of CuO, Fe₃O₄ and CuO-Fe₃O₄ are illustrated in Figure 6.9 . The Nyquist plots of the three thin films are similar except for the diameters of the semicircles. Impedance spectroscopy is divided to the high and low frequency region. The high frequency of the spectrum is related to charge transfer phenomenon, while low frequency activity is attributed to mass transfer processes.¹³⁹ The CuO nanoneedle arrays demonstrate the lowest diameter of semicircle, while interconnected Fe₃O₄ nanoflakes display the largest diameter. Here, the main reason for such behavior can be attributed to the highest electrical conductivity of CuO nanoneedle arrays and lowest conductivity of Fe₃O₄ nanoflakes. The highest conductivity of CuO Nanoneedle can be explained based of the existence of the residual copper, which is a result of incomplete anodization process and conversion reaction with lithium.¹⁰⁶ It can be concluded that in CuO-Fe₃O₄ hybrid, CuO

nanoneedle arrays used as scaffold for growth of Fe_3O_4 , behaves as good 1D electron pathway and improve the electronic conductivity of the hybrid anode material.

Figure 6.9 Nyquist plots of CuO, Fe_3O_4 and CuO- Fe_3O_4 core-shell electrodes obtained by application of a sine wave At amplitude of 10.0 mV over the frequency range 10 kHz–0.1 Hz.

In order to further examine the stability of CuO- Fe_3O_4 core-shell hybrid structure, lithium ion battery cells cycled at 1C rate for 100 cycles were opened in glove box and studies using SEM (see Figure 6.10). It can be observed that CuO- Fe_3O_4 hybrid have retained their free-standing nanowire morphology and while some agglomeration can be observed, connecting some wires together, the open structure is retained and no breakage and deformation is visible. It needs to be noted that the diameters of nanoneedles have increased to about 300-400 nm, which is a result of undergoing reaction of CuO- Fe_3O_4 with lithium during cycling.¹²⁶

Figure 6.10 (A-B) SEM images of CuO- Fe_3O_4 core-shell hybrid after Charge/discharge at (1C) between 0.05-3.00 V (vs Li/Li^+) for 100 cycles.

The reason for such outstanding electrochemical properties can be related to the intrinsic properties of CuO and the unique nanostructure of CuO nanoneedle arrays.

Figure 6.11 Schematic drawing of (A) CuO nanoneedle arrays fabricated by anodization of high purity Cu foil, (B) Fe₃O₄-CuO core-shell fabricated by electrodeposition of Fe₃O₄ at -1.1 V on CuO nanoneedle arrays, (C) Fe₃O₄-CuO 3D network hybrids fabricated by electrodeposition of Fe₃O₄ at -1.2 V on CuO nanoneedle arrays.

According to the presented results, it can be concluded that Fe₃O₄-CuO hybrids have superior electrochemical performance compared to the individual components (CuO and Fe₃O₄). The authors believe that the high capacity, perfect stability and ultrafast charging/discharging capability of coaxial Fe₃O₄-CuO hybrids comes from the smart selection of two compatible components with promising properties and their intelligent integration to unique hierarchical architectures. As can be observed in the schematic drawing in Figure 6.11, the free-standing ultra-fast CuO nanoneedle arrays as core provides 1D electronic pathway, structural spacer and superior rate capabilities due to the existence of copper cores formed by incomplete anodization and lithium conversion reactions.¹⁰⁶ On the other hand, the mesoporous Fe₃O₄ nanocrystals with high specific capacity are grown directly on CuO with perfect adhesion, while maintaining the

open structure. This allows buffering of huge volume swings at high cycling rates and penetration of the electrolyte to the depth of the 3D structure. The mesoporosity of both components decreases the Li^+ ions diffusion length and provide active sites for reaction. This results in high delivered capacity with exceptional cycling stability at high cycling rates. Compared to 2D thin films or 3D nanowire arrays the presented hybrids presents much higher areal capacity, due to the efficient loading of additional active material in the vertical dimension, while maintaining similar Li ion transport efficiency and porosity.

Two types of $\text{Fe}_3\text{O}_4\text{-CuO}$ hybrids with core-shell and hierarchical 3D network was fabricated and investigated in this study. As discussed, at 1C rate initially both hybrids presented similar electrochemical properties, but with increase in cycle number the gradual capacity fade in the initial cycles became more rapid in the hierarchical $\text{Fe}_3\text{O}_4\text{-CuO}$ 3D network. Nevertheless, the capacity was stabilized after the 33th cycle, delivering stable capacity thereafter. Similar situation was observed when the hybrids were examined for their rate capabilities. Both hybrids exposed similar behaviors up to 1C, but with increase of rate to 2C and higher rates the hierarchical $\text{Fe}_3\text{O}_4\text{-CuO}$ 3D network started to drop to lower specific capacities. Additionally, when the rate was again decreased to 0.2 C the core-shell $\text{Fe}_3\text{O}_4\text{-CuO}$ retrieved its initial capacity, while the hierarchical $\text{Fe}_3\text{O}_4\text{-CuO}$ 3D network could not recover completely. The reason for such behavior can be the fact that in the hierarchical $\text{Fe}_3\text{O}_4\text{-CuO}$ 3D network with interconnected nanoflakes, Fe_3O_4 plays a more dominant role and influences the electrochemical performance with its poorer rate capabilities, while in core-shell $\text{Fe}_3\text{O}_4\text{-CuO}$ this short coming is suppressed. These results demonstrate the importance of electrode engineering and their huge influence on electrochemical properties.

6.5 *Conclusion*

Herein, we report a facile, template free two-step electrochemical method to fabricate free-standing coaxial $\text{Fe}_3\text{O}_4\text{-CuO}$ hybrid electrodes grown directly on copper substrate. The electrodes are made of free-standing CuO nanoneedle arrays electrochemically coated with mesoporous

Fe_3O_4 nanocrystals. The Fe_3O_4 -CuO electrodes were directly used as lithium-ion battery anodes without use of any binder. The electrochemical properties of two types of core-shell and hierarchical 3D network of Fe_3O_4 -CuO hybrids were thoroughly studied and compared with the single phase CuO and Fe_3O_4 nanostructures as the hybrid building blocks. The Fe_3O_4 -CuO hybrids demonstrated superior properties at 1C rate and perfect rate capability when tested to up to 15C. Excellent electrochemical performance of Fe_3O_4 -CuO hybrids comes from their smart selection and unique hierarchical architecture. The three-dimensional mesoporous Fe_3O_4 nanocrystals offers high surface area for electrochemical reaction, while the one-dimensional CuO nanoneedle arrays with direct contact to the current collector serve both as structural spacer to buffer the strain during lithiation/delithiation and act as a good electron pathway to improve electronic conductivity. Further constructive design and development of such hierarchical hybrids can open new opportunities in energy storage application and other fields such as sensing and photoconversion.

7 Conclusion and future work

7.1 Conclusion

In this thesis, a rational design and development of advanced nanostructured copper oxide based hybrid anodes with two main electrochemical reactions of alloying and conversion was carried out. The concentration of this work was to develop facile, green, template free electrochemical fabrication processes for fabrication of coaxial, binder-free, free-standing hybrid anodes with high energy density, good cycling stability; especially at high cycling rates and good rate capability with practical application.

Detailed investigation of synergetic effects of the hybrids constituents and the important parameters influencing the electrochemical performance such as nanostructure, porosity, architecture was carried out. Development and application of different types of hybrids by combining chemically distinct materials with explicit electrochemical properties were pursued with the aim to achieve multi-functionality or expose novel enhanced electrochemical properties. Schematic drawing of summary of the copper oxide based hybrids developed in the presented thesis is presented in Figure 7.1.

Copper oxide was selected as the suitable core and scaffold for growth of metallic compound hybrid. CuO nanoneedle arrays were fabricated by a simple anodization process. In electrochemical examination, when tested at 1C, CuO nanoneedle array anodes demonstrated outstanding stability, delivering 559 mAh/g specific capacity to up to 200 cycles, while illustrating perfect rate capability to up to 50 C. It is believed that the residual copper of the incomplete anodization during production and irreversible conversion reaction during cycling behaves as a good electron pathway and improves the electronic conductivity of the anode material, resulting in outstanding cycling stability and rate capability.

Figure 7.1 Schematic drawing of summary of the copper oxide based hybrids developed in the presented thesis.

Sb nanoflakes bundles with high uniformity and purity were formed using pulse galvanostatic method. Antimony is a promising anode material with high electrical conductivity which undergoes alloying reaction upon interaction with lithium during the charge/discharge process. Although binder free Sb nanoplates exposed high initial capacity close to the theoretical value (660 mAh/g), the property could not be maintained and after nine cycles the electrode faded abruptly to reach capacities lower than 100 mAh/g after 70 cycles. To develop an anode with improved electrical conductivity and electrochemical stability, free-standing Sb/Cu₂Sb/Cu hybrid electrodes were grown directly on copper substrate by a two-step electrochemical method, using

$\text{Cu}(\text{OH})_2$ nanoneedle arrays as scaffold for Sb deposition. The aim of this attempt was to fabricate Sb-CuO core-shell nanowires. However, application of a reductive current resulted in reduction of copper hydroxide to copper and formation of $\text{Cu}_2\text{Sb}/\text{Cu}$ core-shell during heat treatment. It was observed that compared to pure Sb nanoplates, Sb/ $\text{Cu}_2\text{Sb}/\text{Cu}$ hybrids demonstrated improved cycling stability and enhanced rate capability to up to 20 C. The authors believe that this improvement is due to application of free-standing Cu core which provides 1D electronic pathway and structural spacer. While, the mesoporous Cu_2Sb nanocrystals with direct contact to the copper core and strong structural relationship with the lithiated phase; Li_2CuSb , leads to enhanced rate capability and a more stable electrochemical performance.

Next, a safe fabrication route was utilized to fabricate free-standing several micron lengths, core-shell Ge- Cu_2O hybrid nanowire arrays. The aim was to achieve a highly stable anode with high specific capacity and fast diffusion rates. The Ge- Cu_2O hybrid nanowire arrays with conversion-alloying reactions were developed by combining electrochemical anodization and CVD growth. The Ge shell with 50-80 nm thickness was highly mesoporous with good adhesion to the Cu_2O core. At 0.5C and 1C large improvement in electrochemical performance was observed in core-shell Ge- Cu_2O hybrid compared to Ge nanoparticles; which demonstrated fast fading electrochemical properties. In-situ generation of GeO_2 was observed in Ge- Cu_2O hybrid electrodes from the initial cycle. The formation of GeO_2 was explained based on the different electroactive response of hybrid's building block towards Li^+ ; with Cu_2O undergoing conversion reaction and Ge undergoing alloying reaction with the capability to react electrochemically with Li_2O . The superior electrochemical performance of Ge- Cu_2O hybrid comes from their smart selection and unique hierarchical architecture. Ge shell with high theoretical capacity and uniform mesoporosity affords short diffusion distances and achievement of high specific capacities. Direct growth of 1D Cu_2O nanoneedle arrays on Cu substrates improves contact and enhances electrical conductivity resulting in better rate capabilities. The open interspaces between the core-shell nanowires allow quick infiltration of electrolyte into the structure, partially accommodating the volume expansion during lithiation and alleviating material loss.

Finally, two types of free-standing coaxial $\text{Fe}_3\text{O}_4\text{-CuO}$ conversion hybrids, with core-shell and hierarchical 3D network architecture were developed using a facile, template-free, two-step electrochemical method. Interconnected Fe_3O_4 nanoflakes delivered high initial capacity, but faded fast when tested at high cycling rates. Nevertheless, the $\text{Fe}_3\text{O}_4\text{-CuO}$ hybrids demonstrated superior properties at 1C rate and perfect rate capability when tested to up to 15C. For example core-shell $\text{Fe}_3\text{O}_4\text{-CuO}$ hybrid delivered a high initial discharge capacity of 1208 mAh/g which reduced to 868 mAh/g in the second cycle. The hybrid demonstrated perfect stability, delivering 954 mAh/g discharge capacity with 99% Coulombic efficiency after 100 cycles. It is believed that the excellent electrochemical properties of $\text{Fe}_3\text{O}_4\text{-CuO}$ hybrids come from their unique hierarchical architecture. The three-dimensional mesoporous Fe_3O_4 nanocrystals offer high surface area for electrochemical reaction, while the one-dimensional CuO nanoneedle arrays with perfect rate capability and direct contact to the current collector serve both as structural spacer to buffer the strain during lithiation/delithiation and act as good electron pathway to improve electronic conductivity.

The discussed findings highlights the many possibilities and advantages of deposition routes and demonstrates the large opportunities of hybrid electrodes to overcome the limiting intrinsic properties of single component electrodes and develop the next generation Lithium ion batteries with enhanced properties in all aspects.

7.2 *Future work*

Based on the findings of the present work, further investigation and development of template free electrodeposition technique can be encouraged. Fabrication of free-standing nanostructured thin-films is largely investigated in many fields, e.g., energy storage and conversion, photovoltaic. Electrochemical technique is a simple, cheap and fast method which can be performed in room temperature under air atmosphere. Generally, electrodeposition usually needs application of hard templates to fabricate nanostructure, e.g. anodized aluminum oxides to produce nanowire arrays^{97, 98}, or polystyrene sphere for fabrication of porous nanostructures which need to be

removed afterwards. However, as presented template free methods like pulse plating, high over-potential conditions can be successfully utilized to grow different types of nanostructured electrodes and hybrids, e.g., nanoflake, nanowires, cubes, ... of different materials, e.g., CuO, Sb, Fe₃O₄, ... The authors believe that the developed template free fabrication routes is applicable to many other promising materials and hybrids for different applications, e.g. Sn, Co₃O₄, TiO₂, TiO₂-Fe₃O₄, TiO₂-SnO₂.

Growth and application of many one-dimensional nanomaterials and hybrids for energy conversion and storage is reported in large scale. However, the 3D interconnected nanostructures, in addition to having the advantage of open structure and short diffusion length, the problem of complete disconnection and loss of active material is largely subsided due to the 3D interconnection. The 3D electrode also has the advantage of higher material loading compared to 2D electrodes. In the current thesis successful fabrication of Fe₃O₄ 3D network, composed of interconnected flakes was pursued using electrodeposition. Based on this observation, further detailed investigation of 3D interconnected nanostructured hybrids of promising electroactive materials such as Si, Fe₃O₄, Co₃O₄ is encouraged. The process is simple and straight forward and allows fast and cheap template free formation of binder-free three dimensional nanostructures directly grown on current collector.

With the prevalence of portable electronic the claim for rechargeable energy storage devices with high energy density and low-weight has been raising rapidly. Many different strategies has been suggested and examined in the last decade. However, finally it has come to this point that limited by the intrinsic properties of materials the single component nanostructures may not meet the high expectations. Based on the presented study of the influencing parameters smart design and development of many different hybrid electrodes with 1D, 2D and 3D nanostructures and combination of different types of electroactive materials such as TiO₂-SnO₂, Fe₂O₃-SnO₂, Fe₃O₄-SnO₂, SnO₂-Co₃O₄ can be encouraged. Careful examination of hybrid's interface, evolution of hybrid constituent's in terms of chemical composition, phase and nanostructure during lithiation and the synergetic properties of the hybrid's building block can deepen our understanding of

hybrid electrodes. Physical and mathematical calculation in addition to simulation studies of the hybrid interfaces, electronic and ionic conductivity can open whole new possibilities to novel superior hybrids. The investigation of structural change and stress build up in different hybrid systems, composed of different materials with different morphologies such as core-shell wire or particles can help develop novel electroactive hybrid electrodes.

Understanding and application of the proposed strategies can open new opportunities to develop the next generation energy conversion and storage devices, which can meet the high energy demands of today and tomorrow.

8 References:

1. Tarascon, J. M.; Armand, M., Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, 414, (6861), 359-367.
2. David Linden; Reddy, T., *Handbook of Batteries*. McGraw-Hill Inc.: New York, 1995.
3. Hayner, C. M.; Zhao, X.; Kung, H. H., Materials for rechargeable lithium-ion batteries. *Annual Review of Chemical and Biomolecular Engineering* **2012**, 3, 445-471.
4. Jeong, G.; Kim, Y. U.; Kim, H.; Kim, Y. J.; Sohn, H. J., Prospective materials and applications for Li secondary batteries. *Energy and Environmental Science* **2011**, 4, (6), 1986-2002.
5. Holzwarth, N. A. W.; Louie, S. G.; Rabi, S., Lithium-intercalated graphite: Self-consistent electronic structure for stages one, two, and three. *Physical Review B* **1983**, 28, (2), 1013.
6. Patil, A.; Patil, V.; Wook Shin, D.; Choi, J. W.; Paik, D. S.; Yoon, S. J., Issue and challenges facing rechargeable thin film lithium batteries. *Materials Research Bulletin* **2008**, 43, (8-9), 1913-1942.
7. Obrovac, M. N.; Christensen, L.; Le, D. B.; Dahn, J. R., Alloy design for lithium-ion battery anodes. *Journal of the Electrochemical Society* **2007**, 154, (9).
8. Huggins, R. A., Lithium alloy negative electrodes. *Journal of Power Sources* **1999**, 81-82, 13-19.
9. Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novák, P., Insertion electrode materials for rechargeable lithium batteries. *Advanced Materials* **1998**, 10, (10), 725-763.
10. Winter, M.; Besenhard, J. O., Electrochemical lithiation of tin and tin-based intermetallics and composites. *Electrochimica Acta* **1999**, 45, (1), 31-50.
11. Besenhard, J. O.; Yang, J.; Winter, M., Will advanced lithium-alloy anodes have a chance in lithium-ion batteries? *Journal of Power Sources* **1997**, 68, (1), 87-90.
12. Mao, O.; Turner, R. L.; Courtney, I. A.; Fredericksen, B. D.; Buckett, M. I.; Krause, L. J.; Dahn, J. R., Active/Inactive Nanocomposites as Anodes for Li-Ion Batteries. *Electrochemical and Solid-State Letters* **1999**, 2, (1), 3-5.
13. Aricò, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; Van Schalkwijk, W., Nanostructured materials for advanced energy conversion and storage devices. *nature materials* **2005**, 4, (5), 366-377.
14. Zhang, S.; Ding, M. S.; Xu, K.; Allen, J.; Jow, T. R., Understanding solid electrolyte interface film formation on graphite electrodes. *Electrochemical and Solid-State Letters* **2001**, 4, (12), A206-A208.
15. Peled, E., Film forming reaction at the lithium/electrolyte interface. *Journal of Power Sources* **1983**, 9, (3), 253-266.
16. Guo, Y. G.; Hu, J. S.; Wan, L. J., Nanostructured materials for electrochemical energy conversion and storage devices. *Advanced Materials* **2008**, 20, (23), 2878-2887.
17. Beaulieu, L. Y.; Hatchard, T. D.; Bonakdarpour, A.; Fleischauer, M. D.; Dahn, J. R., Reaction of Li with alloy thin films studied by in situ AFM. *Journal of the Electrochemical Society* **2003**, 150, (11).
18. Bruce, P. G.; Scrosati, B.; Tarascon, J. M., Nanomaterials for rechargeable lithium batteries. *Angewandte Chemie - International Edition* **2008**, 47, (16), 2930-2946.
19. Guo, Y. G.; Hu, Y. S.; Sigle, W.; Maier, J., Superior Electrode Performance of Nanostructured Mesoporous TiO₂ (Anatase) through Efficient Hierarchical Mixed Conducting Networks. *Advanced Materials* **2007**, 19, (16), 2087-2091.
20. Shaju, K. M.; Jiao, F.; Débart, A.; Bruce, P. G., Mesoporous and nanowire Co₃O₄ as negative electrodes for rechargeable lithium batteries. *Physical Chemistry Chemical Physics* **2007**, 9, (15), 1837-1842.

21. Park, M. S.; Wang, G. X.; Kang, Y. M.; Wexler, D.; Dou, S. X.; Liu, H. K., Preparation and electrochemical properties of SnO₂ nanowires for application in lithium-ion batteries. *Angewandte Chemie - International Edition* **2007**, 46, (5), 750-753.
22. Chan, C. K.; Peng, H.; Liu, G.; McIlwrath, K.; Zhang, X. F.; Huggins, R. A.; Cui, Y., High-performance lithium battery anodes using silicon nanowires. *Nature Nanotechnology* **2008**, 3, (1), 31-35.
23. Du, N.; Zhang, H.; Chen, B.; Wu, J.; Ma, X.; Liu, Z.; Zhang, Y.; Yang, D.; Huang, X.; Tu, J., Porous Co₃O₄ Nanotubes Derived From Co₄(CO)₁₂ Clusters on Carbon Nanotube Templates: A Highly Efficient Material For Li-Battery Applications. *Advanced Materials* **2007**, 19, (24), 4505-4509.
24. Park, M. H.; Kim, K.; Kim, J.; Cho, J., Flexible dimensional control of high-capacity Li-Ion-battery anodes: from 0D hollow to 3D porous germanium nanoparticle assemblies. *Advanced Materials* **2010**, 22, (3), 415-418.
25. Cao, A. M.; Hu, J. S.; Liang, H. P.; Wan, L. J., Self-Assembled Vanadium Pentoxide (V₂O₅) Hollow Microspheres from Nanorods and Their Application in Lithium-Ion Batteries. *Angewandte Chemie* **2005**, 117, (28), 4465-4469.
26. Ji, L.; Lin, Z.; Alcoutlabi, M.; Zhang, X., Recent developments in nanostructured anode materials for rechargeable lithium-ion batteries. *Energy and Environmental Science* **2011**, 4, (8), 2682-2689.
27. Débart, A.; Dupont, L.; Poizot, P.; Leriche, J. B.; Tarascon, J. M., A Transmission Electron Microscopy Study of the Reactivity Mechanism of Tailor-Made CuO Particles toward Lithium. *Journal of the Electrochemical Society* **2001**, 148, (11), A1266-A1274.
28. Sahay, R.; Suresh Kumar, P.; Aravindan, V.; Sundaramurthy, J.; Chui Ling, W.; Mhaisalkar, S. G.; Ramakrishna, S.; Madhavi, S., High aspect ratio electrospun CuO nanofibers as anode material for lithium-ion batteries with superior cycleability. *Journal of Physical Chemistry C* **2012**, 116, (34), 18087-18092.
29. Chen, X.; Zhang, N.; Sun, K., Facile fabrication of CuO mesoporous nanosheet cluster array electrodes with super lithium-storage properties. *Journal of Materials Chemistry* **2012**, 22, (27), 13637-13642.
30. Wang, Z.; Su, F.; Madhavi, S.; Lou, X. W., CuO nanostructures supported on Cu substrate as integrated electrodes for highly reversible lithium storage. *Nanoscale* **2011**, 3, (4), 1618-1623.
31. Lockman, Z.; Ismail, S.; Sreekantan, S.; Schmidt-Mende, L.; MacManus-Driscoll, J. L., The rapid growth of 3 µm long titania nanotubes by anodization of titanium in a neutral electrochemical bath. *Nanotechnology* **2010**, 21, (5).
32. Allam, N. K.; Feng, X. J.; Grimes, C. A., Self-assembled fabrication of vertically oriented Ta₂O₅ nanotube arrays, and membranes thereof, by one-step tantalum anodization. *Chemistry of Materials* **2008**, 20, (20), 6477-6481.
33. Allam, N. K.; Shankar, K.; Grimes, C. A., Photoelectrochemical and water photoelectrolysis properties of ordered TiO₂ nanotubes fabricated by Ti anodization in fluoride-free HCl electrolytes. *Journal of Materials Chemistry* **2008**, 18, (20), 2341-2348.
34. Ruckh, T.; Porter, J. R.; Allam, N. K.; Feng, X.; Grimes, C. A.; Popat, K. C., Nanostructured tantalum as a template for enhanced osseointegration. *Nanotechnology* **2009**, 20, (4).
35. Allam, N. K.; Grimes, C. A., Electrochemical fabrication of complex copper oxide nanoarchitectures via copper anodization in aqueous and non-aqueous electrolytes. *Materials Letters* **2011**, 65, (12), 1949-1955.

36. Chen, X.; Zhang, N.; Sun, K., Facile fabrication of CuO 1D pine-needle-like arrays for super-rate lithium storage. *Journal of Materials Chemistry* **2012**, 22, (30), 15080-15084.
37. Liu, X.; Li, Z.; Zhang, Q.; Li, F.; Kong, T., Preparation of CuO/C core-shell nanowires and its application in lithium ion batteries. *Materials Letters* **2012**, 80, (0), 37-39.
38. Zheng, S.-F.; Hu, J.-S.; Zhong, L.-S.; Song, W.-G.; Wan, L.-J.; Guo, Y.-G., Introducing Dual Functional CNT Networks into CuO Nanomicrospheres toward Superior Electrode Materials for Lithium-Ion Batteries. *Chemistry of Materials* **2008**, 20, (11), 3617-3622.
39. Wang, B.; Wu, X. L.; Shu, C. Y.; Guo, Y. G.; Wang, C. R., Synthesis of CuO/graphene nanocomposite as a high-performance anode material for lithium-ion batteries. *Journal of Materials Chemistry* **2010**, 20, (47), 10661-10664.
40. Dailly, A.; Ghanbaja, J.; Willmann, P.; Billaud, D., Lithium insertion into new graphite-antimony composites. *Electrochimica Acta* **2003**, 48, (8), 977-984.
41. Park, C. M.; Kim, J. H.; Kim, H.; Sohn, H. J., Li-alloy based anode materials for Li secondary batteries. *Chemical Society Reviews* **2010**, 39, (8), 3115-3141.
42. Kim, M. G.; Cho, J., Reversible and high-capacity nanostructured electrode materials for li-ion batteries. *Advanced Functional Materials* **2009**, 19, (10), 1497-1514.
43. Scrosati, B., Recent advances in lithium ion battery materials. *Electrochimica Acta* **2000**, 45, (15-16), 2461-2466.
44. Stjerndahl, M.; Bryngelsson, H.; Gustafsson, T.; Vaughey, J. T.; Thackeray, M. M.; Edström, K., Surface chemistry of intermetallic AlSb-anodes for Li-ion batteries. *Electrochimica Acta* **2007**, 52, (15), 4947-4955.
45. Zhao, H.; Yin, C.; Guo, H.; He, J.; Qiu, W.; Li, Y., Studies of the electrochemical performance of Sn-Sb alloy prepared by solid-state reduction. *Journal of Power Sources* **2007**, 174, (2), 916-920.
46. Fransson, L. M. L.; Vaughey, J. T.; Benedek, R.; Edström, K.; Thomas, J. O.; Thackeray, M. M., Phase transitions in lithiated Cu₂Sb anodes for lithium batteries: An in situ X-ray diffraction study. *Electrochemistry Communications* **2001**, 3, (7), 317-323.
47. Fransson, L. M. L.; Vaughey, J. T.; Edström, K.; Thackeray, M. M., Structural transformations in intermetallic electrodes for lithium batteries. An in situ x-ray diffraction study of lithiated MnSb and Mn₂Sb. *Journal of the Electrochemical Society* **2003**, 150, (1).
48. Fan, X. Y.; Zhuang, Q. C.; Wei, G. Z.; Huang, L.; Dong, Q. F.; Sun, S. G., One-step electrodeposition synthesis and electrochemical properties of Cu₆Sn₅ alloy anodes for lithium-ion batteries. *Journal of Applied Electrochemistry* **2009**, 39, (8), 1323-1330.
49. Grugeon, S.; Laruelle, S.; Dupont, L.; Tarascon, J. M., An update on the reactivity of nanoparticles co-based compounds towards Li. *Solid State Sciences* **2003**, 5, (6), 895-904.
50. Cui, G.; Gu, L.; Zhi, L.; Kaskhedikar, N.; Van Aken, P. A.; Müllen, K.; Maier, J., A germanium-carbon nanocomposite material for lithium batteries. *Advanced Materials* **2008**, 20, (16), 3079-3083.
51. Chan, C. K.; Zhang, X. F.; Cui, Y., High capacity Li ion battery anodes using Ge nanowires. *Nano Letters* **2008**, 8, (1), 307-309.
52. Lee, H.; Cho, J., Sn₇₈Ge₂₂@Carbon Core-Shell Nanowires as Fast and High-Capacity Lithium Storage Media. *Nano Letters* **2007**, 7, (9), 2638-2641.
53. Zhang, W.-M.; Wu, X.-L.; Hu, J.-S.; Guo, Y.-G.; Wan, L.-J., Carbon Coated Fe₃O₄ Nanospindles as a Superior Anode Material for Lithium-Ion Batteries. *Advanced Functional Materials* **2008**, 18, (24), 3941-3946.

54. Behera, S. K., Enhanced rate performance and cyclic stability of Fe₃O₄-graphene nanocomposites for Li ion battery anodes. *Chemical Communications* **2011**, 47, (37), 10371-10373.
55. Xiong, Q. Q.; Tu, J. P.; Lu, Y.; Chen, J.; Yu, Y. X.; Wang, X. L.; Gu, C. D., Three-dimensional porous nano-Ni/Fe₃O₄ composite film: Enhanced electrochemical performance for lithium-ion batteries. *Journal of Materials Chemistry* **2012**, 22, (35), 18639-18645.
56. Liu, C.; Li, F.; Ma, L.-P.; Cheng, H.-M., Advanced Materials for Energy Storage. *Advanced Materials* **2010**, 22, (8), E28-E62.
57. Kang, B.; Ceder, G., Battery materials for ultrafast charging and discharging. *Nature* **2009**, 458, (7235), 190-193.
58. Song, T.; Cheng, H.; Choi, H.; Lee, J.-H.; Han, H.; Lee, D. H.; Yoo, D. S.; Kwon, M.-S.; Choi, J.-M.; Doo, S. G.; Chang, H.; Xiao, J.; Huang, Y.; Park, W. I.; Chung, Y.-C.; Kim, H.; Rogers, J. A.; Paik, U., Si/Ge Double-Layered Nanotube Array as a Lithium Ion Battery Anode. *ACS Nano* **2011**, 6, (1), 303-309.
59. Zhou, W.; Tay, Y. Y.; Jia, X.; Yau Wai, D. Y.; Jiang, J.; Hoon, H. H.; Yu, T., Controlled growth of SnO₂@Fe₂O₃ double-sided nanocombs as anodes for lithium-ion batteries. *Nanoscale* **2012**, 4, (15), 4459-4463.
60. Djenizian, T.; Hanzu, I.; Knauth, P., Nanostructured negative electrodes based on titania for Li-ion microbatteries. *Journal of Materials Chemistry* **2011**, 21, (27), 9925-9937.
61. Ortiz, G. F.; Hanzu, I.; Lavela, P.; Tirado, J. L.; Knauth, P.; Djenizian, T., A novel architected negative electrode based on titania nanotube and iron oxide nanowire composites for Li-ion microbatteries. *Journal of Materials Chemistry* **2010**, 20, (20), 4041-4046.
62. Wu, X.; Zhang, S.; Wang, L.; Du, Z.; Fang, H.; Ling, Y.; Huang, Z., Coaxial SnO₂@TiO₂ nanotube hybrids: From robust assembly strategies to potential application in Li⁺ storage. *Journal of Materials Chemistry* **2012**, 22, (22), 11151-11158.
63. Liu, X.-M.; Huang, Z. d.; Oh, S. w.; Zhang, B.; Ma, P.-C.; Yuen, M. M. F.; Kim, J.-K., Carbon nanotube (CNT)-based composites as electrode material for rechargeable Li-ion batteries: A review. *Composites Science and Technology* **2012**, 72, (2), 121-144.
64. Praveen, B. M.; Venkatesha, T. V., Electrodeposition and properties of Zn-Ni-CNT composite coatings. *Journal of Alloys and Compounds* **2009**, 482, (1-2), 53-57.
65. Nam, K. W.; Lee, C. W.; Yang, X. Q.; Cho, B. W.; Yoon, W. S.; Kim, K. B., Electrodeposited manganese oxides on three-dimensional carbon nanotube substrate: Supercapacitive behaviour in aqueous and organic electrolytes. *Journal of Power Sources* **2009**, 188, (1), 323-331.
66. Wu, Z.-S.; Zhou, G.; Yin, L.-C.; Ren, W.; Li, F.; Cheng, H.-M., Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy* **2012**, 1, (1), 107-131.
67. Hsieh, C.-T.; Lin, C.-Y.; Lin, J.-Y., High reversibility of Li intercalation and de-intercalation in MnO-attached graphene anodes for Li-ion batteries. *Electrochimica Acta* **2011**, 56, (24), 8861-8867.
68. Zhu, X.; Zhu, Y.; Murali, S.; Stoller, M. D.; Ruoff, R. S., Nanostructured Reduced Graphene Oxide/Fe₂O₃ Composite As a High-Performance Anode Material for Lithium Ion Batteries. *ACS Nano* **2011**, 5, (4), 3333-3338.
69. Zhu, J.; Sharma, Y. K.; Zeng, Z.; Zhang, X.; Srinivasan, M.; Mhaisalkar, S.; Zhang, H.; Hng, H. H.; Yan, Q., Cobalt Oxide Nanowall Arrays on Reduced Graphene Oxide Sheets with Controlled Phase, Grain Size, and Porosity for Li-Ion Battery Electrodes. *The Journal of Physical Chemistry C* **2011**, 115, (16), 8400-8406.

70. Jiang, J.; Li, Y.; Liu, J.; Huang, X.; Yuan, C.; Lou, X. W., Recent advances in metal oxide-based electrode architecture design for electrochemical energy storage. *Advanced Materials* **2012**, 24, (38), 5166-5180.
71. Liu, R.; Sang, B. L., MnO₂/poly(3,4-ethylenedioxythiophene) coaxial nanowires by one-step coelectrodeposition for electrochemical energy storage. *Journal of the American Chemical Society* **2008**, 130, (10), 2942-2943.
72. Guo, Z. P.; Wang, J. Z.; Liu, H. K.; Dou, S. X., Study of silicon/polypyrrole composite as anode materials for Li-ion batteries. *Journal of Power Sources* **2005**, 146, (1-2), 448-451.
73. Cao, F. F.; Deng, J. W.; Xin, S.; Ji, H. X.; Schmidt, O. G.; Wan, L. J.; Guo, Y. G., Cu-Si nanocable arrays as high-rate anode materials for lithium-ion batteries. *Advanced Materials* **2011**, 23, (38), 4415-4420.
74. Park, K.-S.; Kang, J.-G.; Choi, Y.-J.; Lee, S.; Kim, D.-W.; Park, J.-G., Long-term, high-rate lithium storage capabilities of TiO₂ nanostructured electrodes using 3D self-supported indium tin oxide conducting nanowire arrays. *Energy & Environmental Science* **2011**, 4, (5), 1796-1801.
75. Wang, W.; Tian, M.; Abdulagatov, A.; George, S. M.; Lee, Y. C.; Yang, R., Three-dimensional Ni/TiO₂ nanowire network for high areal capacity lithium ion microbattery applications. *Nano Letters* **2012**, 12, (2), 655-660.
76. Liu, R.; Duay, J.; Lee, S. B., Heterogeneous nanostructured electrode materials for electrochemical energy storage. *Chemical Communications* **2011**.
77. Zhou, W.; Cheng, C.; Liu, J.; Tay, Y. Y.; Jiang, J.; Jia, X.; Zhang, J.; Gong, H.; Hng, H. H.; Yu, T.; Fan, H. J., Epitaxial Growth of Branched α -Fe₂O₃/SnO₂ Nano-Heterostructures with Improved Lithium-Ion Battery Performance. *Advanced Functional Materials* **2011**, 21, (13), 2439-2445.
78. Liu, J.; Jiang, J.; Cheng, C.; Li, H.; Zhang, J.; Gong, H.; Fan, H. J., Co₃O₄ Nanowire@MnO₂ Ultrathin Nanosheet Core/Shell Arrays: A New Class of High-Performance Pseudocapacitive Materials. *Advanced Materials* **2011**, 23, (18), 2076-2081.
79. Zhou, S.; Liu, X.; Wang, D., Si/TiSi₂ heteronanostructures as highcapacity anode material For li ion batteries. *Nano Letters* **2010**, 10, (3), 860-863.
80. Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions. In Pergamon Press: New York, 1966.
81. Allen J. Bard; Faulkner, L. R., Electrochemical Methods: Fundamentals and Applications, 2nd Edition. In John Wiley: New York, 2001.
82. Yin, Z.; Wu, S.; Zhou, X.; Huang, X.; Zhang, Q.; Boey, F.; Zhang, H., Electrochemical deposition of ZnO nanorods on transparent reduced graphene oxide electrodes for hybrid solar cells. *Small* **2010**, 6, (2), 307-312.
83. Wu, S.; Yin, Z.; He, Q.; Huang, X.; Zhou, X.; Zhang, H., Electrochemical deposition of semiconductor oxides on reduced graphene oxide-based flexible, transparent, and conductive electrodes. *Journal of Physical Chemistry C* **2010**, 114, (27), 11816-11821.
84. Therese, G. H. A.; Kamath, P. V., Electrochemical Synthesis of Metal Oxides and Hydroxides. *Chemistry of Materials* **2000**, 12, (5), 1195-1204.
85. Saadat, S.; Zhu, J.; Shahjamali, M. M.; Maleksaeedi, S.; Tay, Y. Y.; Tay, B. Y.; Hng, H. H.; Ma, J.; Yan, Q., Template free electrochemical deposition of ZnSb nanotubes for Li ion battery anodes. *Chemical Communications* **2011**, 47, (35), 9849-9851.
86. Hao Sim, D.; Rui, X.; Chen, J.; Tan, H.; Lim, T. M.; Yazami, R.; Hng, H. H.; Yan, Q., Direct growth of FeVO₄ nanosheet arrays on stainless steel foil as high-performance binder-free Li ion battery anode. *RSC Advances* **2012**, 2, (9), 3630-3633.

87. Rui, X.; Sim, D.; Xu, C.; Liu, W.; Tan, H.; Wong, K.; Hng, H. H.; Lim, T. M.; Yan, Q., One-pot synthesis of carbon-coated VO₂(B) nanobelts for high-rate lithium storage. *RSC Advances* **2012**, 2, (3), 1174-1180.
88. Xu, C.; Zeng, Y.; Rui, X.; Xiao, N.; Zhu, J.; Zhang, W.; Chen, J.; Liu, W.; Tan, H.; Hng, H. H.; Yan, Q., Controlled soft-template synthesis of ultrathin C@FeS nanosheets with high-Li-storage performance. *ACS Nano* **2012**, 6, (6), 4713-4721.
89. Zhang, W.; Zeng, Y.; Xiao, N.; Hng, H. H.; Yan, Q., One-step electrochemical preparation of graphene-based heterostructures for Li storage. *Journal of Materials Chemistry* **2012**, 22, (17), 8455-8461.
90. Song, M.-K.; Park, S.; Alamgir, F. M.; Cho, J.; Liu, M., Nanostructured electrodes for lithium-ion and lithium-air batteries: the latest developments, challenges, and perspectives. *Materials Science and Engineering: R: Reports* **2011**, 72, (11), 203-252.
91. Shi, W.; Rui, X.; Zhu, J.; Yan, Q., Design of Nanostructured Hybrid Materials Based on Carbon and Metal Oxides for Li Ion Batteries. *The Journal of Physical Chemistry C* **2012**.
92. Wu, H. B.; Chen, J. S.; Hng, H. H.; Wen Lou, X., Nanostructured metal oxide-based materials as advanced anodes for lithium-ion batteries. *Nanoscale* **2012**, 4, (8), 2526-2542.
93. Yin, Z.; Wu, S.; Zhou, X.; Huang, X.; Zhang, Q.; Boey, F.; Zhang, H., Electrochemical deposition of ZnO nanorods on transparent reduced graphene oxide electrodes for hybrid solar cells. *Small* 6, (2), 307-312.
94. Sundaram, R. S.; Gómez-Navarro, C.; Balasubramanian, K.; Burghard, M.; Kern, K., Electrochemical modification of grapheme. *Advanced Materials* **2008**, 20, (16), 3050-3053.
95. Hung, K. H.; Tzeng, S. S.; Kuo, W. S.; Wei, B.; Ko, T. H., Growth of carbon nanofibers on carbon fabric with Ni nanocatalyst prepared using pulse electrodeposition. *Nanotechnology* **2008**, 19, (29).
96. Taberna, P. L.; Mitra, S.; Poizot, P.; Simon, P.; Tarascon, J. M., High rate capabilities Fe₃O₄-based Cu nano-architected electrodes for lithium-ion battery applications. *Nat Mater* **2006**, 5, (7), 567-573.
97. Duan, H.; Gnanaraj, J.; Chen, X.; Li, B.; Liang, J., Fabrication and characterization of Fe₃O₄-based Cu nanostructured electrode for Li-ion battery. *Journal of Power Sources* **2008**, 185, (1), 512-518.
98. Chou, S.; Cheng, F.; Chen, J., Electrochemical Deposition of Ni(OH)₂ and Fe-Doped Ni(OH)₂ Tubes. *European Journal of Inorganic Chemistry* **2005**, 2005, (20), 4035-4039.
99. Bartlett, P. N.; Baumberg, J. J.; Birkin, P. R.; Ghanem, M. A.; Netti, M. C., Highly Ordered Macroporous Gold and Platinum Films Formed by Electrochemical Deposition through Templates Assembled from Submicron Diameter Monodisperse Polystyrene Spheres. *Chemistry of Materials* **2002**, 14, (5), 2199-2208.
100. Sahay, R.; Sundaramurthy, J.; Suresh Kumar, P.; Thavasi, V.; Mhaisalkar, S. G.; Ramakrishna, S., Synthesis and characterization of CuO nanofibers, and investigation for its suitability as blocking layer in ZnO NPs based dye sensitized solar cell and as photocatalyst in organic dye degradation. *Journal of Solid State Chemistry* **2012**, 186, (0), 261-267.
101. Kim, Y.-S.; Hwang, I.-S.; Kim, S.-J.; Lee, C.-Y.; Lee, J.-H., CuO nanowire gas sensors for air quality control in automotive cabin. *Sensors and Actuators B: Chemical* **2008**, 135, (1), 298-303.

102. Wijesundera, R. P., Fabrication of the CuO/Cu₂O heterojunction using an electrodeposition technique for solar cell applications. *Semiconductor Science and Technology* **2010**, 25, (4).
103. Ionica, C. M.; Lippens, P. E.; Fourcade, J. O.; Jumas, J. C., Study of Li insertion mechanisms in transition metal antimony compounds as negative electrodes for Li-ion battery. *Journal of Power Sources* **2005**, 146, (1-2), 478-481.
104. Zhao, X. B.; Cao, G. S., Study of Zn₄Sb₃ as a negative electrode for secondary lithium cells. *Electrochimica Acta* **2001**, 46, (6), 891-896.
105. Li, Y.; Tan, B.; Wu, Y., Mesoporous Co₃O₄ Nanowire Arrays for Lithium Ion Batteries with High Capacity and Rate Capability. *Nano Letters* **2007**, 8, (1), 265-270.
106. Liu, D.; Garcia, B. B.; Zhang, Q.; Guo, Q.; Zhang, Y.; Sepehri, S.; Cao, G., Mesoporous Hydrous Manganese Dioxide Nanowall Arrays with Large Lithium Ion Energy Storage Capacities. *Advanced Functional Materials* **2009**, 19, (7), 1015-1023.
107. Morales, J.; Sánchez, L.; Martín, F.; Ramos-Barrado, J. R.; Sánchez, M., Nanostructured CuO thin film electrodes prepared by spray pyrolysis: a simple method for enhancing the electrochemical performance of CuO in lithium cells. *Electrochimica Acta* **2004**, 49, (26), 4589-4597.
108. Park, J. C.; Kim, J.; Kwon, H.; Song, H., Gram-Scale Synthesis of Cu₂O Nanocubes and Subsequent Oxidation to CuO Hollow Nanostructures for Lithium-Ion Battery Anode Materials. *Advanced Materials* **2009**, 21, (7), 803-807.
109. Wang, H.; Pan, Q.; Zhao, J.; Yin, G.; Zuo, P., Fabrication of CuO film with network-like architectures through solution-immersion and their application in lithium ion batteries. *Journal of Power Sources* **2007**, 167, (1), 206-211.
110. Pan, Q.; Jin, H.; Wang, H.; Yin, G., Flower-like CuO film-electrode for lithium ion batteries and the effect of surface morphology on electrochemical performance. *Electrochimica Acta* **2007**, 53, (2), 951-956.
111. Xiang, J. Y.; Tu, J. P.; Qiao, Y. Q.; Wang, X. L.; Zhong, J.; Zhang, D.; Gu, C. D., Electrochemical Impedance Analysis of a Hierarchical CuO Electrode Composed of Self-Assembled Nanoplates. *The Journal of Physical Chemistry C* **2011**, 115, (5), 2505-2513.
112. Wang, C.; Wang, D.; Wang, Q.; Wang, L., Fabrication of three-dimensional porous structured Co₃O₄ and its application in lithium-ion batteries. *Electrochimica Acta* **2010**, 55, (22), 6420-6425.
113. Laruelle, S.; Grugeon, S.; Poizot, P.; Dollé, M.; Dupont, L.; Tarascon, J. M., On the origin of the extra electrochemical capacity displayed by MO/Li cells at low potential. *Journal of the Electrochemical Society* **2002**, 149, (5), A627-A634.
114. Wang, X.; Tang, D.-M.; Li, H.; Yi, W.; Zhai, T.; Bando, Y.; Golberg, D., Revealing the conversion mechanism of CuO nanowires during lithiation-delithiation by in situ transmission electron microscopy. *Chemical Communications* **2012**, 48, (40), 4812-4814.
115. Aicantara, R.; Fernandez-Madrigal, F. J.; Lavcla, P.; Tirado, J. L.; Jumas, J. C.; Olivier-Fourcade, J., Electrochemical reaction of lithium with the CoSb₃ skutterudite. *Journal of Materials Chemistry* **1999**, 9, (10), 2517-2521.
116. Zhu, J.; Sun, T.; Chen, J.; Shi, W.; Zhang, X.; Lou, X.; Mhaisalkar, S.; Hng, H. H.; Boey, F.; Ma, J.; Yan, Q., Controlled Synthesis of Sb Nanostructures and Their Conversion to CoSb₃ Nanoparticle Chains for Li-Ion Battery Electrodes. *Chemistry of Materials* **2010**, 22, (18), 5333-5339.
117. Bryngelsson, H.; Eskhult, J.; Nyholm, L.; Edström, K., Thin films of Cu₂Sb and Cu₉Sb₂ as anode materials in Li-ion batteries. *Electrochimica Acta* **2008**, 53, (24), 7226-7234.

118. Huang, X.; Zhu, Y.; Dou, X.; Li, G., Tuning peculiar antimony micro- and nano-morphology via a novel electrodeposition approach. *Materials Letters* **2008**, 62, (2), 249-251.
119. Park, C. M.; Yoon, S.; Lee, S. I.; Kim, J. H.; Jung, J. H.; Sohn, H. J., High-rate capability and enhanced cyclability of antimony-based composites for lithium rechargeable batteries. *Journal of the Electrochemical Society* **2007**, 154, (10).
120. Park, C. M.; Sohn, H. J., Novel antimony/aluminum/carbon nanocomposite for high-performance rechargeable lithium batteries. *Chemistry of Materials* **2008**, 20, (9), 3169-3173.
121. Park, C. M.; Sohn, H. J., Quasi-intercalation and facile amorphization in layered ZnSb for Li-ion batteries. *Advanced Materials* 22, (1), 47-52.
122. Yoon, S.; Park, C. M.; Sohn, H. J., Electrochemical characterizations of germanium and carbon-coated germanium composite anode for lithium-ion batteries. *Electrochemical and Solid-State Letters* **2008**, 11, (4), A42-A45.
123. Peña, J. S.; Sandu, I.; Joubert, O.; Pascual, F. S.; Areán, C. O.; Brousse, T., Electrochemical reaction between lithium and β -quartz GeO_2 . *Electrochemical and Solid-State Letters* **2004**, 7, (9), A278-A281.
124. Kim, C. H.; Jung, Y. S.; Lee, K. T.; Ku, J. H.; Oh, S. M., The role of in situ generated nano-sized metal particles on the coulombic efficiency of MGeO_3 (M = Cu, Fe, and Co) electrodes. *Electrochimica Acta* **2009**, 54, (18), 4371-4377.
125. Zhang, C. Q.; Tu, J. P.; Huang, X. H.; Yuan, Y. F.; Chen, X. T.; Mao, F., Preparation and electrochemical performances of cubic shape Cu_2O as anode material for lithium ion batteries. *Journal of Alloys and Compounds* **2007**, 441, (1-2), 52-56.
126. Cui, G.; Gu, L.; Zhi, L.; Kaskhedikar, N.; van Aken, P. A.; Müllen, K.; Maier, J., A Germanium–Carbon Nanocomposite Material for Lithium Batteries. *Advanced Materials* **2008**, 20, (16), 3079-3083.
127. Bazin, L.; Mitra, S.; Taberna, P. L.; Poizot, P.; Gressier, M.; Menu, M. J.; Barnabé, A.; Simon, P.; Tarascon, J. M., High rate capability pure Sn-based nano-architected electrode assembly for rechargeable lithium batteries. *Journal of Power Sources* **2009**, 188, (2), 578-582.
128. Golodnitsky, D.; Nathan, M.; Yufit, V.; Strauss, E.; Freedman, K.; Burstein, L.; Gladkikh, A.; Peled, E., Progress in three-dimensional (3D) Li-ion microbatteries. *Solid State Ionics* **2006**, 177, (26-32 SPEC. ISS.), 2811-2819.
129. Zeng, W.; Zheng, F.; Li, R.; Zhan, Y.; Li, Y.; Liu, J., Template synthesis of $\text{SnO}_2/[\alpha]\text{-Fe}_2\text{O}_3$ nanotube array for 3D lithium ion battery anode with large areal capacity. *Nanoscale* **2012**, 4, (8), 2760-2765.
130. Saadat, S.; Tay, Y. Y.; Zhu, J.; Teh, P. F.; Maleksaeedi, S.; Shahjamali, M. M.; Shakerzadeh, M.; Srinivasan, M.; Tay, B. Y.; Hng, H. H.; Ma, J.; Yan, Q., Template-free electrochemical deposition of interconnected ZnSb nanoflakes for Li-Ion battery anodes. *Chemistry of Materials* **2011**, 23, (4), 1032-1038.
131. Lian, P.; Zhu, X.; Xiang, H.; Li, Z.; Yang, W.; Wang, H., Enhanced cycling performance of Fe_3O_4 -graphene nanocomposite as an anode material for lithium-ion batteries. *Electrochimica Acta* **2010**, 56, (2), 834-840.
132. Taberna, P. L.; Mitra, S.; Poizot, P.; Simon, P.; Tarascon, J. M., High rate capabilities Fe_3O_4 -based Cu nano-architected electrodes for lithium-ion battery applications. *nature materials* **2006**, 5, (7), 567-573.
133. Duan, H.; Chen, X.; Li, B.; Liang, J., Growth morphology study of cathodically electrodeposited Fe_3O_4 thin films at elevated temperatures. *Materials Research Bulletin* **2010**, 45, (11), 1696-1702.

134. Mitra, S.; Poizot, P.; Finke, A.; Tarascon, J. M., Growth and Electrochemical Characterization versus Lithium of Fe_3O_4 Electrodes Made by Electrodeposition. *Advanced Functional Materials* **2006**, 16, (17), 2281-2287.
135. Zhang, Q.; Shi, Z.; Deng, Y.; Zheng, J.; Liu, G.; Chen, G., Hollow $\text{Fe}_3\text{O}_4/\text{C}$ spheres as superior lithium storage materials. *Journal of Power Sources* **2012**, 197, 305-309.
136. Wang, P. C.; Ding, H. P.; Bark, T.; Chen, C. H., Nanosized $\alpha\text{-Fe}_2\text{O}_3$ and Li-Fe composite oxide electrodes for lithium-ion batteries. *Electrochimica Acta* **2007**, 52, (24), 6650-6655.
137. Jin, S.; Deng, H.; Long, D.; Liu, X.; Zhan, L.; Liang, X.; Qiao, W.; Ling, L., Facile synthesis of hierarchically structured $\text{Fe}_3\text{O}_4/\text{carbon}$ micro-flowers and their application to lithium-ion battery anodes. *Journal of Power Sources* **2011**, 196, (8), 3887-3893.
138. Wang, L.; Yu, Y.; Chen, P. C.; Zhang, D. W.; Chen, C. H., Electrospinning synthesis of $\text{C}/\text{Fe}_3\text{O}_4$ composite nanofibers and their application for high performance lithium-ion batteries. *Journal of Power Sources* **2008**, 183, (2), 717-723.
139. Sharma, Y.; Sharma, N.; Subba Rao, G. V.; Chowdari, B. V. R., Studies on spinel cobaltites, FeCo_2O_4 and MgCo_2O_4 as anodes for Li-ion batteries. *Solid State Ionics* **2008**, 179, (15-16), 587-597.

Publication List

1. Saadat, S.; Zhu, J.; Shahjamali, M. M.; Maleksaeedi, S.; Tay, Y. Y.; Tay, B. Y.; Hng, H. H.; Ma, J.; Yan, Q., Template free electrochemical deposition of ZnSb nanotubes for Li ion battery anodes. *Chemical Communications* **2011**, 47, (35), 9849-9851.
2. Saadat, S.; Tay, Y. Y.; Zhu, J.; Teh, P. F.; Maleksaeedi, S.; Shahjamali, M. M.; Shakerzadeh, M.; Srinivasan, M.; Tay, B. Y.; Hng, H. H.; Ma, J.; Yan, Q., Template-free electrochemical deposition of interconnected ZnSb nanoflakes for Li-Ion battery anodes. *Chemistry of Materials* **2011**, 23, (4), 1032-1038.
3. Shahjamali, M. M.; Bosman, M.; Cao, S.; Huang, X.; Saadat, S.; Martinsson, E.; Aili, D.; Tay, Y. Y.; Liedberg, B.; Loo, S. C. J.; Zhang, H.; Boey, F.; Xue, C., Gold Coating of Silver Nanoprisms. *Advanced Functional Materials* **2012**, 22, (4), 849-854
4. Saadat, S.; Zhu, J.; Yazami, Y.; Sim, D.; Hng, H. H.; Yan, Q.; Coaxial Fe₃O₄/CuO Hybrids Nanowires as Ultra Fast Charge/Discharge Lithium-ion Battery Anodes. *Journal of Materials Chemistry A* 2013.
5. Saadat, S.; Zhu, J.; Hng, H. H.; Yan, Q., Fabrication of interconnected Fe₃O₄ nanotubes for Li ion battery anodes. Ready for submission.
6. Saadat, S.; Zhu, J.; Hng, H. H.; Yan, Q., Fabrication of free-standing Ge-Cu₂O hybrid for Li ion battery anodes. Ready for submission.