Iron oxide based anode material for lithium ion battery

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**IRON OXIDE BASED ANODE MATERIAL FOR
LITHIUM ION BATTERY**

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Aug 2017

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

Doctor of Philosophy

Aug 2017

Statement of Originality

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

4th Aug 2017

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ABSTRACT

Iron oxide is intensively studied as a potential anode material of lithium ion battery. Although it has a high theoretical capacity, the potential application is still limited due to its volumetric instability, relative high working voltage and low 1st cycle efficiency.

In this thesis, strategies to alleviate these issues in iron oxide are addressed, such as morphology design, elemental modification and lithium addition.

1D rod-like morphology of iron oxide is firstly investigated as one of the optimized structure to overcome volumetric instability. It is seen that tuning the size of the nanorod led to optimal electrochemical performance, which is due to better structural retaining ability of the particles. It was seen that intermediate sized nanorod showed $\sim 1000 \text{mAh g}^{-1}$ capacity at the end of 50 cycles which is more than powder iron oxide.

Elemental modification of iron oxide has also proven to be an effective strategy to lower the reaction voltage of hematite. Among several of tested material, Mg and Ti modified sample has shown the greatest potential also on enhancing the capacity at higher current density region. A capacity of 556mAh g^{-1} at a delithiation current rate of 3C is achieved for Mg modified nanorod, which is five times higher than for pure hematite.

Further synthesis of iron oxide microsphere, nanosphere and chunky-like particles showed has shown an unexpected high reversible capacity of $\sim 800 \text{mAh g}^{-1}$, which is not fully understood up to date. However, it can be inferred from these studies that in addition to particle morphology, there are other intrinsic factors that dominate the electrochemical behavior of iron oxide.

The last section presents a lithium addition strategy that successfully forms a pre-lithiated form of iron oxide that has proven to increase the 1st cycle efficiency of iron oxide material from $\sim 68\%$ to $\sim 80\%$.

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TABLE OF CONTENTS

ABSTRACT.....	v
ACKNOWLEDGEMENTS	vii
TABLE CAPTIONS	xiii
FIGURE CAPTIONS.....	xv
ABBREVIATIONS	xxi
1. INTRODUCTION	1
1.1 BACKGROUND	1
1.2 PROBLEM STATEMENT	3
1.2.1 BACKGROUND INFORMATION.....	3
1.2.2 LIMITATION OF CURRENT ANODE MATERIAL	4
1.2.3 POTENTIAL ANODE MATERIAL	4
1.3 MOTIVATION	4
1.3.1 MATERIAL VOLUME CHANGE	4
1.3.2 CONDUCTIVITY	5
1.3.3 FIRST CYCLE EFFICIENCY	5
1.3.4 SCALABILITY	5
1.4 RESEARCH SCOPE AND OBJECTIVE	6
1.4.1 INTRINSIC DEVELOPMENT	6
1.4.2 EXTRINSIC DEVELOPMENT	6
1.5 THESIS STRUCTURE.....	6
2. LITERATURE REVIEW	9
2.1 ANODE MATERIAL DEVELOPMENT.....	9
2.1.1 INTERCALATION MATERIALS.....	9
2.1.2 ALLOY\DE-ALLOYING MATERIALS	10
2.1.3 CONVERSION REACTION MATERIALS	11
2.2 IRON OXIDES	13
2.2.1 HEMATITE	13
2.2.2 MAGNETITE	16
2.3 EXTRINSIC MODIFICATION OF IRON OXIDE	16
2.3.1 CARBON COMPOSITE	16
2.3.2 ELEMENTAL MODIFICATION	17
2.3.3 PRE-LITHIATION	18

2.4	PROPOSED WORKING PACKAGE	19
3.	EXPERIMENTAL DETAILS	21
3.1	MATERIAL SYNTHESIS	21
3.1.1	SYNTHESIS OF HEMATITE NANOROD	21
3.1.2	SYNTHESIS OF ELEMENTAL MODIFIED HEMATITE WITH DIAMINES	21
3.1.3	HEMATITE SYNTHESIS WITH ADDITION OF NaOH	24
3.1.4	LITHIUM ADDITION	25
3.2	MATERIAL CHARACTERIZATION	28
3.2.1	X-RAY DIFFRACTION (XRD) ANALYSIS	28
3.2.2	FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM) ANALYSIS	28
3.2.3	TRANSMISSION ELECTRON MICROSCOPY (TEM) ANALYSIS	28
3.2.4	ENERGY DISPERSIVE X-RAY (EDX) ANALYSIS	28
3.2.5	X-RAY FLUORESCENCE (XRF) ELEMENTAL ANALYSIS	29
3.2.6	ULTRAVIOLET-VISIBLE (UV-VIS) ANALYSIS	29
3.3	ELECTROCHEMICAL CELL ASSEMBLY AND TESTING	29
3.3.1	CYCLIC VOLTAMMETRY (CV)	30
3.3.3	RATE PERFORMANCE TEST	30
3.3.4	EX-SITU CHARACTERIZATION OF ELECTRODE	31
4.	EXPERIMENTAL RESULTS	33
4.1	HEMATITE NANOROD SYNTHESIS ASSISTED BY DIAMINE SERIES ..	33
4.1.1	MATERIAL CHARACTERIZATIONS	33
4.1.2	ELECTROCHEMICAL PERFORMANCE	40
4.2	HEMATITE MODIFICATION IN NANOROD	45
4.2.2	TRIAL ON DIFFERENT ADDITIVE ELEMENTS	45
4.2.3	MG MODIFIED HEMATITE NANOROD	51
4.2.3	TI MODIFIED HEMATITE NANOROD	62
4.3	HEMATITE MICROSPHERE SYNTHESIS	69
4.3.1	MATERIAL CHARACTERIZATIONS	69
4.3.2	ELECTROCHEMICAL PERFORMANCE	72
4.4	HEMATITE MODIFICATION IN MICROSPHERES AND CHUNK-LIKE PARTICLE	75
4.4.1	TI MODIFICATION ON HEMATITE MICROSPHERE	75

4.4.2	MG MODIFICATION ON CHUNKY-LIKE HEMATITE	80
4.5	LITHIUM ADDITION	86
4.5.1	COATING OF HEMATITE WITH LITHIUM OXALATE	86
4.5.2	TWO-STEP SYNTHESIS OF LITHIUM INCORPORATED IRON OXIDE..	88
4.5.3	THREE-STEP SYNTHESIS OF LITHIUM INCORPORATED IRON OXIDE	91
5.	DISCUSSION	95
5.1	EFFECT OF NANOROD SIZE ON HEMATITE.....	95
5.2	ELEMENTAL MODIFICATION ON HEMATITE NANOROD	101
5.3	ELECTROCHEMICAL PERFORMANCE COMPARISON FROM MICROPARTICLE, NANOPARTICLE AND CHUNKY-LIKE PARTICLE.....	104
5.4	LITHIUM ADDITION	105
6.	CONCLUSION	107
6.1	SCIENTIFIC CONTRIBUTION	109
6.2	TECHNOLOGICAL CONTRIBUTION	109
6.3	FUTURE WORK.....	110
6.3.1	ELECTROCHEMICAL PROPERTY OF HEMATITE	110
6.3.2	PRE-LITHIATION	110
6.3.3	LONGTERM DEVELOPMENT	110
	REFERENCE.....	112

TABLE CAPTIONS

Table 2.1: Electrochemical performance of different hematite morphology in literature

Table 2.2: Literature about iron oxide/carbon nanocomposites

Table 2.3: Electrochemical performance of lithiated iron oxide in literature

Table 3.1: Syntheses for different hematite modification approaches assisted by DIP

Table 3.2: Syntheses for Mg modified hematite assisted by DIP

Table 3.3: Syntheses for Ti modified hematite assisted by DIP

Table 3.4: Syntheses for Mg or Ti modified hematite assisted by NaOH

Table 3.5: Syntheses of lithium oxalate coated iron oxide

Table 3.6: Syntheses of lithium incorporated iron oxide

Table 4.1: Physicochemical characteristics of α -Fe₂O₃ synthesized with different SCAs and various Fe³⁺ concentrations

Table 4.2: Electrochemical data of α -Fe₂O₃ synthesized with different SCAs and various Fe³⁺ concentrations

Table 4.3: Lattice parameters obtained from Rietveld refinement of XRD data for different additive elements and DIP as SCA

Table 4.4: Lattice parameters from Rietveld refinement of XRD data and XRF data for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 10%

Table 4.5: Rod length and aspect ratio for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 5%

Table 4.6: Estimated band gap for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of 0 to 10%

Table 4.7: Lattice parameters from Rietveld refinement of XRD data and XRF data for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 10%

Table 4.8: Estimated band gap for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Ti modification levels of 0 to 10%

Table 4.9: Lattice parameters obtained from Rietveld refinement for iron oxide synthesized with different NaOH amount

Table 4.10: Lattice parameters obtained from Rietveld refinement for different Ti modified hematite assisted by NaOH

Table 4.11: Ti composition measured by EDX in Ti modified hematite assisted by NaOH

Table 4.12: Lattice parameters obtained from Rietveld refinement of XRD data for hematite with 10% Mg adding levels with 4ml NaOH

Table 4.13: Mg composition measured by EDX in hematite with 10% Mg addition

Table 4.14: Lattice parameters obtained from Rietveld refinement of XRD data for hematite with different Mg adding levels synthesized with 12ml NaOH

Table 4.15: Lithiation\delithiation capacity for repeated cell for C1 and C2

Table 4.16: Lithiation\delithiation capacity for repeated cell for L1Ar and L2Ar

Table 4.17: Lithiation\delithiation capacity for repeated cell for L3 and L4Ar

FIGURE CAPTIONS

Figure 1.1. Comparison of different energy storage system.

Figure 1.2. Volumetric (Wh/L) and Gravimetric (Wh/kg) energy densities of current battery systems.

Figure 1.3. Working principle of lithium ion battery.

Figure 4.1. Schematic illustration of applied SCAs containing two vicinal amine groups and different H₃C-groups.

Figure 4.2. a) XRD patterns for α -Fe₂O₃ nanoparticles synthesized with various Fe³⁺ concentrations and DIP and b) different diamine derivatives as SCA and varied Fe³⁺ concentrations.

Figure 4.3. FESEM images of α -Fe₂O₃ nanoparticles obtained with DIP as SCA and varied Fe³⁺ concentration of a) 0.1M, b) 0.5M, c) 0.8M, d) 1.0M, e) 1.5M and f) 2.0M, magnification: 50000.

Figure 4.4. Aspect ratio vs. Fe³⁺ concentration for α -Fe₂O₃ nanoparticles obtained with DIP and EDA as SCA (the aspect ratio for spherical particles is set to 1; 20 nanorods were taken for estimation of the aspect ratio for each Fe³⁺ concentration

Figure 4.5. FESEM images of α -Fe₂O₃ nanoparticles obtained with EDA as SCA and varied Fe³⁺ concentration of a) 0.1M, b) 0.5M, c) 0.8M, d) 1.0M, e) 1.5M and f) 2.0M, magnification: 50000.

Figure 4.6. FESEM images of α -Fe₂O₃ nanoparticles obtained with a) EDA, b) DIP, c) NMD and d) DAB, Fe³⁺ concentration was kept at 1.5M, magnification: 50000.

Figure 4.7. FESEM images of α -Fe₂O₃ nanoparticles obtained with a) EDA, b) DIP and c) DAB, Fe³⁺ concentration was kept at 0.5M, magnification: 50000.

Figure 4.8. Cyclic voltammogram profile of nanorod shaped α -Fe₂O₃ (obtained with 1.5M Fe³⁺ concentration and EDA as SCA).

Figure 4.9. (a) Galvanostatic delithiation/lithiation profiles (1st, 2nd and 5th cycle) for α -Fe₂O₃-E1.5 and (b) 1st and 2nd cycle comparison for α -Fe₂O₃-E0.5, α -Fe₂O₃-E1.5, α -Fe₂O₃-D0.5, α -Fe₂O₃-D0.8, α -Fe₂O₃-D1.5 and α -Fe₂O₃-B1.5.

Figure 4.10. (a) Cycling performance and (b) rate testing of α -Fe₂O₃-E0.5, α -Fe₂O₃-E1.5, α -Fe₂O₃-D0.5, α -Fe₂O₃-D0.8, α -Fe₂O₃-D1.5 and α -Fe₂O₃-B1.5.

Figure 4.11. XRD pattern for V, Sr and Ba added samples (The unlabeled peaks are from hematite Fe₂O₃ or Goethite FeOOH)

Figure 4.12. XRD pattern for different elements added, and DIP as SCA

Figure 4.13. FESEM image for studied additive elements and DIP as SCA

Figure 4.14. Cycling and rate test of different modified hematite.

Figure 4.15. XRD patterns for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 20%.

Figure 4.16. Change of a) lattice parameter, and b) cell volume for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 10%.

Figure 4.17. FESEM images for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of a) 0%, b) 1%, c) 3%, d) 5%, e) 7%, and f) 10%.

Figure 4.18. TEM images for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 10%.

Figure 4.19. FESEM images for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of a) 15%, and b) 20%; and FESEM images for iron oxide nanoparticles obtained from synthesis approaches with Mg modification level of 10% and NaOH_(aq) as pH controller and c) FeCl₃·6H₂O, and d) Fe(NO₃)₃·9H₂O as precursors.

Figure 4.20. a) Absorption and b) Tauc Mott plot of UV–Vis spectra (direct transition) for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of 0 to 10%.

Figure 4.21. a) 1st cycle CV curves, b) 1st and 2nd cycle galvanostatic curves, c) cycling performance, and d) rate capability for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of 0 to 10%.

Figure 4.22. First 10 cycles of ΔE value for Mg modified hematite nanorod.

Figure 4.23. XRD pattern for different Ti modification levels and DIP as SCA

Figure 4.24. Change cell volume against real Ti content for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Ti modification level of 0 to 10%.

Figure 4.25. FESEM image for different Ti modification levels and DIP as SCA

Figure 4.26. Tauc Mott plot of UV–Vis spectra (direct transition) for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Ti modification levels of 0 to 10%.

Figure 4.27. a) CV, b) galvanostatic curve, c) cycling test, b) rate test and e) ΔE value for Ti modified samples with DIP as SCA

Figure 4.28. XRD pattern for iron oxide synthesized with different NaOH amount.

Figure 4.29. XRD pattern from different precursors.

Figure 4.30. FESEM image for hematite with different NaOH amount.

Figure 4.31. FESEM image hematite particle using different precursors.

Figure 4.32. a) galvanostatic b) cycling and c) rate test for different iron precursors

Figure 4.33. a) cycling and b) rate test for different NaOH amount

Figure 4.34. XRD pattern for different Ti modified hematite assisted by NaOH

Figure 4.35. EDX pattern for different Ti modified hematite assisted by NaOH

Figure 4.36. FESEM image for different Ti modified hematite assisted by NaOH.

Figure 4.37. a) galvanostatic b) Cycling c) rate test and d) ΔE value for Ti modified hematite assisted by NaOH.

Figure 4.38. XRD pattern for hematite with 10% Mg adding levels synthesized with 4ml NaOH

Figure 4.39. XRD pattern for hematite with different Mg adding levels synthesized with 12ml NaOH

Figure 4.40. FESEM image for hematite with different Mg modification levels synthesized with 12ml NaOH.

Figure 4.41. a) galvanostatic curve, b) cycling, c) rate and d) ΔE value for hematite with Mg modified sample synthesized with 12ml NaOH

Figure 4.42. XRD pattern for lithium oxalate contained hematite.

Figure 4.43. FESEM image of lithium oxalate coated hematite particle.

Figure 4.44. XRD pattern for two-step synthesized lithium incorporated iron oxide.

Figure 4.45. FESEM image of a) lithium incorporated iron oxide (L1Ar) and b) comparison sample (L2Ar).

Figure 4.46. a) Cycling and b) rate test for two-step synthesized lithium incorporated iron oxide.

Figure 4.47. XRD pattern for three-step synthesized lithium incorporated iron oxide.

Figure 4.48. FESEM image of hydrothermally synthesized magnetite (L3) and lithium incorporated products (L4Ar).

Figure 4.49. a) Cycling and b) rate test for three-step synthesized lithium incorporated iron oxide.

Figure 5.1. Schematic illustration of the α -FeOOH nanorod formation process assisted by diamine derivatives as SCA according to literature

Figure 5.2. Different hydroxyl groups found on surfaces of iron oxides according to literature

Figure 5.3. Post-cycling FESEM images.

Figure 5.4. Cycling performance of intermediate sized nanorod electrode (E1.5) with hematite as active material (active material ratio is 40%)

Figure 5.5. FESEM of electrode from hematite nanorod as active material (40%)

Figure 5.6. XRD pattern of fresh electrode and electrode after 1 cycle.

Figure 5.7. EDX mapping using TEM of 5% Mg added nanorod after 10 cycles.

ABBREVIATIONS

EV	Electric Vehicles
BEV	Battery Electric Vehicles
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy-dispersive X-ray spectroscopy
TGA	Thermogravimetric analysis
TEM	Transmission Electron Microscopy
XRF	X-Ray Fluorescence
UV-vis	Ultraviolet-visible light spectrum
CV	Cycling Voltammetry
SCA	Shape Controlling Agent
EDA	Ethylene Diamine
DIP	1,2-Diaminopropane
DIB	2,3-diaminobutane
NMD	N-methylethylene diamine
SEI	Solid Electrolyte Interface
DI water	Deionized Water
LIB	Lithium Ion Battery
PVDF	Polyvinylidene Difluoride
NMP	N-methyl-2-Pyrrolidone
CMC	Carboxymethyl cellulose
TIPP	Titanium (IV) Isopropoxide
TEOS	Tetraethyl Orthosilicate

1. INTRODUCTION

1.1 BACKGROUND

In the 21st century, an ever-increased energy demand has drawn great intention on human society. On one hand, we are still highly depending on fossil fuel, which is a non-renewable energy source, while on the other hand, carbon dioxide emission associated with fossil fuel is treated as the main reason for global warming in recent years [1]. Thus, it has become a main challenge to lower the dependency on fossil fuels.

A lot of renewable energy sources has been studied including solar energy, biomass, tidal energy and so on [2]. However, energy generation is hardly coincided with energy demand in terms of time window and locations. Thus, it is also of vital importance to develop an efficient system for energy storage capability. Among all the current energy storage devices, battery is considered as one of the optimal in terms of energy density and power density [3], as shown in figure 1.1 below.

Figure 1.1. Comparison of different energy storage system. [3] (Reprinted with permission from Royal Society of Chemistry)

Moreover, in the current revolution to replace fossil fuel, automotive industry stands right in the center, as vehicles are one of the major consumption source of fossil fuel due to their internal combustion engine. Fortunately, in recent years,

electric vehicles (EV) are intensively studied in both academic and industrial field. As the energy source, batteries are one of the most essential component in EV development. However, the driving range of EV is still much behind traditional vehicles with internal combustion (IC) engine, due to the limitation of energy density of battery. Thus, to meet the critical demand of long driving range EV as well as other applications (such as renewable energy storage), an innovation and/or improvement of battery with high energy density is more than necessary.

During more than 100 years of development, several battery systems have been developed for both primary and secondary (also known as rechargeable batteries) battery. Among the various rechargeable battery systems in the commercial market, *viz.* lead-acid, nickel cadmium (Ni-Cd), nickel metal hydride (Ni-MH) [4], lithium ion battery (LIB) are treated as most promising battery systems for EV applications, as shown in figure 1. 2.

Figure 1. 2. Volumetric (Wh/L) and Gravimetric (Wh/kg) energy densities of current battery systems. [5] (Reprinted with permission from Nature)

1.2 PROBLEM STATEMENT

1.2.1 BACKGROUND INFORMATION

The basic working principle of lithium ion battery is shown in figure 1.3 below:

Figure 1.3. Working principle of lithium ion battery. [5] (Reprinted with permission from Nature)

In a lithium ion battery cell, lithium ions are the charge carrier inside the battery. Two electrodes (namely cathode and anode) are made from materials that can accommodate lithium ions at different potential. The voltage gradient between the positive and negative electrode will lead to spontaneous lithium ion migration, which convert the chemical energy stored in lithium ion battery into electrical energy, also known as “discharge process”. The opposite process could be achieved by applying a voltage to force lithium ions to migrate in a reverse direction, converting electrical energy into chemical energy stored in lithium ion battery, also known as “charge process”.

Currently, most commercial lithium ion battery are composed of a lithiated metal oxide as cathode (such as LiCoO₂), graphite as anode, and 1M LiPF₆ in organic carbonate solvent (such as Ethylene Carbonate and Dimethyl carbonate) as

electrolyte, as firstly commercialized by Sony in 1990 [4] with following reaction equation:

1.2.2 LIMITATION OF CURRENT ANODE MATERIAL

As the anode material, graphite is perfect in conductivity, stability, safety and cost. However, the theoretical capacity of graphite is limited to 372mAh g^{-1} , which can hardly fit for future demand of higher energy density. Thus, for the next generation high energy density lithium ion battery system, an alternative anode with much higher capacity must be applied.

1.2.3 POTENTIAL ANODE MATERIAL

Iron oxide is considered as one of the most promising anode material for next generation lithium ion batteries, as on one hand, they have higher theoretical capacity ($\sim 1000\text{mAh g}^{-1}$ [6]) and on the other hand, they are extremely cost competitive and have minimum safety concerns compared to other material.

1.3 MOTIVATION

Although iron oxide has much higher theoretical capacity than graphite, it still suffers from issues such as large volumetric instability, low conductivity and relatively high working voltage again Li^+/Li .

1.3.1 MATERIAL VOLUME CHANGE

The mechanism of energy storage for graphite in lithium ion batteries come from insertion/desertion of lithium ions into carbon layer, the structural change during

cycling is minimal and reversible. However, iron oxides undergo conversion reaction with lithium detailed explanation is provided in chapter 2 accompanied by a large irreversible volume change leading to its poor cycling performance as compared to graphite. It is crucial to minimize this problem during material design for practical application of iron oxide anode.

1.3.2 CONDUCTIVITY

Iron oxides are typical semiconductors ($10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at room temperature), so a conductive additive (such as acetylene black, graphene etc) is necessary to enhance its conductivity as an electrode. These conductivities are usually either added during the electrode preparation process or in some approaches, iron oxide/carbon composite, such as carbon coated iron oxide nanoparticle, where there is intimate mixture and contact between the iron oxide and carbon are hierarchically produced to enhance its conductivity.

1.3.3 FIRST CYCLE EFFICIENCY

In general, iron oxide suffers from severe 1st cycle coulombic loss. During the 1st discharge, the electrolyte will decompose irreversibly at voltage plateau around 0.8 V (vs Li), forming lithium containing solid electrolyte interphase (SEI). SEI is a complex layer composed of lithium carbonate and lithium fluoride and other lithiated organic carbonate products. [7, 8] Such phenomenon for iron oxide will generally lead to a higher-than-theoretical capacity for the 1st discharge process, while a large capacity difference will be presented between 1st discharge and 1st charge process. Such instability in anode side will affect the efficiency greatly in full battery, as part of lithium ions provided from cathode will be irreversibly trapped and lose their activity.

1.3.4 SCALABILITY

In research field, nano-structuring is one of the most effect strategy to overcome the above-mentioned limitations of iron oxide, especially conductivity and

volumetric instability. However, in nanostructure design, methods that could have precise control over morphology will generally lead to low yield and multi-step process, thus to looking for future industrialization process, the experimental design need to have a balance between precise control and facileness.

1.4 RESEARCH SCOPE AND OBJECTIVE

To make iron oxide the next generation lithium ion battery anode, development for iron based oxide material must be implemented. In general, there are 2 strategies that is proposed for development of iron based oxide, namely intrinsic development and extrinsic development.

1.4.1 INTRINSIC DEVELOPMENT

Intrinsic development refers to strategies that does not involve any foreign element, the focus is on design of iron based oxide itself. Intrinsic development is mainly about morphology design and nano-structuring. In this thesis, it mainly consists of optimization of nanorod morphology of iron oxide, and design of micro-particles.

1.4.2 EXTRINSIC DEVELOPMENT

Extrinsic development refers to methodology that involve other element as additive or incorporated in design iron oxide anode. It mainly consists of design of iron based composite material, design of ternary iron oxide and modification of iron oxide with other elements. In this thesis, elemental modification is selected as main strategy due to its facileness and effectiveness. Lithium addition is selected as the other strategy targeting on solve the limitation of low 1st cycle efficiency.

1.5 THESIS STRUCTURE

The structure of the thesis is as follows:

Chapter 1 provides a brief introduction of whole thesis, mainly about the background and limitation of iron oxides, and use of strategy such as nano-structuring, elemental modification and Lithium addition to overcome those limitations.

Chapter 2 is the literature review of research activities, starting from 3 mechanism of anode material, namely intercalation, alloying\de-alloying and conversion reaction material. This chapter also explains the consideration of selecting iron oxides in conversion reaction category as the base material in this thesis. Furthermore, the current literatures in designing iron oxides for anode material of LIB is analyzed to identify the research gap.

Chapter 3 describes the methodology of all the research activities involved in this thesis. The first part in this chapter provide the synthesis procedure of different experiments, including hematite nanorod and micro-sphere synthesis, elemental modification experiments and lithium addition experiments. Material characterization technics and battery assembly procedures for above topics are also presented.

Chapter 4 provides the experimental result from experiments described in chapter 3, including material characterization outcome such as morphology, crystallinity and so on. Battery test data is also presented in this section.

Chapter 5 is the discussion chapter, where experimental results are analyzed, including both intrinsic and extrinsic modification experiment of iron oxide.

Chapter 6 concludes all the research activity and draws the conclusion of this thesis. Potential future works are also shared if more research will be carried out in related aspects.

2. LITERATURE REVIEW

2.1 ANODE MATERIAL DEVELOPMENT

For development toward higher energy density and fast charging capability, intensive studies have been implemented on anode material development ever since the invention of lithium ion battery. Up to date, there are generally 3 categories of anode materials according to their Li- reaction mechanism- (i) intercalation, (ii) alloying-dealloying and (iii) conversion reaction based anode.

2.1.1 INTERCALATION MATERIALS

Typical example of intercalation carbon based materials are graphite [9] and graphene [10-13], a lot of researches are also in process of developing titanium based oxide, such as TiO_2 [14-18] and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) [19-23]. For intercalation materials, lithium ion storage is achieved by intercalating lithium ions inside the crystalline lattice of host material. Intercalation materials have excellent volumetric stability during lithiation-delithiation cycling, the volume expansion for TiO_2 and LTO are only 4% [14] and 1% respectively [24]. Such property leads to ultra-long cycling life and remarkable high rate performance of LIB. Recently, researchers have achieved a stable cycling life of 10000 cycles for TiO_2 half-cell at current density of 8.4 A g^{-1} (25C) [15]. There are also commercial products with LTO anode in the market already, due to its superior property such as cycling stability and high rate performance. However, the general limitation of intercalation materials is that they have a relatively low theoretical capacity (372 mAh g^{-1} for graphite and less than 200 mAh g^{-1} for Ti based oxide materials), leading to low energy density of the full cell. (Graphene has a doubled intercalation theoretical capacity of graphite [25], but the main limitation is the high production cost and scalability.) Furthermore, titanium based anode material has a relatively high working potential, both TiO_2 and LTO have a working plateau around 1.6 V against Li^+/Li electrode, (All the voltage value in this report is against Li^+/Li electrode unless otherwise stated.) which would lower the working voltage of full cell, which

eventually further reduce the energy density of the battery. Thus, for intercalation material such as titanium based oxide, they are promising future anode material for those applications where the need for power density and cycle life outweighs the need for energy density. But for applications such as EV, where energy density plays a crucial role in material innovation, intercalation materials would not fit in the requirement.

2.1.2 ALLOY\DE-ALLOYING MATERIALS

For this category, the most studied materials are Si [26-30] based and Sn [31-34] based materials. These materials could form lithiated alloy such as $\text{Li}_{4.4}\text{Si}$ for Si based material and $\text{Sn}_{4.4}\text{Li}$ for Sn, achieving lithium storage property. In general, alloying/de-alloying materials have very high theoretical capacity ($\sim 900 \text{ mAh g}^{-1}$ for Sn and $\sim 4000 \text{ mAh g}^{-1}$ for Si). Except for high theoretical capacity, they have another advantage in reaction potential. In general, alloying materials have a reaction plateau of around 0.4 V-0.9 V [35], which is much lower than titanium based intercalation materials, and close to graphite ($\sim 0.1 \text{ V}$) anode [36]. Such properties make them a strong target material for high energy applications. However, the main limitation is the stability of material during electrochemical cycling. In the example of Si, the volumetric expansion of Si material during electrochemical cycling could be as high as 300% [29], leading to contact loss of the active material over current collector, which results in a severe capacity decay of the material. Intensive studies have been implemented on modification of alloying materials, majorly Si. The general strategy is nano-structuring and Si based composite material design. Cui and his group is the pioneer in this field. They have developed Si hollow tubes which could keep a capacity of 1000 mAh g^{-1} after 6000 cycles with current density of 12 C (1 C = 4000 mA g^{-1} for Si) [37]. They also developed carbon-silicon core-shell structure, which gives capacity around 2000 mAh g^{-1} for 50 cycles with current density of 0.2 C [38]. However, the cost of this category of material remains a key challenge.

2.1.3 CONVERSION REACTION MATERIALS

In this type of material, Li storage is achieved by conversion reactions. In general, metal oxides are the main member of this category, together with nitrides, sulfides and so on. When placed as anode material of LIB, 1 mole conversion based materials (M_xA_y) will intake xy mole of electrons and lithium ion, converting M_xA_y into a composite composed of metallic M particles dispersed in Li_yA phase. A general reaction formula could be concluded for these materials: [39]

where M^{y+} is the metal ion, while A^{x-} is oxide ion or other anions such as S^{x-} , P^{x-} and so on. From the reaction equation, the capacity of conversion material could be calculated based on Faraday's law, where for 1 mole material, $Q = Fn$. F is Faraday constant with value of 96500 C mol^{-1} and n is the number of electrons that is involved in the reaction.

$$\text{Specific Capacity (mAh g}^{-1}\text{)} = \frac{96500 \times xy}{MW(TMOs)} \quad (2.2)$$

Based on the above equation, there are 2 criteria to obtain a target material with high theoretical capacity:

1. High cation charge for the metal ions.
2. Relatively low atomic number. (MW)

Among all the conversion materials, transition metal oxides are mostly studied in literature. Back in 2000, Tarascon and his group firstly discovered reversible conversion reaction by using nano-sized CoO as new anode material for lithium ion battery. [40] An intensive effort has then been implemented in TMOs, such as cobalt oxides [40-47], iron oxide [48-65], manganese oxide [66-70], chromium oxide [71, 72], nickel oxide [40, 73-80] and so on.

Except for oxides, other products such as sulfides, nitride and phosphides, are also studied.

Sulfides has been studied by different groups [81, 82]. In the example of iron sulfide, FeS and FeS₂ has a satisfactory theoretical capacity of 500 mAh g⁻¹ and 600 mAh g⁻¹ respectively, but either a severe capacity decay is observed [82] or a large amount of carbon phase need to be introduced into the system. [81]

Nitride is also considered for future anode material of LIB [83] as conversion based materials. However, either a high energy process such as sputtering [83-85], or an annealing process involving unsafe NH₃ containing gas atmosphere [86, 87] is required for transition metal nitride synthesis, which limits their industrialization potential.

Phosphides are also reported as anode material [88, 89], they have shown high theoretical capacity (around 1000 mAh g⁻¹ depending on the formula and cation) and relatively low working voltage (0.6 V-0.8 V). But the volumetric expansion of 300% during galvanostatic cycles [88] and their instability in contact with electrolyte [90] limits the potential in near future.

Thus, transition metal oxides (TMO) are still considered as most promising candidate in all conversion reaction material family.

In conclusion, conversion reaction based TMOs have a theoretical capacity in the range of 700 mAh g⁻¹ to 1000 mAh g⁻¹, which is much higher than intercalation materials, while comparable to most alloying materials. (Si has a theoretical capacity of 4000 mAh g⁻¹, but in most of literatures, the stable capacity obtained is still around 1000 mAh g⁻¹.) The volumetric expansion of TMOs is around 100%, which limits their long-term cycling stability. The lithiation voltage plateau of TMOs is generally in the range of 0.5 V-1.5 V, while the delithiation voltage plateau is generally in the range of 1.6 V-2 V, which is between alloying materials and titanium based intercalation materials. The most attractive property of TMOs, especially iron oxide, is the abundance of material and low processing cost.

Thus, after consideration of various categories, TMOs are selected as target material for research in this thesis.

2.2 IRON OXIDES

Iron oxides are selected as the research focus in TMOs, due to their high theoretical capacity, low cost, low toxicity and abundance of raw materials compared other TMOs.

The main form of iron oxide that is studied as anode material of LIB in research field are hematite ($\alpha\text{-Fe}_2\text{O}_3$) [48-51, 53, 54, 56-65] and magnetite (Fe_3O_4) [52, 55, 91-94].

2.2.1 HEMATITE

As a most common phase of iron oxides, hematite is also most intensively studied to overcome the limitation. In general, hematite will have a three-step reaction as anode material of LIB:

Initially, lithium ion intercalated into the $\alpha\text{-Fe}_2\text{O}_3$ matrix without changing its hexagonal crystal structure leading to a compound described as $\text{Li}_x\text{Fe}_2\text{O}_3$ (2.3). Then, $\text{Li}_x\text{Fe}_2\text{O}_3$ is transformed into a cubic $\text{Li}_2\text{Fe}_2\text{O}_3$ structure with further intercalation of lithium ions (2.4). Subsequently, a conversion reaction takes place, changing Fe^{2+} ion to metallic Fe, associated with conversion reaction of lithium intercalation to form Li_2O . [48] Due to the volumetric expansion during the phase change from hematite. Hematite suffers from poor cycling life. An electrode made from commercially available Fe_2O_3 powder will lose around 80% of the capacity after 50 galvanostatic charge-discharge cycles. [95] Nano-structuring is one of the main strategy to enhance the cycling stability of hematite. Morphologies such as nanowires, nanorod, nanosphere, nanoflakes and so on are developed to enhance the electrochemical performance, as listed in table 2.1 below:

Table 2.1. Electrochemical performance of different hematite morphology in literature.

Morphology	Initial lithiation capacity (mAh g⁻¹)	Capacity retaining (mAh g⁻¹)/ cycling	First cycle columbic efficiency	Discharging rate	Ref.
Commercial sample (Sigma-Aldrich)	1200	200/50 th	67%	0.1C	[95]
Nanowire	1303	456/100 th	73%	0.1C	[96]
Nanorod	1191	908/30 th	77%	0.2C	[97]
Multi-shell nanosphere	1450	1000/100 th	75%	0.4C	[61]
Nanoflake	1230	680/80 th	54%	0.1C	[98]
Mesoporous nanoparticle	1606	540/230 th	77%	0.5C	[99]
Nano-spindle	1379	911/50 th	69%	0.2C	[100]
Nanotube	1415	510/100 th	not specified	0.2C	[50]

Different synthesis strategies are also applied for morphology control, including precipitation and sol-gel approaches. The hydro-/solvo-thermal synthesis route is described as an advantageous synthesis procedure, due to homogenous nucleation/growth processes and highly crystallized products.[101-103] With respect to combining a synthesis method with morphology controlling aspects, inorganic ions as well as organic reagents including e.g. phosphates, sulfates, chlorides, fluorides, benzenediols, nitrilotriacetic acid and diamine derivatives are successfully applied as shape controlling agents (SCA) to obtain α -Fe₂O₃ with several morphologies enclosed by different crystal facets. [102, 104-108] The diamine-assisted hydrothermal synthesis of α -Fe₂O₃ nanorod is a beneficial, low-cost, and time-efficient combination of an efficient SCA and a powerful synthesis

tool. Applied diamine derivatives are normally water-soluble and can be easily removed. The resulting $\alpha\text{-Fe}_2\text{O}_3$ is free from nitrogen as described in literature (elemental analysis).[109] Expensive and tedious to upscale structure-directing approaches involving sacrificial hard templates can be avoided. The aspect ratio of the resulting nanorod morphology can be adjusted by the type of diamine derivative and further reaction parameters. Li et al. applied hydrothermal synthesis assisted by 1,2-diaminopropane (DIP) as SCA to get single crystalline $\alpha\text{-Fe}_2\text{O}_3$ nanorods with high and controllable aspect ratios,[102] and Lin et al. demonstrated that such obtained $\alpha\text{-Fe}_2\text{O}_3$ nanorods outperform submicrometer- and micrometer-sized particles in terms of electrochemical performance in LIBs.[97] Also, ethylene diamine (EDA) is presented in literature in the hydrothermal synthesis of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles leading to shuttle-like nanorod morphology.[108] In the presence of diamines, the reaction mixture's pH is raised to provide a supportive medium for the phase transformation of FeOOH to $\alpha\text{-Fe}_2\text{O}_3$. In addition, diamines form chelate complexes with ferric ions in solution leading to a directional dependency of OH^- -attacks for subsequent hydrolysis processes, which results in a targeted growth direction of iron oxide products.[110] Furthermore, diamines directly coordinate to lattice ferric species and the complexes are released into solution. Since it is understood that this coordination will specifically take place on $\alpha\text{-Fe}_2\text{O}_3$ surface facets with only singly coordinated hydroxyl groups,[111] this interaction mechanism can be targeted applied to direct the crystal growth in specific growth directions. It was found that DIP outperforms EDA as SCA, and the vicinal position of the two amine groups seems to be crucial for the shape controlling, since it was reported that 1,3-diaminopropane shows little effect on directing the crystal growth of $\alpha\text{-Fe}_2\text{O}_3$. It was assumed that this phenomenon could be attributed to the lower steric hindrance of EDA or 1,3-diaminopropane. [102] To gain a deeper understanding of the role of diamines in the shape controlled synthesis of $\alpha\text{-Fe}_2\text{O}_3$, a detailed test series including EDA, DIP, 2,3-diaminobutane (DAB), and N-methylethylene diamine (NMD) is presented. The effect of the growing number of H_3C -groups which enhance the electron density (+M effect) at the reactive diamine unit, but at the same time increase the steric hindrance is

investigated. N-methylethylene diamine was included, since it is a constitutional isomer to DIP and allows investigations in terms of the position of the H₃C-group.

2.2.2 MAGNETITE

Except for hematite, magnetite is another most usual form of iron oxide. Magnetite has slightly lower theoretical capacity (926 mAh g⁻¹), as the oxidation state is partially in 2+ state. Like hematite, magnetite also suffers from large volume change during galvanostatic cycling. Thus, the majority articles about magnetite on LIB application used magnetite\carbon composite material in response to its poor cycling performance.[6, 52, 112]

Although compared to hematite, magnetite has a limitation of slightly lowered theoretical capacity due to the presence of Fe²⁺, it has the potential to be applied as base material for pre-lithiation, which will be discussed in lithium addition sections.

2.3 EXTRINSIC MODIFICATION OF IRON OXIDE

2.3.1 CARBON COMPOSITE

Another promising strategy on extrinsic modification of iron oxide are approaches is to embed iron oxide into a ductile, conductive second phase with volume buffer capabilities. One of the top choices for a second phase are molecular sp² derived architectures of carbon to form hematite/carbon nanocomposites. The combination of hematite and sp² derived carbons provides several advantages such as:

1. Provide a dispersed conducting phase for iron oxide to enhance overall conductivity and better electrical contact [113].
2. Provide strong mechanical support for brittle TMOs during lithiation\delithiation process, due to excellent mechanical properties (ductile and elastic) of carbon materials [114]
3. Stabilize the SEI formation as carbons would be a stable layer surrounding the active material and act as a support material to preserve the electrode material's integrity especially for TMO nanostructures (e.g. hematite), since

they intrinsically exhibit high surface to volume ratios and high surface free energies, which are suspected to catalyze undesired side reactions at the solid-electrolyte interphase associated with material degradation [115].

4. Carbon materials provide extra capacity for lithium insertion [116].

Several carbon derivatives have been presented in the synthesis of hematite/carbon nanocomposites, e.g. 2D graphene, 1D carbon nanofibers, 1D carbon nanotubes (CNT), amorphous carbon and carbon coatings, as summarized in table 2.2.

Table 2.2. Literature about iron oxide/carbon nanocomposites

Active material	Carbon or Fe ₂ O ₃ content	Initial capacity (mAh g ⁻¹)	Capacity retaining (mAh g ⁻¹)/ cycling	Current density	Ref.
α-Fe₂O₃ nanoparticles anchored on Graphene sheets	60 wt% Fe ₂ O ₃	1554	~1000 /100	0.05C	[117]
α-Fe₂O₃ nanorods/CNFs	5 wt% CNF	1278	960/30	0.2C	[118]
Fe₂O₃/SWCNT membrane	88.0 wt% Fe ₂ O ₃	2097	1242/90	0.05C	[119]
Fe₃O₄/carbon nanospindle	78.5 wt% Fe	~1000	~600 /50	0.5C	[52]
Hollow-structured α-Fe₂O₃ dispersed inside amorphous Carbon	5.3% Carbon based material	1420	1210 /50	0.05C	[120]

However, it is noted that for iron oxide\carbon composite, extra synthesis procedures are always presented, or expensive precursors such as CNT or graphene oxide (GO) will be used, which is not favored for potential commercialization. Thus, more study is need for a facile extrinsic strategy.

2.3.2 ELEMENTAL MODIFICATION

Another extrinsic modification is partial substitution of Fe³⁺ ions by elements with higher or lower valence state to generate electronic defects and synthesize p- or n-

type materials, which potentially exhibit enhanced initial electronic conductivity compared to the pristine hematite.

Studies regarding modification experiments on TMOs correlating the electrochemical performance in LIBs are hardly presented in literature. Li et al. reported a Cu modified Mn_2O_3 hollow crystal for LIB anode. They discovered that Cu modified sample retained a capacity of 642 mAh g^{-1} at 0.1C after 100 cycles, which is almost 2 times the value of unmodified ones. [121] Similar effect is also observed by Hashem et al. in Al, Cu or Mg modified MnO_2 [122] and Mai et al. in Co modified NiO. [123]

For hematite, Jin et al. reported a morphology controlled molten salt synthesis approach to obtain Sn^{4+} modified hematite nanodisc. No change in morphology was observed during modification experiments and the resulting material (5% modification level) exhibits a decrease in charge-transfer impedance, increased conductivity, and enhanced charge-discharge cycling stability (899 mAh g^{-1} after 100 cycles at a current density of 0.1 C) [124]. However, it should also be mentioned that Ling et al. observed a significant electron-hole recombination within the first few picoseconds for Sn modified hematite nanostructures, which was revealed by ultrafast spectroscopy studies [125]. A second example for modification experiments on hematite to enhance the electrochemical performance in LIB is provided by Li et al. In their work, Zn is successfully modified into the hematite lattice, resulting in an enhanced capacity of 560 mAh g^{-1} after 500 cycles at a current density of 1 C. [126]

However, to the best of our knowledge, a systematic study on different potential additive elements for hematite is still lacking investigation up to date.

2.3.3 PRE-LITHIATION

Another point need to be addressed for iron oxide is the low 1st cycle efficiency. The procedure proposed is to provide extra lithium source at anode side to compensate lithium ion loss. In previous literatures, lithium-iron-oxides are also studied as anode material of lithium ion batteries. For example, Zeng et al.

successfully synthesized $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ nanoparticles using hydrothermal and subsequent annealing method, which shows a reversible capacity of 991 mAh g^{-1} after 50 cycles at current density of 0.1 C, with 1st cycle efficiency of around 68%. [127] Similarly, Büyükyazi et al. synthesized LiFeO_2 nano-architectures through electro-spinning with metal alkoxides source. [128] Some other researchers also successfully synthesized these 2 materials and applied it for anode material of LIB, [129, 130] as shown in table 2.3 below.

Table 2.3. Electrochemical performance of lithiated iron oxide in literature

Phase and Morphology	Initial lithiation capacity (mAh g^{-1})	First cycle columbic efficiency	Capacity retaining (mAh g^{-1})/ cycling	Current Density	Ref.
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ /nanoparticle	~1100	~68%	991/50 th	0.1C	[127]
LiFeO_2 /nano-architecture	~1600	~66%	756/50 th	0.1C	[128]
LiFeO_2 with C /nanoparticle	1626	74%	540/200 th	1C	[130]

A stable and satisfactory cycling performance is successfully obtained for up-mentioned literature, but none of them has shown any improvement in 1st cycle efficiency.

2.4 PROPOSED WORKING PACKAGE

The proposed working package of this thesis based on research gap in literatures areas follow:

1. Synthesis of hematite nanorod with diamine series to obtain an optimized condition for electrochemical performance.
2. A systematic study of elemental modification on hematite.

3. Synthesis a pre-lithiated iron oxide to test if the 1st cycle efficiency could be enhanced.

3. EXPERIMENTAL DETAILS

This chapter summarized all the experimental details from material synthesis, characterization and respective electrochemical testing as anode material of LIB.

3.1 MATERIAL SYNTHESIS

3.1.1 SYNTHESIS OF HEMATITE NANOROD

As analyzed in previous section, diamine assisted hydrothermal synthesis are applied to obtain hematite nanorod structure. In a typical procedure, 32 mL of DIP (99%, Aldrich) was added drop wise into 18 ml of 1.5 M of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, Riedel-de Haën) under constant magnetic stirring. The solution was then transferred to a 100 ml autoclave with teflon-lined stainless steel for hydrothermal treatment at 180 °C for 16hrs. The product was naturally cooled down to room temperature after reaction, and collected by centrifuge process with deionized water and ethanol. The sample was dried overnight at 60 °C, and a red color product was obtained. For a systematic study, the concentration of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was varied, while the ratio between iron ions and organic SCA was kept constant. The effectiveness of the SCA was compared by using ethylene diamine (EDA, 99%, Aldrich), 2,3-diaminobutane (DAB, 95%, Otava), and N-methylethylene diamine (NMD, 95%, Aldrich) instead of DIP.

3.1.2 SYNTHESIS OF ELEMENTAL MODIFIED HEMATITE WITH DIAMINES

Subsequent experiment is carried out based on previous nanorod synthesis with modifications. Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Cu^{2+} , Ni^{2+} , Al^{3+} , V^{3+} , Co^{3+} , Si^{4+} , Ti^{4+} and Sn^{4+} were tested as potential additive elements. In a typical synthesis, a direct, diamine-assisted hydrothermal method was applied to synthesize modified hematite with nanorod morphology. In a typical procedure, 9 mL DIP (Aldrich, 99%) was added drop wise into a 16ml solution of 0.95 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Riedel-de

Haën, 99%) and 0.05 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99%, 5% Mg modification level) under constant magnetic stirring. The resulting red colloidal solution was then transferred to a 45 ml autoclave with Teflon-lined stainless steel for hydrothermal treatment at 180 °C for 16 hours. The product was naturally cooled down to room temperature after the reaction, and collected by centrifuge process with deionized water and ethanol. The sample was dried overnight at 60 °C, and the product with red color was obtained.

Modification with other elements were also carried out by replacing the Mg precursor with respective metal precursors such as CaCl_2 (Sigma-Aldrich, 99%), Tris(ethylenediamine) cobalt(III) chloride (Sigma-Aldrich, 98%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich, 99%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, 99%), VCl_3 (Aldrich, 98%), $\text{Ba}(\text{NO}_3)_2$ (Sigma-Aldrich, 99%), $\text{Sr}(\text{NO}_3)_2$ (Sigma-Aldrich, 99%) and Titanium (IV) Isopropoxide (TIPP, Aldrich, 97%). In the case of Ti modification, the TIPP was dissolved in 5 ml absolute EtOH (Merck, 99.9%) before adding it into 27 ml of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution. An annealing process was applied for products at 400 °C for 3 hours in air that exhibit a FeOOH phase to complete the crystallization process. The detailed synthesis procedures are listed in table 3,1 below:

Table 3.1: Syntheses for different hematite modification approaches assisted by DIP

Procedur e Number	Amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (mmol)	Additive element type	Amount of additive element (mmol)	Amount of DIP (mL)	Water amount (mL)
Mg5	30.40 (95%)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.60 (5%)	9	16
Ca5	30.40 (95%)	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	1.60 (5%)	9	16
Ba5	30.40 (95%)	$\text{Ba}(\text{NO}_3)_2$	1.60 (5%)	9	16
Sr5	30.40 (95%)	$\text{Sr}(\text{NO}_3)_2$	1.60 (5%)	9	16
Cu5	30.40 (95%)	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	1.60 (5%)	9	16
Ni5	30.40 (95%)	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.60 (5%)	9	16

Al5	30.40 (95%)	Ba(NO ₃) ₂	1.60 (5%)	9	16
V5	30.40 (95%)	Sr(NO ₃) ₂	1.60 (5%)	9	16
Co5	30.40 (95%)	Tris(EDA) cobalt(III) chloride	1.60 (5%)	9	16
Ti5	30.40 (95%)	TIPP in 5ml EtOH	1.60 (5%)	9	13.5
Si5	30.40 (95%)	TEOS in 5ml EtOH	1.60 (5%)	9	13.5
Sn5	30.40 (95%)	SnCl ₄ ·4H ₂ O	3.20 (10%)	9	16

Further systematic study of modification was carried out on Mg and Ti by varying the molar ratio between additive elements and iron ion, as summarized in table 3.2 and table 3.3 below.

Table 3.2: Syntheses for Mg modified hematite assisted by DIP

Procedure Number	Amount of FeCl ₃ ·6H ₂ O (mmol)	Additive element type	Amount of additive element (mmol)	Amount of DIP (mL)	Water amount (mL)
0	32.00 (100%)	-	-	9	16
Mg1	31.68 (99%)	Mg(NO ₃) ₂ ·6H ₂ O	0.32 (1%)	9	16
Mg3	31.04 (97%)	Mg(NO ₃) ₂ ·6H ₂ O	0.96 (3%)	9	16
Mg5	30.40 (95%)	Mg(NO ₃) ₂ ·6H ₂ O	1.60 (5%)	9	16
Mg7	29.76 (93%)	Mg(NO ₃) ₂ ·6H ₂ O	2.24 (7%)	9	16
Mg10	28.80 (90%)	Mg(NO ₃) ₂ ·6H ₂ O	3.20 (10%)	9	16
Mg15	27.20 (85%)	Mg(NO ₃) ₂ ·6H ₂ O	4.80 (15%)	9	16
Mg20	25.60 (80%)	Mg(NO ₃) ₂ ·6H ₂ O	6.40 (20%)	9	16

Table 3.3: Syntheses for Ti modified hematite assisted by DIP

Procedure Number	Amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (mmol)	Additive element type	Amount of additive element (mmol)	Amount of DIP (mL)	Water amount (mL)
Ti1	31.68 (99%)	TIPP in 5ml EtOH	0.32 (1%)	9	13.5
Ti3	31.36 (97%)	TIPP in 5ml EtOH	0.96 (3%)	9	13.5
Ti5	30.40 (95%)	TIPP in 5ml EtOH	1.60 (5%)	9	13.5
Ti7	29.68 (93%)	TIPP in 5ml EtOH	2.32 (7%)	9	13.5
Ti10	28.80 (90%)	TIPP in 5ml EtOH	3.20 (10%)	9	13.5

3.1.3 HEMATITE SYNTHESIS WITH ADDITION OF NaOH

Comparison study was also carried out with similar hydrothermal procedure, with Mg and Ti as additive elements. In this series, 0.3 mol NaOH pellets (Aldrich, 99.5%) were dissolved in 50 ml DI water to form a 6 M NaOH solution. 16ml of 6 M NaOH solution were drop wisely added into the solution with Fe and additive element ions, instead of 18 ml DIP. In addition, KOH (Aldrich, 98%) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were also used instead of NaOH and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in some cases for comparison, which will be specifically mentioned in result and discussion chapters. The detailed experimental analysis is listed in table 3.4 below.

Table 3.4: Syntheses for Mg or Ti modified hematite assisted by NaOH

Procedure Number	Amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (mmol)	Additive element type (in 2.5ml Abs EtOH)	Amount of additive element (mmol)	Amount of $\text{NaOH}_{(\text{aq})}$ (mL)	Water amount (mL)
N4	16.00 (100%)	-	-	4	16
N8	16.00	-	-	8	16

Procedure Number	Amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (mmol)	Additive element type (in 2.5ml Abs EtOH)	Amount of additive element (mmol)	Amount of $\text{NaOH}_{(\text{aq})}$ (mL)	Water amount (mL)
	(100%)				
N12	16.00 (100%)	-	-	12	16
N16	16.00 (100%)	-	-	16	16
N8Ti1	15.84 (99%)	TIPP	0.16 (1%)	8	13.5
N8Ti3	15.52 (97%)	TIPP	0.48 (3%)	8	13.5
N8Ti5	15.20 (95%)	TIPP	0.80 (5%)	8	13.5
N8Ti7	14.86 (93%)	TIPP	1.14 (7%)	8	13.5
N8Ti10	14.40 (90%)	TIPP	1.60 (10%)	8	13.5
N8Mg10	14.40 (90%)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.60 (10%)	8	16
N4Mg10	14.40 (90%)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.60 (10%)	8	16
N12Mg1	15.84 (99%)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.16 (1%)	8	16
N12Mg5	15.20 (95%)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.80 (5%)	8	16
N12Mg10	14.40 (90%)	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1.60 (10%)	8	16

3.1.4 LITHIUM ADDITION

Similar with many other anode materials, iron oxide suffers from low 1st cycle columbic efficiency as described in previous chapter. Thus, it is necessary to develop a strategy to overcome this limitation. In this thesis, a chemical lithium addition strategy is proposed. Coating and incorporating of lithium ion into iron oxide is a promising strategy to compensate the lithium ion loss during SEI formation.

3.1.4.1 COATING APPROACH

The first strategy is to coat on pre-synthesized hematite particle. In a typical synthesis, 400 mg of pre-synthesized hematite microparticle (N8 in section 3.1.3,

table 7) and 80 mg of lithium acetate (Sigma-Aldrich, 99%) were dispersed in 2.5ml of absolute EtOH with continuous magnetic stirring. Then a separate solution was prepared by dissolving 39 mg of oxalic acid (Sigma-Aldrich, 98%) into 1ml of absolute EtOH. The oxalic acid solution was then added into iron oxide dispersed solution drop wisely under continuously magnetic stirring. After 30minutes of stirring, the solution was collected and centrifuged 3 times in absolute EtOH to exclude any unfinished residue substance, and red powder could be obtained with a drying process in vacuum oven at 60 °C overnight.

For comparison, another sample was prepared with extra lithium source and oxalic acid as a variable to justify the effectiveness of coating, as shown in table 3.5 below.

Table 3.5: Syntheses of lithium oxalate coated iron oxide

	Fe₂O₃	Li Acetate	EtOH	Oxalic acid	EtOH
C1	400 mg	0.0800 g	2.5 ml	39.19 mg	1 ml
C2	400 mg	0.2649 g	2.9 ml	129.75 mg	1.5 ml

3.1.2.2 TWO-STEP SYNTHESIS OF LITHIUM INCORPORATED IRON OXIDE

Incorporation of lithium into iron oxide is also tested. It is already discussed in the literature review part that addition of lithium into hematite has already proven ineffective on 1st cycle efficiency enhancement. Thus, in this part, precursors with Fe²⁺ is used, aiming at a lithiated compound contained partially Fe²⁺.

In first approach, a two-step synthesis route was proposed. In a typical synthesis, 3.48g of iron (II) acetate (Aldrich, 98%) and 1.32g of lithium acetate were dissolved in 20ml of absolute EtOH, while a separate solution 2 was prepared by dissolving 0.99g of oxalic acid in 5ml absolute EtOH. Then solution 2 was added into iron/lithium ion solution with continuous magnetic stirring. The mixture was then loaded into a 45ml stainless steel autoclave with Teflon-lined for

hydrothermal treatment at 180°C for 16 hours. The product was naturally cooled down to room temperature after the reaction, and collected by centrifuge process with absolute EtOH. A comparison sample without lithium acetate and oxalic acid was also prepared with the same procedure, to justify the effectiveness of lithium content addition, as shown in table 3.6 below.

Table 3.6: Syntheses of lithium incorporated iron oxide

	Iron (II) acetate	Lithium acetate	Oxalic acid solution	ABS EtOH (mL)
L1	3.4786 g	1.3196 g	0.99 g in 5 ml ABS EtOH	20
L2	3.4786 g	0	0	20

The obtained black powders were then transferred into a ceramic boat and placed in Ar tube furnace and annealed at temperature of 400°C for 10 hours with ramping rate of 5 °C minute⁻¹. The annealed samples are denoted as L1Ar and L2Ar respectively.

3.1.2.3 Three-step synthesis of lithium incorporated iron oxide

A three-step synthesis approach is also proposed. In this approach, magnetite was synthesized in the first step, then lithium source was added into as-prepared magnetite samples. In a typical synthesis, 0.83 g of iron (II) acetate and 0.25 g of urea (Aldrich, 99%) were dissolved in 24 ml of DI water, the mixture was then loaded into a 45 ml stainless steel autoclave with Teflon-lined for hydrothermal treatment at 180 °C for 16 hours. The product was naturally cooled down to room temperature after the reaction, and collected by centrifuge process with DI water and absolute EtOH, followed by vacuum drying in vacuum oven at 60 °C overnight. The obtained black powder is denoted as L3.

300 mg of sample L3 and 180 mg of lithium acetate were dispersed into 15ml of absolute EtOH with continuous magnetic stirring. The mixture was then put on a hot plate at 80 °C under stirring to evaporate EtOH. The dried solid content was transferred into a ceramic boat and placed in Ar tube furnace and annealed at

temperature of 400 °C for 10 hours with ramping rate of 5 °C minute⁻¹. The annealed sample is denoted as L4Ar.

3.2 MATERIAL CHARACTERIZATION

3.2.1 X-RAY DIFFRACTION (XRD) ANALYSIS

Crystallographic characterization was carried out by XRD using a Shimadzu XRD-6000 diffractometer operating at 40 kV and 40 mA using Cu K_{α1} radiation ($\lambda = 0.154$ nm) with a copper target and a nickel filter. TOPAS is used as analysis tool for Rietveld refinement.[131] Essential information such as lattice parameter and cell volume about the material could be obtained.

3.2.2 FIELD EMISSION SCANNING ELECTRON MICROSCOPY (FESEM) ANALYSIS

The surface morphology and microstructure were investigated by FESEM using a JEOL 6340F with an accelerating voltage of 5 kV in the secondary electron imaging mode. For FESEM sample preparation, the samples were dispersed in ethanol, and dripped on a silicon wafer by a pipette. After drying in an oven at 60 °C overnight, the as-prepared samples were placed in a carbon tape, and coated with Pt twice, 60 s each.

3.2.3 TRANSMISSION ELECTRON MICROSCOPY (TEM) ANALYSIS

TEM imaging was conducted at 200 kV using a JEOL JEM-2100F TEM. TEM samples were prepared by depositing powdered materials on holey-carbon coated copper-grids after ultrasonication for 3 min in ethanol.

3.2.4 ENERGY DISPERSIVE X-RAY (EDX) ANALYSIS

EDX analysis incorporated in FESEM or TEM is applied as semi-quantitative elemental analysis tool. A working voltage of 20 kV and working distance of 15 mm is applied during the measurement. In the spectrum, elemental X-ray energies

(in KeV) from each element are plotted against the intensity of characteristic X-rays from each element, thus assisting in an elemental analysis of a sample from the EDX spectrum.

3.2.5 X-RAY FLUORESCENCE (XRF) ELEMENTAL ANALYSIS

XRF measurements were performed using a sequential wavelength dispersive XRF Spectrometer AXS SRS 3400 (Bruker), equipped with a Rh-Tube with maximum output of 3 kW. The maximum tube voltage and current are 60 kV and 50 mA, respectively. Analysis and quantification were carried out using the software SpectraPlus V 1.6.

3.2.6 ULTRAVIOLET–VISIBLE (UV-VIS) ANALYSIS

UV-vis spectra are obtained by using the reflectance mode in Shimatzu UV-2501 PC with a Light Source of 50 W halogen lamp and Deuterium lamp. The scan range is set from 800 nm to 400 nm. The absorbance spectrum is deduced from reflection spectrum, and Tauc plot is applied to obtain the absorption edge, which is referring to the band gap of the material.

3.3 ELECTROCHEMICAL CELL ASSEMBLY AND TESTING

There are 2 ratios of active material ratio in the anode electrode used in this thesis. At first, for the pure hematite nanorod, the electrodes were prepared with 40% active martial, 40% of conductive additives (Super P Li carbon, Timcal) and 20% of PVDF binder (Kynar 2801). In all other experiment, the anodes were then prepared by mixing 60% of synthesized modified hematite powder, with 20% of conductive additives and 20% of PVDF binder. Different content is mixed in NMP (Sigma-Aldrich, 99.5%) as the solvent to form the slurry. The slurry was mixed under magnetic stirring overnight to achieve a homogenous mixture. The as-prepared slurry was coated on a copper foil by doctor blade technique with a gap width of 300 μ m. The coated sample was then transferred into an oven at 60°C overnight. Then it was roll-pressed with 20 tones and cut into circular pieces with

diameter of 12 mm. The electrodes were assembled into half-cells for electrochemical performance test. Coin cells (CR2016) with lithium foil (~0.59 mm thickness, Hohsen Corp., Japan) as counter and reference electrode were assembled in an argon filled glovebox (Mbraun, Unilab, USA, H₂O, O₂ < 1 ppm.). LiPF₆ (1 M) in ethylene carbonate/diethyl carbonate (Danvec, 1:1 v%) was used as the electrolyte (75 μ L) and a Celgard 2400 (24 μ m) membrane as the separator.

3.3.1 CYCLIC VOLTAMMETRY (CV)

The CV measurements were performed by Solartron electrochemical workstation (1470E and SI 1255B analyzer coupled with a potentiostat), at voltage range from 0.05 V to 3 V. The scan rate was set as 0.1 mV s⁻¹. In the tested half-cell, delithiation curve refers to the reduction reaction, where iron oxide is reduced to metallic iron by electron intake, while lithiation curve refers to the oxidation reaction, where the reverse reaction happened. All the potential measured or presented in this thesis is based on voltages versus Li⁺/Li electrode as reference electrode. (Li⁺/Li has a potential of -3.04 V using SHE as reference electrode.)

3.3.2 CYCLING PERFORMANCE TEST

Galvanostatic cycling test was performed on a Multichannel Battery Tester (Neware Technology Limited) in the range of 0.05 V to 3 V, with current density of 100 mA g⁻¹ (0.1 C), where 1C is defined as to full lithiate or delithiate of the electrode in the time of 1 hour. In the case of iron oxide, 1 C is approximately equal to current density of 1000 mA g⁻¹, as iron oxides' theoretical capacity is around 1000 mAh g⁻¹. All cells were tested for 50 galvanostatic cycles continuously to monitor the cycling stability of material.

3.3.3 RATE PERFORMANCE TEST

Rate performance test refers to repeated galvanostatic cycling test with gradually increasing current density. In this thesis, a constant testing pattern was applied: the lithiation current density was always set at 0.1C for every galvanostatic cycles, while delithiation current was varied. Specifically, the delithiation current density

was set as 0.1 C for the first 5 cycles, while gradually increase to 3 C through 0.33 C, 0.5 C, 1 C, 2 C, and capacity check at 0.1 C was finally implemented to identify if the capacity could be recovered. The electrode run 4 cycles under each mentioned current density. Such design is mainly due to the uneven need of power density during charge and discharge process in real applications. In EV field, the discharge power density is one of the main limitation for LIB. Thus, a fully lithiation of product before next delithiation is required to study the delithiation response under different current density. In conclusion, such procedure is designed for the optimization of delithiation capacity in different current density.

3.3.4 EX-SITU CHARACTERIZATION OF ELECTRODE

Selected electrodes were also collected after cycling for further analysis. To achieve this, coin cells were collected and transferred into glovebox after completion of the testing procedure. The cell was then disassembled, and the electrode was retrieved. The retrieved electrode was rinsed with DEC (Aldrich, 99%) to remove electrolyte and corresponding lithiated salt, and dried inside glovebox for 2 days. Then the electrode was transferred out and respective characterization including XRD, FESEM and TEM were applied.

For TEM measurement, the retrieved electrode was peeled off from current collector, and dispersed in absolute EtOH with ultrasonication for 10 minutes to obtain homogeneous dispersion. The dispersion was then dropped on a holey carbon coated copper grid and vacuum-dried overnight before testing. The operation process is same as previously described in section 3.2.3.

4. EXPERIMENTAL RESULTS

4.1 HEMATITE NANOROD SYNTHESIS ASSISTED BY DIAMINE SERIES

4.1.1 MATERIAL CHARACTERIZATIONS

For all the SCA related pure hematite nanorod synthesis, the samples are named following the pattern $\alpha\text{-Fe}_2\text{O}_3\text{-D.0.5}$, where D is the abbreviation of SCA types (E for EDA, D for DIP, B for DAB, and N for NMD), and 0.5 is the concentration of iron ions in solution before synthesis. The hydrothermal synthesis parameters of all here discussed samples are set to 1:13 as the molar ratio of FeCl_3/SCA and $180^\circ\text{C}/16\text{hrs}$ as the reaction temperature/time which were optimized towards fully crystalized pure phase products in preliminary test series and are in good agreement with reported $\alpha\text{-Fe}_2\text{O}_3$ synthesis.[102] A systematic study is applied to study Fe^{3+} concentration effect and various SCAs on crystal phase formation and morphology of the obtained $\alpha\text{-Fe}_2\text{O}_3$. All applied diamine derivatives are schematically illustrated in Figure 4.1.

Figure 4.1: Schematic illustration of applied SCAs containing two vicinal amine groups and different H_3C -groups.

Figure 4.2a illustrates exemplarily the XRD patterns of samples obtained from a test series with DIP as SCA and varied Fe^{3+} concentration ($\alpha\text{-Fe}_2\text{O}_3\text{-D0.1}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D0.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D1.0}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D1.5}$, and $\alpha\text{-Fe}_2\text{O}_3\text{-D2.0}$), whereas Figure 4.2b shows exemplarily the XRD pattern of samples obtained from a test series with a

fixed Fe^{3+} concentration of 1.5 M with different SCA ($\alpha\text{-Fe}_2\text{O}_3\text{-E1.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D1.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-B1.5}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-N1.5}$).

Figure 4.2: (a) XRD patterns for $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles synthesized with various Fe^{3+} concentrations and DIP and (b) different diamine derivatives as SCA and varied Fe^{3+} concentrations.

The obtained pattern could be perfectly indexed to $\alpha\text{-Fe}_2\text{O}_3$ (JAPDS card No. 330664), the reflections are strong and spiky, suggesting good crystallinity of material. Lattice constants are calculated using Rietveld refinement and found to be in the range of 5.030 Å to 5.033 Å for lattice constant a , and 13.748 Å to 13.757 Å for lattice constant c (Table), which is in perfect agreement with reported values. [58, 132] The obtained R_{Bragg} values vary from ~3% to ~7%, indicating a good reliability of the refined data. No reflections of detectable impurities are observed indicating pure hematite phase has been successfully synthesized through above procedure.

FESEM was applied to examine the morphology of the final $\alpha\text{-Fe}_2\text{O}_3$ products. Figure displays the morphology evolution with increased Fe^{3+} concentration from 0.1 M to 2.0 M and DIP as SCA. At Fe^{3+} concentration of 0.1 M nanoparticles with diameters of ~100nm are obtained. When the Fe^{3+} concentration is increased to 0.5M, a 1-D rod-like morphology starts to form with rod length of ~240 nm resulting in an aspect ratio of ~2.6. Increasing the Fe^{3+} concentration to 0.8 M leads to an elongated nanorod shape with rod length of ~320 nm and an aspect ratio of ~4.7. At higher Fe^{3+} concentration from 1.04.3M to 2.0 M, further pronounced

elongated nanorods with length of ~ 400 nm and aspect ratios in the range of 4.9 to 5.7 are obtained.

Figure 4.3: FESEM images of α - Fe_2O_3 nanoparticles obtained with DIP as SCA and varied Fe^{3+} concentration of a) 0.1 M, b) 0.5 M, c) 0.8 M, d) 1.0 M, e) 1.5 M and f) 2.0 M, magnification: 50000.

EDA is also tested as alternative SCA in the synthesis procedure instead of DIP to study the effect of side methyl group. All other reaction parameters are kept constant. In general, the Fe^{3+} concentration vs. aspect ratio dependency shows an analogical profile shape as obtained for DIP, but shorter rod length for each tested Fe^{3+} concentration. In detail, at lower Fe^{3+} concentration of 0.1 M and 0.5 M, nanoparticles with diameters of ~ 100 nm are obtained with EDA as SCA. When the Fe^{3+} concentration is increased to 0.8 M, nanorods with length of ~ 275 nm and aspect ratio of ~ 2.9 are achieved. Further increase of the Fe^{3+} concentration up to 2.0 M leads to a comparable rodlike morphology with rod length of ~ 280 nm and aspect ratios of ~ 3.0 .

Figure 4.4: Aspect ratio vs. Fe^{3+} concentration for $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles obtained with DIP and EDA as SCA (the aspect ratio for spherical particles is set to 1; 20 nanorods were taken for estimation of the aspect ratio for each Fe^{3+} concentration; a certain fluctuation margin cannot be excluded especially due to a natural variation in the rod length of about 20%).

Figure 4.5: FESEM images of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles obtained with EDA as SCA and varied Fe^{3+} concentration of a) 0.1 M, b) 0.5 M, c) 0.8 M, d) 1.0 M, e) 1.5 M and f) 2.0 M, magnification: 50000.

DAB and NMD were also tested as SCA, as a further comparison to DIP and ethylene diamine to allow investigations in the effectiveness of methyl side group.

NMD assisted hydrothermal approaches did not lead to a nanorod morphology, but spherical shaped particles with ~ 100 nm in diameter (Fe^{3+} conc.:1.5M, Figure c). When compare to its structural isomer DIP, it can be concluded that the H_3C -shift from C to N suppresses the ferric complex formation due to steric hindrance and therefore the directional dependency of the crystal growth is inhibited.

Figure 4.6: FESEM images of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles obtained with a) EDA, b) DIP, c) NMD and d) DAB, Fe^{3+} concentration was kept at 1.5 M, magnification: 50000.

Further synthesis procedures are applied in Fe^{3+} concentration test series with lower concentrations to confirm the ability among different SCAs. For DIP-assisted synthesis, the nanorod formation starts with comparatively low Fe^{3+} concentrations of 0.5 M leading to products with ~ 240 nm in length and aspect ratios of ~ 2.6 , while application of other here discussed diamine derivatives results in spherical particles only with diameters of ~ 100 nm under the same conditions (Figure).

Figure 4.7: FESEM images of α -Fe₂O₃ nanoparticles obtained with a) EDA, b) DIP and c) DAB, Fe³⁺ concentration was kept at 0.5M, magnification: 50000.

In conclusion, DIP is noticed to be the most effective SCA according to shape controlling ability, while EDA and DAB have shown similar intermediate ability. NMD has shown no shape controlling ability in above procedures. Table 4.1 below summarized relevant information from all involved synthesis experiments.

Table 4.1: Physicochemical characteristics of α -Fe₂O₃ synthesized with different SCAs and various Fe³⁺ concentrations.

Test series	Sample ID	Fe ³⁺ conc. (M)/SCA	Lattice constant a (Å)	Lattice constant c (Å)	R _{Bragg} value (%)	Rod length (nm)	Aspect ratio
Varied Fe³⁺ conc., fixed SCA (EDA)	α-Fe₂O₃-E0.1	0.1/EDA	5.031(2)	13.752(1)	6.406	spherical particle	-
	α-Fe₂O₃-E0.5	0.5/EDA	5.033(4)	13.753(6)	5.158	spherical particle	-
	α-Fe₂O₃-E0.8	0.8/EDA	5.033(5)	13.757(0)	4.838	275	2.9
	α-Fe₂O₃-E1.0	1.0/EDA	5.033(2)	13.755(2)	5.184	280	3.0
	α-Fe₂O₃-E1.5	1.5/EDA	5.033(6)	13.757(4)	6.672	276	3.0
	α-Fe₂O₃-E2.0	2.0/EDA	5.030(7)	13.749(7)	5.819	277	2.9
Varied Fe³⁺	α-Fe₂O₃-D0.1	0.1/DAP	5.031(1)	13.750(9)	4.636	spherical particle	-

conc., fixed SCA (DAP)	α-Fe₂O₃- D0.5	0.5/DAP	5.031(3)	13.748(4)	5.209	237	2.6
	α-Fe₂O₃- D0.8	0.8/DAP	5.030(7)	13.749(2)	2.997	320	4.7
	α-Fe₂O₃- D1.0	1.0/DAP	5.030(2)	13.753(3)	4.496	397	5.7
	α-Fe₂O₃- D1.5	1.5/DAP	5.031(8)	13.750(5)	3.645	394	5.0
	α-Fe₂O₃- D2.0	2.0/DAP	5.032(2)	13.754(4)	4.467	399	4.9
Varied SCA, fixed Fe³⁺ conc. (0.5M)	α-Fe₂O₃- E0.5	0.5/EDA	5.033(4)	13.753(6)	5.158	spherical particle	-
	α-Fe₂O₃- D0.5	0.5/DAP	5.031(3)	13.748(4)	5.209	237	2.6
	α-Fe₂O₃- B0.5	0.5/DAB	5.033(2)	13.750(8)	7.067	particle	-
	α-Fe₂O₃- N0.5	0.5/N- MED	Not synthesized, since even higher Fe ³⁺ concentration of 1.5M did not lead to nanorod morphology.				
Varied SCA, fixed Fe³⁺ conc. (1.5M)	α-Fe₂O₃- E1.5	1.5/EDA	5.033(6)	13.757(4)	6.672	276	3.0
	α-Fe₂O₃- D1.5	1.5/DAP	5.031(8)	13.750(5)	3.645	394	5.0
	α-Fe₂O₃- B1.5	1.5/DAB	5.032(1)	13.751(0)	5.073	256	2.8
	α-Fe₂O₃- N1.5	1.5/N- MED	5.031(4)	13.748(1)	7.019	spherical particle	-

Aspect ratio is not calculated for samples without nanorod morphology, DAP: DIP, EDA: ethylene diamine, DAB: 2,3-diaminobutane, N-MED: N-methylethylene diamine

4.1.2 ELECTROCHEMICAL PERFORMANCE

Since similar morphologies are obtained in several cases for SCA assisted hematite synthesis, selected samples with different rod-size are tested for electrochemical property,

To investigate the reaction mechanism of nano-shaped hematite particle with lithium ions, cycling voltammetry (CV) tests are applied. The obtained data for all samples are sufficiently congruent and figure 4.8 exemplarily shows the cyclic voltammetry curve for the first three cycles of $\alpha\text{-Fe}_2\text{O}_3\text{-E1.5}$ in the voltage range of 3.00 V to 0.05 V at a scan rate of 0.1 mV s^{-1} .

Figure 4.8: Cyclic voltamogram profile of nanorod shaped $\alpha\text{-Fe}_2\text{O}_3$ (obtained with 1.5M Fe^{3+} concentration and EDA as SCA).

For the first cathodic sweep, there are 3 peaks present at 1.5 V, 1.1 V and 0.7 V respectively. At 1.5 V, the peak corresponds to lithium ion intercalation into the $\alpha\text{-Fe}_2\text{O}_3$ matrix to form a lithiated structure of $\text{Li}_x\text{Fe}_2\text{O}_3$ without change the lattice structure, further lithiation at 1.1 V involves an electrochemical reaction associated with the phase transformation from $\text{Li}_x\text{Fe}_2\text{O}_3$ to cubic $\text{Li}_2\text{Fe}_2\text{O}_3$. [133] Subsequently, a spiky peak at about 0.7 V is presented, indicating the reduction reaction and formation of Fe^0 , associated with conversion reaction of lithium intercalation to

form Li_2O and electrolyte decomposition with SEI formation.[113] From the second cathodic cycle onwards, the peaks from 1.5 V to 1.3 V and at 1.1 V do not appear and also the peak at 0.7 V shifts slightly into the higher voltage range with decreased intensity most likely due to the irreversibility of the redox reaction as stated in the literature.[134] For the first anodic sweep, broad oxidation peaks at 1.6 V and 1.8 V are observed, corresponding to the oxidation of Fe^0 to $\text{Fe}^{2+}/\text{Fe}^{3+}$. [59]

The galvanostatic delithiation/lithiation profiles of $\alpha\text{-Fe}_2\text{O}_3$ with nanorod morphology at 0.1 C between the voltage window of 0.05 V to 3.00 V are shown in figure 4.9.

The obtained data are in good agreement with the CV profiles. In general, all $\alpha\text{-Fe}_2\text{O}_3$ samples exhibit two slopes for the first discharge curve from the starting voltage to around 1.3 V and from around 1.1 V to 0.8 V, which corresponds to the intercalation of lithium into $\alpha\text{-Fe}_2\text{O}_3$, resulting in $\text{Li}_x\text{Fe}_2\text{O}_3$ and cubic $\text{Li}_2\text{Fe}_2\text{O}_3$, respectively.[48, 63] A strong and stable plateau at around 0.8 V indicates the reduction of Fe^{2+} to Fe^0 and formation of amorphous Li_2O . [134] As exemplarily illustrated for $\alpha\text{-Fe}_2\text{O}_3\text{-E1.5}$ (Figure 4.10a), all samples exhibit a significant capacity loss at the first lithiation cycle. The first lithiation capacities for $\alpha\text{-Fe}_2\text{O}_3\text{-E0.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-E1.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D0.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D0.8}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D1.5}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-B1.5}$ are around 1400-1500 mAh g^{-1} , the capacities of the 1st delithiation cycle are about 1100 mAh g^{-1} , and the respective columbic efficiencies are about 75%. The exact values for each sample can be found in Table 4.2. The initial capacity loss might be attributed to the irreversible loss of lithium due to SEI formation.[56]

Figure 4.9: (a) Galvanostatic delithiation/lithiation profiles (1st, 2nd and 5th cycle) for $\alpha\text{-Fe}_2\text{O}_3\text{-E1.5}$ and (b) 1st and 2nd cycle comparison for $\alpha\text{-Fe}_2\text{O}_3\text{-E0.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-E1.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D0.5}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D0.8}$, $\alpha\text{-Fe}_2\text{O}_3\text{-D1.5}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-B1.5}$.

Figure 4.10: (a) Cycling performance and (b) rate testing of α - Fe_2O_3 -E0.5, α - Fe_2O_3 -E1.5, α - Fe_2O_3 -D0.5, α - Fe_2O_3 -D0.8, α - Fe_2O_3 -D1.5 and α - Fe_2O_3 -B1.5.

Table 4.2: Electrochemical data of α -Fe₂O₃ synthesized with different SCAs and various Fe³⁺ concentrations.

Sample ID	1 st cycle lithiation capacity (mAh g ⁻¹)	1 st cycle delithiation capacity (mAh g ⁻¹)	1 st cycle columbic efficiency (%)	50 th cycle lithiation capacity (mAh g ⁻¹)	50 th cycle delithiation capacity (mAh g ⁻¹)
α -Fe ₂ O ₃ -E0.5	1465	1066	73	1001	986
α -Fe ₂ O ₃ -E1.5	1545	1132	73	1072	1053
α -Fe ₂ O ₃ -D0.5	1479	1087	73	1086	1062
α -Fe ₂ O ₃ -D0.8	1494	1143	77	957	935
α -Fe ₂ O ₃ -D1.5	1526	1121	73	848	829
α -Fe ₂ O ₃ -B1.5	1422	1020	72	1034	1017

The cycling performance of α -Fe₂O₃-E0.5, α -Fe₂O₃-E1.5, α -Fe₂O₃-D0.5, α -Fe₂O₃-D0.8, α -Fe₂O₃-D1.5 and α -Fe₂O₃-B1.5 at 0.1 C are illustrated in Figure showing exceptional cycle stabilities around 1000 mAh g⁻¹ for 50 cycles. The data demonstrate that especially samples with intermediate rod lengths (α -Fe₂O₃-E1.5, α -Fe₂O₃-D0.5 and α -Fe₂O₃-B1.5) in the range of ~240 nm up to ~280 nm show higher capacities over spherical α -Fe₂O₃ nanoparticles (α -Fe₂O₃-E0.5) or samples with longer rod lengths of approximately ~320 nm (α -Fe₂O₃-D0.8) and ~390 nm (α -Fe₂O₃-D1.5).

The rate test is also implemented to examine the samples' capacity under higher current density. The samples α -Fe₂O₃-E1.5, α -Fe₂O₃-D0.5 and α -Fe₂O₃-B1.5 with intermediate nanorod length of ~280 nm, ~240 nm and ~260 nm show charge capacities of 746, 770 and 740 mAh g⁻¹ at a charge current density of 3C, which outperform over nanoparticles (590 mAh g⁻¹) and longer rods with ~320 nm (696 mAh g⁻¹) and ~390 nm (655 mAh g⁻¹). The samples from intermediate sized nanorod also show a better capacity recover (~1000 mAh g⁻¹) when 0.1 C is applied after 3 C period, compared with longer rod and nanoparticles.

In conclusion, for all the tested samples, intermediate sized nanorod with rod length around 260 nm and aspect ratio around 3 has shown the most satisfactory electrochemical performance in both cycling stability and high rate response.

4.2 HEMATITE MODIFICATION IN NANOROD

4.2.2 TRIAL ON DIFFERENT ADDITIVE ELEMENTS

4.2.1.1 MATERIAL CHARACTERIZATION

Hematite modification trial is firstly implemented on elements including Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , Ni^{2+} , Al^{3+} , Co^{3+} , V^{3+} , Ti^{4+} , Si^{4+} and Sn^{4+} , an annealing process in air was carried out for Ti^{4+} added sample to obtain a pure hematite phase.

It is found that when the as-mentioned elements are added into the system, V^{3+} , Sr^{2+} and Ba^{2+} will lead to an impurity phase, namely VOOH (standard JCPDS card no. 159172), SrCO_3 (standard JCPDS card no. 050418) and BaCO_3 (standard JCPDS card no. 0451471) as shown in figure 4.11 below. It could be concluded that the as mentioned 3 elements are preferably forming another phase rather than being incorporated into hematite lattice. Thus, no further investigation is carried out on these elements.

Figure 4.11. XRD pattern for V, Sr and Ba added samples (The unlabeled peaks are from hematite Fe_2O_3 or Goethite FeOOH)

The remaining elements, including Mg^{2+} , Ca^{2+} , Al^{3+} , Co^{3+} , V^{3+} , Ti^{4+} , Si^{4+} and Sn^{4+} , are found to form a single hematite (standard JCPDS card no. 330664), phase when added into the system, as shown in figure 4.12 below. The lattice parameter of the pure phase hematite is also obtained through refinement as shown in table 4.3 below.

Figure 4.12. XRD pattern for different elements added, and DIP as SCA

Table 4.3. Lattice parameters obtained from Rietveld refinement of XRD data for different additive elements and DIP as SCA

Sample	a(Å)	c(Å)	Cell volume(Å ³)
Unmodified	5.030(2)	13.744(5)	301.1
5% Ca	5.032(1)	13.763(9)	301.8
5% Al	5.023(7)	13.729(6)	299.9
5% Co	5.030(8)	13.753(5)	301.3
5% Cu	5.030(0)	13.744(3)	301.1
5% Ni	5.031(2)	13.747(6)	301.2
5% Mg	5.047(1)	13.778(8)	303.9
5% Ti	5.028(2)	13.747(6)	300.9
5% Si	5.022(7)	13.755(1)	300.4
5% Sn	5.048(3)	13.786(5)	304.3

Compared with unmodified samples, a small increase in lattice constant is observed for Ca, Mg, Sn modified hematite, while an obvious decrease for Al added samples is found, which could be explained by the ionic radius, since Ca^{2+} , Mg^{2+} and Sn^{4+} are larger than Fe^{3+} while Al^{3+} is smaller (ionic radius for Ca^{2+} , Mg^{2+} , Sn^{4+} , Al^{3+} and Fe^{3+} is 114 pm, 86 pm, 83 pm, 67.5 pm and 78.5 pm respectively [135]). Thus, it could be concluded that both ions have been successfully incorporated into the hematite lattice.

As for Co^{3+} , Cu^{2+} , Ni^{2+} and Ti^{4+} , the lattice parameter is very close to unmodified samples. It is difficult to obtain a solid proof of successful modification.

Thus, a qualitative EDX is carried out to examine the chemical composition of the obtained solids from Co^{3+} , Cu^{2+} and Ni^{2+} modification approaches.

From EDX spectrum, no additive element content is discovered in Co^{3+} , Cu^{2+} and Ni^{2+} modification experiment, which could lead to a conclusion these 3 elements, Co^{3+} , Cu^{2+} and Ni^{2+} are not presented in the samples in the detectable range. Most of the respective ions possibly remain in solution, and washed away during centrifuge process. Thus, Co^{3+} , Cu^{2+} and Ni^{2+} added samples are not further investigated. But the presence of titanium could clearly be observed in figure 15d, which could be a direct proof that titanium is present in the system, so titanium added sample is further investigated as potential modified sample.

FESEM image from each promising additive element are shown in figure 4.13 below.

Figure 4.13. FESEM image for studied additive elements and DIP as SCA

It could be noticed that except for Si added sample, all other studied samples successfully maintained rodlike morphology, with length around 280 nm and width around 100 nm. For Si added samples, a 2D plate-like morphology is observed,

with around 300 nm in diameter and around 30 nm in thickness. All samples are then tested for electrochemical performance.

4.1.2.2 ELECTROCHEMICAL TEST

The cycling and rate test is quickly investigated with 60% active material ratio as stated in the experimental section to justify the effectiveness of such modification, as shown in figure 4.14 below. For the cycling curve, both lithiation and delithiation capacity are drawn in the graph, while for rate test, only delithiation capacity is present as the different current density is only applied on delithiation process.

Figure 4.14. Cycling and rate test of different modified hematite.

It could be observed from above data that Mg is found to be the most effective additives among all the tested samples. The reversible capacity after 50 cycles is doubled from around 200 mAh g⁻¹ to 400 mAh g⁻¹. Furthermore, the rate test also suggested that Mg contained samples deliver a much better high rate response of 400 mAh g⁻¹ at delithiation current density of 3 C, compared to unmodified sample of 100 mAh g⁻¹ under same conditions. Ti modified sample also shows an enhanced delithiation capacity of 300 mAh g⁻¹ on high rate response, but no observable increase in cycling capacity is presented. Thus, Mg and Ti are selected as promising elements for a detailed study.

4.2.3 MG MODIFIED HEMATITE NANOROD

4.2.3.1 MATERIAL CHARACTERIZATION

Mg added samples are named according to Mg addition amount from 1% Mg until 20% Mg. It is notified that the real Mg content is different from the amount added, but for simplicity of naming systems, Mg adding amount is used to describe the respective samples.

Figure 4.15 shows the XRD pattern obtained from Mg added hematite, up to Mg addition level of 10%, a single hematite phase (standard JCPDS card no. 330664) without impurities is confirmed, further Mg addition of 15% and 20% lead to the presence of a second phase consisting of MgO (standard JCPDS card no. 8041920). Lattice parameters are calculated with Rietveld refinement for samples that have shown pure hematite phase. Lattice parameters are found to increase with increased Mg modification level of 0 to 10%, specifically, *a* increases from 5.030 Å for unmodified sample to 5.053 Å for 10% Mg added sample. Similarly, for the lattice parameter *c*, the value increased from 13.744 to 13.792 Å within the test series of 0 to 10% Mg modification. The increment in lattice constants is attributed to the relatively larger ionic radius in the octahedral state of Mg²⁺ (0.72 Å) as for the host ion Fe³⁺ (0.645 Å) [136], and confirms the incorporation of Mg into the hematite structure. *R*_{Bragg} values are in range of 4.739 to 7.598%, which indicates a good reliability of the refined data (Table 4.4).

Figure 4.15: XRD patterns for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 20%.

Table 4.4: Lattice parameters from Rietveld refinement of XRD data and XRF data for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 10%.

Mg modification level (%)	a (Å)	c (Å)	Cell volume (Å³)	R_{Bragg} value (%)	Calculated atomic ratio (Mg:Fe)
0	5.030(3)	13.744(5)	301.1	4.739	
1	5.032(0)	13.749(4)	301.5	6.969	0.86:100
3	5.039(1)	13.759(8)	302.8	5.338	2.24:100
5	5.042(9)	13.768(2)	303.2	5.345	3.73:100
7	5.046(4)	13.777(6)	303.7	7.598	4.21:100
10	5.053(5)	13.792(2)	305.0	6.787	6.45:100

Elemental analysis is carried out for Mg modified sample by XRF to confirm the presence of Mg, as shown in table 4.4. The real Mg content is shown to increase for higher Mg adding level samples, with partial Mg loss during the hydrothermal synthesis. A close to linear relationship of lattice parameters obtained from Rietveld refinement and Mg proportion is observed (figure 4.16).

Figure 4.16: Change of a) lattice parameter, and b) cell volume for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 10%.

Morphology examination of Mg modified products is conducted with FESEM and TEM. 20 nanorods were taken for determination of rod lengths and diameter. Mg-

free samples exhibit an averaged rod length of ~280 nm (Fe^{3+} conc. of 1.0 M, DIP), which is in consistency with optimized nanorod in previous section. A Mg modification level of 5% leads to rod lengths of ~310 nm, and the aspect ratio decreases from ~4.0 (unmodified samples) to ~3.2 (table 4.5). At a Mg modification level of 10%, the morphology turns into hollow nanocubes with diameters of ~200 nm, while 7% Mg leads to an intermediate state between nanorods and hollow nanocubes (figure 4.17 and 4.18). For 15% and 20% of Mg, an additional 2D plate-like morphology appears (figure 4.19). Thus, the theoretical Mg uptake-limit for hematite with preserved nanorod shape morphology for the here presented DIP-assisted synthesis approach, is ~5%, while a pure hematite crystal phase is preserved up to a Mg modification level of ~10%.

Table 4.5: Rod length and aspect ratio for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 5%, (20 nanorods were taken for each determination; fluctuation margin cannot be excluded especially due to a natural variation in the nanorod size of about 20%).

Mg modification level (%)	Average rod length (nm)	Standard deviation of rod length (nm)	Average rod width (nm)	Standard deviation of rod width (nm)	Calculated aspect ratio
0	284	52	73	10	3.9
1	295	66	74	8	4.0
3	312	59	89	15	3.5
5	316	45	99	12	3.2
7	Intermediate between nanorods and nanocubes				
10	Cubic morphology

Figure 4.17: FESEM images for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of a) 0%, b) 1%, c) 3%, d) 5%, e) 7%, and f) 10%.

Figure 4.18: TEM images for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 10%.

Figure 4.19: FESEM images for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of a) 15%, and b) 20%; and FESEM mages for iron oxide nanoparticles obtained from synthesis approaches with Mg modification level of 10% and $\text{NaOH}_{(\text{aq})}$ as pH controller and c) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and d) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as precursors.

The formation of iron oxide nanocubes is discussed in literature. For instance, acidic conditions (strong hydrogen interaction between hematite nanoparticles) are reported to support the aggregation of nanoparticles into cubic morphologies [137]. A nanocube morphology can also be obtained by oxidative decomposition of Prussian blue nanocubes [138]. In addition, Cl^- ions have been discussed as a factor for the formation of a cube-like morphology [54]. Thus, reactants are successively replaced. For the first approach, no DIP as shape controlling agent is applied, but 16 ml 6 M NaOH to control the pH. In a second approach, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was used as precursor instead of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. As shown by FESEM (figure 20), similar nanocubes have been formed in both cases, suggesting that Cl^- and DIP are not responsible for the nanocube formation. Besides this, a cube-like morphology is also not obtained in approaches, in which Mg is replaced by other di-valent additive elements such as Ca, suggesting that the presence of Mg has a substantial effect in morphology directing.

As discussed before, Changes in the electronic conductivity involve a variation of the band gap that determines the activation energy that is needed to transfer electrons from the valance band to the conduction band. The shift in band gap can be investigated via UV-Vis absorption using Tauc Mott Plot:

$$\alpha h\nu = A(h\nu - E_g)^n \quad [139], [140] \quad (4.1)$$

where, A is a constant related to the density of electronic states above and below the band gap, α is the absorption coefficient, E_g is the optical band gap, $h\nu$ is the absorbed photon energy, n is 2 for indirect transition, and 0.5 for direct transition. The absorption spectrum is obtained by converting the measured diffusion reflectance using Kubelka-Munk remission function [141]. There are generally two regions in the measured wavelength range [142]. The first region (400 - 500 nm) corresponds to the excitation of two neighboring cations, associated with a partially local d-d transition and charge-transfer effect. The second region (500 - 750 nm) corresponds to local d-d transitions. The Tauc Mott plot with direct transition for samples with a Mg modification level from 0 to 10% is presented in figure 4.20. The direct band gap can be roughly estimated as intersection between the elongated absorption edge in the Tauc Mott plot and the x-axis [139], [140], as exemplified

with the dashed line in Figure b. The higher the Mg modification level, a trend to reduced band gaps is observed resulting in 2.131 eV for unmodified hematite and 1.970 eV for samples with 10% Mg (table 4.6). These results confirm an enhancement in the electronic conductivity through Mg modification of hematite.

Figure 4.20: a) Absorption and b) Tauc Mott plot of UV–Vis spectra (direct transition) for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of 0 to 10%. For the ordinate of b, arbitrary units are used, although α and $\alpha h\nu$ have a unit of m^{-1} and eV m^{-1} , respectively. However, the α value obtained using Kubelka-Munk remission function is a relative value).

Table 4.6: Estimated band gap for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of 0 to 10%.

	0% Mg	1% Mg	3% Mg	5% Mg	7% Mg	10% Mg
Estimated band gap (eV)	2.131	2.120	2.109	2.088	2.032	1.970

4.2.2.2 ELECTROCHEMICAL TESTS

Lithiation/delithiation processes are studied by cyclic voltammetry (CV) from 3.00 to 0.005V (scan rate of 0.1mV s^{-1}). Figure 2.21a shows the 1st cycle CV curve for samples obtained from Mg modification levels of 0 to 10% Mg (2nd cycle CV curve of all samples, and first 3 cycles for a sample with 5% Mg to be found in ESI). The first cathodic sweep exhibits a small broad peak at 1.4 V that is assigned to the intercalation of Li^+ into the hematite structure, forming hexagonal $\text{Li}_x\text{Fe}_2\text{O}_3$. A shoulder peak at 1.0 V indicates the formation of cubic $\text{Li}_2\text{Fe}_2\text{O}_3$ with further Li^+ intercalation into Fe_2O_3 . An intense peak at 0.7 V is observed, indicating the conversion reaction that leads to metallic iron and lithium oxide. The total reaction can be summarized as $\text{Fe}_2\text{O}_3 + 6\text{Li}^+ + 6\text{e}^- \rightarrow 2\text{Fe} + 3\text{Li}_2\text{O}$ [48], [63], [39]. From the second cathodic cycle onwards, the peak at 0.7 V slightly shifts to higher voltages with decreased intensity, indicating the partial irreversibility of the reaction [134]. For the first anodic sweep, an overlap of two broad peaks is observed at 1.6 V and 1.8 V that is assigned to the oxidation of Fe to FeO and Fe_2O_3 [59]. Figure 24b illustrates the 1st and 2nd cycle delithiation/lithiation profiles for samples with Mg modification levels of 0 to 10% at 0.1 C. The obtained data are in good agreement with CV.

Figure 4.21: a) 1st cycle CV curves, b) 1st and 2nd cycle galvanostatic curves, c) cycling performance, and d) rate capability for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification levels of 0 to 10%.

The cycling performance at a current rate of 0.1 C for samples obtained from Mg modification levels of 0 to 10% Mg are presented in figure 4.21c. Capacity values are based on the whole electrode. The 1st cycle coulombic efficiencies for all samples are in the range 74 - 76% , which is in good agreement with typical values reported in literature for iron oxides [134], [63]. The coulombic efficiencies for subsequent cycles are above 98%. A general increasing trend of the cycling stability is observed the higher the Mg content. A reversible capacity of 203 mAh g⁻¹ is obtained after 50 cycles for Mg-free samples, while 5% Mg modification leads to a capacity of 325 mAh g⁻¹ under the same conditions. With a Mg modification level of 10% a reversible capacity of 650 mAh g⁻¹ is achieved, which is more than 2 times higher than for the unmodified sample in long term cycling.

The rate testing for samples obtained from Mg modification levels of 0 to 10% Mg are presented in figure 4.21d. At higher current rate of 3 C, the unmodified sample shows a delithiation capacity of 109mAh g⁻¹, while 1% Mg leads to 65 mAh g⁻¹, further Mg modification of 3%, 5%, 7%, and 10% result in 192 mAh g⁻¹, 478 mAh g⁻¹, 556 mAh g⁻¹, and 427 mAh g⁻¹. The capacity of all Mg modified samples can be retained when operated again at 0.1 C after running at 3 C, suggesting a good capacity recovering ability for the Mg modified samples. For unmodified hematite, although it shows good capacity retaining ability at 1st cycle at 0.1 C after high current rate section (3 C), a pronounced capacity drop is observed.

Figure 4.22 below shows the average ΔE value, calculated by the following equation:

$$average \Delta E = \left(\frac{Energy_{lithiation}}{Capacity_{lithiation}} \right) - \left(\frac{Energy_{delithiation}}{Capacity_{delithiation}} \right) \quad (4.2)$$

In this equation, lithiation\delithiation energy and respective capacity are obtained from battery testing software after galvanostatic cycling directly. Figure 11 below shows the first 10 cycle of ΔE value for Mg modified hematite nanorod.

Figure 4.22. First 10 cycles of ΔE value for Mg modified hematite nanorod.

It could be observed that except for 1% Mg added sample, a clear decreasing trend is observed for all other samples along with increasing Mg adding level. Such result is in good agreement from previous cycling and rate data, where a better

electrochemical performance is presented for higher Mg adding level. A detailed discussion will be present in next sections.

4.2.3 TI MODIFIED HEMATITE NANOROD

4.2.3.1 MATERIAL CHARACTERIZATION

Like Mg modification, Ti modified samples are also synthesized in different concentrations to study the potential effect on electrochemical performance.

XRD pattern for Ti modified samples are shown in figure 4.23 below. Samples from 3% Ti onwards were annealed in air at 400 degrees for 3 hours to obtain pure phase hematite structure. The lattice parameter is obtained from Rietveld refinement, as shown in table 4.7 below. A gradual decrease of the lattice parameter a from 5.030 to 5.025 Å is found with increased Ti modification level of 0 to 10%. A similar trend is shown for the lattice parameter c that decrease from 13.756 to 13.734 Å within the test series of 0 to 10% Ti modification. This is possibly due to the iron vacancies in hematite lattice. Ti^{4+} ions have very similar ionic radii compared to Fe^{3+} (75 pm for Ti^{4+} and 78.5 pm for Fe^{3+} [135]), Ti^{4+} carries more positive charge compared to Fe^{3+} . To keep the charge balance, it is very possible that some of the Fe^{3+} sites become vacancies for compensation.

Figure 4.23. XRD pattern for different Ti modification levels and DIP as SCA

Elemental study is also carried out by XRF for Ti modified series, as shown in figure 4.24 below. It could be observed that the real Ti content increases as more Ti source is applied. A close to linear relationship is obtained when cell volume is plotted with obtained real Ti content, which confirms Ti ions are successfully entered hematite lattice.

Table 4.7: Lattice parameters from Rietveld refinement of XRD data and XRF data for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Mg modification level of 0 to 10%.

Ti modification level (%)	a (Å)	c (Å)	Cell volume (Å ³)	R_{Bragg} value (%)	Calculated atomic ratio (Ti:Fe)
0	5.030(2)	13.744(5)	301.2	4.739	
1	5.030(9)	13.756(3)	301.5	5.558	0.52:100
3	5.031(0)	13.749(6)	301.4	5.579	1.6:100
5	5.028(3)	13.747(7)	301.0	5.819	2.9:100
7	5.026(1)	13.738(5)	300.6	3.023	5.2:100
10	5.025(7)	13.734(2)	300.4	5.445	7.5:100

Figure 4.24: Change cell volume against real Ti content for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Ti modification level of 0 to 10%.

FESEM technic is applied to examine the morphology of Ti modified sample, a dramatic morphology change depending on the Ti amount is observed (figure 4.25). 1% Ti modification level leads to nanowire morphology with rod length over 500 nm. At 3% of Ti precursor in the reaction mixture leads to nanorods with a length that is comparable to unmodified hematite nanorods obtained from diamine-assisted hydrothermal synthesis indicating that further addition of Ti seems to lead back to a nanorod morphology. With 5% Ti precursor addition, the morphology almost remains unchanged from 3%. Further increase to 7% and 10% of Ti precursor addition leads to additional long and rigid rods in the micrometer range. From these observations it is noticed that Ti addition may enhanced the shape controlling ability of the diamines under low concentrations. When the Ti concentration is further increased, it may be leading to distortion of nano-structure formation, and lead to a micro-sized second morphology.

Figure 4.25. FESEM image for different Ti modification levels and DIP as SCA

Like Mg modified samples, UV-vis measurements were applied for Ti modified samples to study the band gap shift. The same calculation was also applied to estimate band gap from measured reflection spectrum of material. Figure 4.26 below shows the obtained Tauc plot for Ti modified samples.

Figure 4.26: Tauc Mott plot of UV–Vis spectra (direct transition) for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Ti modification levels of 0 to 10%.

The estimated band gap is shown in table 16 below. It could be observed that a clear decreasing trend is observed. The estimated band gap decreases from 2.131 eV for unmodified to 2.050 eV for 10% Ti addition level. It could also be noted that compare to Mg modified samples, Ti modified sample has a relatively smaller decrement. Thus, electrochemical tests were applied to test the effectiveness of Ti modified samples.

Table 4.8: Estimated band gap for iron oxide nanoparticles obtained from DIP-assisted synthesis approaches with Ti modification levels of 0 to 10%.

	Unmodified	1% Ti	3% Ti	5% Ti	7% Ti	10% Ti
Estimated band gap (eV)	2.131	2.125	2.086	2.083	2.084	2.050

4.2.3.2 ELECTROCHEMICAL PERFORMANCE TEST

Like Mg modification series, electrochemical performance test for Ti modified samples were also carried out. Figure 4.27 below shows the cycling and rate capability test from Ti modified sample.

Figure 30. a) CV, b) galvanostatic curve, c) cycling test, b) rate test and e) ΔE value for Ti modified samples with DIP as SCA

From CV and galvanostatic curve in figure 4.27a and 4.27b, similar 3 step reactions are observed for 1st lithiation, as a typical process for hematite. Lithium intercalated products $\text{Li}_x\text{Fe}_2\text{O}_3$ and cubic $\text{Li}_2\text{Fe}_2\text{O}_3$ forms at voltage around 1.5 V and 1.1 V respectively, followed by a reducing reaction to form metallic iron and Li_2O [133].

For the cycling performance shown in figure 4.27c, the stability for 1% Ti added sample is found to be better than both, unmodified and 3% modified sample, which could be explained by the morphology effect. At around 1%, a nanowire morphology is obtained, which is different from either unmodified or 3% added sample. Thus, morphology is the dominating factor of the cycling stability of the 1% Ti added sample. For 3% and 5% Ti added sample, the cycling stability is similar, suggesting Ti modification is not affecting the cycling stability on this level. Further increase of the Ti addition level to 7% and 10% lead to a clear cycling stability enhancement, the discharge capacity at 50th cycle increases from 185 mAh g⁻¹ for the unmodified to 476 mAh g⁻¹ and 548 mAh g⁻¹ for 7% and 10% Ti added sample, respectively. Although a second morphology of large micro-sized rigid rod starts to form at 7%, the dominating effect for such enhancement is believed to come from the modification effect, as only minor large sized rods are present at 7% modification level.

For the rate capability test in figure 4.27d, an obvious increase in capacity with increasing Ti concentration in the system is observed, especially at high C region. At current density of 3 C, the charge capacity increases from 109 mAh g⁻¹ for the unmodified to 370 mAh g⁻¹ for 10% Ti added sample.

It is interesting to note that for 3% and 5% Ti added sample, although the cycling stability is similar compared to unmodified sample, a notable enhancement of capacity in the high C region is observed in the rate test. Such observation confirms that modification might affect the reaction kinetic of the material, which is more critical at high C region where less reaction time is present to overcome polarization.

Such analysis could be further indicated by the fact that the Ti modified hematite has a lower ΔE value, which could be observed in figure 4.27e. Unmodified sample shows an increase ΔE value, which reaches 0.9 V after 10 cycles. For Ti modified samples, the ΔE value keeps in the range of 0.8 V to 0.85 V, and no increment is observed for most of the samples. It is also noticeable that unlike Mg modified samples, a general decreasing trend is not observed among different Ti concentrations.

4.3 HEMATITE MICROSPHERE SYNTHESIS

4.3.1 MATERIAL CHARACTERIZATIONS

As described in the experimental section, further synthesis of hematite was tested as comparing group without SCA content. 8 ml of 6 M NaOH is added as basic agent to precipitate iron ions in standard procedure (refer as original in the graph). Then comparison is done by varying NaOH amount to study the potential effect of such behavior. Figure 4.28 below shows the XRD pattern from samples synthesized with different NaOH amount. Pure hematite (standard JCPDS card no. 330664) is observed for all the tested samples with good crystallinity

Figure 4.28. XRD pattern for iron oxide synthesized with different NaOH amount.

Further comparison is also applied by varying the precursor chemicals from NaOH to KOH or from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, while other synthesis parameters were kept constant with original sample. The XRD pattern in figure 4.29 below listed the comparison of different samples. Pure hematite (standard JCPDS card no. 330664) is again observed for all the tested samples with good crystallinity.

Figure 4.29. XRD pattern from different precursors.

Rietveld refinement was also applied for all the tested samples, and respective lattice parameters are summarized in table 4.9 below. The lattice parameters are found in the range of 5.030 Å to 5.032 Å for a, while 13.747 Å to 13.753 Å for c. Both values are very close from each sample, which is completely expected as no induced change in lattice parameter such as modification has been introduced.

Table 4.9. Lattice parameters obtained from Rietveld refinement for iron oxide synthesized with different NaOH amount.

Sample	a(Å)	c(Å)	Cell volume(Å ³)
8ml NaOH(original)	5.032(3)	13.753(5)	301.6
4ml NaOH	5.030(2)	13.749(7)	301.2
12ml NaOH	5.031(1)	13.747(8)	301.2
18ml NaOH	5.031(3)	13.749(6)	301.2
With iron nitrate	5.031(7)	13.753(2)	301.4
With KOH	5.030(6)	13.749(4)	301.3

FESEM images of above samples are also taken to study the morphology change, as shown figure 4.30 below.

Figure 4.30. FESEM image for hematite with different NaOH amount.

From the above data, it could be observed that when 8 ml NaOH (refer as original) is applied, a microparticle with surface porosity will be obtained. For less NaOH amount, similar particle with egg-like shape is present, while for 12 ml and 18 ml NaOH level, chunky-like particles in the size range of 300 nm is present.

Figure 4.31 below shows the FESEM image for hematite particles made from different precursor types. Nanoparticles with diameter around 100nm is formed instead of micro-particles when precursors change to KOH or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Thus, it could be concluded that both Cl^- and Na^+ ion is found to be crucial in the formation of micro-sized particle. While when either NaOH or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were replaced by KOH or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, nanoparticles will be present instead.

Figure 4.31. FESEM image hematite particle using different precursors.

In conclusion, 3 different morphologies could be obtained from this comparing group, depending on the amount of NaOH solution applied and type of precursors.

4.3.2 ELECTROCHEMICAL PERFORMANCE

Electrochemical test is also carried out for all the samples with different morphology, to study the morphology change trend and their influence on electronic performance of iron oxide as anode material of lithium ion battery. Figure 35 shows the comparison study of microparticle and nanoparticle synthesized in above procedures.

Figure 4.32. a) galvanostatic b) cycling and c) rate test for different iron precursors

From figure 4.32a, it can be observed that on the 1st cycle, all the samples show a long plateau at around 0.8 V for the lithiation process, while only the original sample (micro-particle) shows a much less intercalation section sloping around 1.5 V or 1.1 V compared to other 2 samples, which is in good agreement with the previous literature [48] that nano-sized particles would have a more pronounced intercalation process on 1st delithiation process.

For the cycling performance as shown in figure 4.32b, up to 50 cycles, no observable decay is present for micro-particle sample (original) after stabilized around 10th cycle. A lithiation capacity of 775 mAh g^{-1} is obtained for the sample after 50 cycles. For the other 2 nanoparticle samples, although the capacity in initial cycles is higher than that of micro-size particle, the cells died off quickly from 20 cycles onwards. This strongly indicates that such micro-sized particles

with surface texture is a superior morphology for lithium storage capability compared to nano-particles.

In the rate capability test in figure 4.32c, the original sample retains a capacity of 438 mAh g⁻¹ at 3 C, which greatly outperform the other 2 nanoparticle samples, indicating an extraordinary high rate capability from this morphology also.

Further electrochemical study is carried out for different NaOH adding amount, as shown in figure 4.33 below.

Figure 4.33. a) cycling and b) rate test for different NaOH amount

From the above data, both cycling and rate capability for all the tested samples are similar. A stable cycling stability and a satisfactory rate performance (above 400 mAh g⁻¹ at current density of 3 C) is obtained. Such results are expected for 4ml and 8ml NaOH added sample, as they both show a similar micro-size particle with surface texture, which has already proven to be a superior morphology. However, the good performance of 12 ml and 18ml NaOH addition is unexpected judged from their unfavorable morphology as shown in figure 4.29 in FESEM section.

In conclusion, micro sized particles with surface texture are found to have superior property in cycling stability and high rate performance compared to nanoparticles, but irregular chunk-like particles have also shown such superior performance. Such behavior is suggesting that morphology may not be the dominating factors to affect the electrochemical performance in these experiments.

4.4 HEMATITE MODIFICATION IN MICROSPHERES AND CHUNK-LIKE PARTICLE

4.4.1 TI MODIFICATION ON HEMATITE MICROSPHERE

4.4.1.1 MATERIAL CHARACTERIZATIONS

Ti is also applied on microspheres to examine the potential effect.

Figure 4.34 shows the XRD pattern of Ti modified sample with NaOH_(aq) to control pH. Pure hematite (standard JCPDS card no. 330664) with good crystallinity was obtained for all the samples, no impurities were found. The lattice parameters and cell volumes were also obtained through Rietveld refinement, and a very possible small decreasing trend of the lattice parameter *a* is observed, with increasing Ti addition level, which confirms that Ti ion is incorporated into hematite lattice, as shown in table 4.10.

Figure 4.34. XRD pattern for different Ti modified hematite assisted by NaOH

Table 4.10. Lattice parameters obtained from Rietveld refinement for different Ti modified hematite assisted by NaOH.

Sample	a(Å)	c(Å)	Cell volume(Å ³)
Unmodified	5.032(5)	13.753(3)	301.6
1% Ti	5.030(3)	13.750(1)	301.4
3% Ti	5.029(2)	13.751(4)	301.2
5% Ti	5.028(8)	13.751(2)	301.1
7% Ti	5.027(6)	13.751(5)	301.0
10% Ti	5.026(7)	13.741(9)	300.6

Further confirmation is carried out by EDX, as shown in figure 4.35 and table 4.11 below. It could be confirmed that Ti is present in the system, while the estimated content is increased gradually from 1.0% to 8.5% for 1% Ti adding until 10% Ti addition.

Figure 4.35. EDX pattern for different Ti modified hematite assisted by NaOH.

Table 4.11. Ti composition measured by EDX in Ti modified hematite assisted by NaOH.

	1% Ti adding	3% Ti adding	5% Ti adding	7% Ti adding	10% Ti adding
Estimated Ti amount by EDX	1.0%	3.7%	4.9%	6.0%	8.5%

Figure 4.36 below shows the FESEM image for Ti added sample without the addition of any SCA, but only NaOH solution to precipitate Fe^{3+} ions. Particles with diameter around $1\mu\text{m}$ could be obtained when no Ti content is added. Some surface texture could also be observed from FESEM images. When Ti content is added in the system, the particles are found to expand in size until 3% of Ti addition, further increase to 5% and 7% Ti adding level leads to more distortion of the particles. With 10% of Ti adding level, irregular particles with diameter around

300 nm are obtained. Thus, it could be concluded that the micro-sized particle is generally retained with some level of expanding and distortion up to 7% of Ti addition. Thus, electrochemical performance test is applied for Ti modified samples until 7% Ti addition to exclude the effect of morphology change.

Figure 4.36. FESEM image for different Ti modified hematite assisted by NaOH.

4.4.1.2 ELECTROCHEMICAL PERFORMANCE

Ti modified sample with NaOH is then tested for their electrochemical performance, as shown in figure 4.37 below.

Figure 4.37. a) galvanostatic b) cycling c) rate test and d) ΔE value for Ti modified hematite assisted by NaOH.

From figure 4.37a, it can be observed that on the 1st cycle, the Ti modified samples show a long plateau at around 0.8 V for the lithiation process, while much less intercalation sloping around 1.5 V or 1.1 V can be observed, which is in good agreement with the previous literature [48].

For the cycling performance as shown in figure 4.37b, up to 50 cycles, no observable decay is present for all the samples, including the unmodified sample. A lithiation capacity of 775 mAh g⁻¹ is obtained for the unmodified sample after 50 cycles.

In the rate capability test in figure 4.37c, the unmodified sample retain a capacity of 438 mAh g^{-1} at 3 C, which is 4 times of the value for unmodified nanorods (109 mAh g^{-1}), indicating an extraordinary high rate capability from this morphology also. Ti added samples show similar trend, but lower capacity ($\sim 330 \text{ mAh g}^{-1}$ to 380 mAh g^{-1} at 3 C), the mechanism for this phenomenon would be expected to be similar to the behavior on cycling performance test.

The average reaction potential for both lithiation and delithiation process in the first 10 cycles are calculated and plotted in figure 4.36d. It could be observed that the ΔE is significantly decreased with up to 3% Ti adding level for the first 10 cycles. The ΔE value decreases from 0.8V for unmodified sample to 0.74V for 7% Ti added sample at the 10th cycle.

In conclusion, micro sized particles with surface texture are found to have superior property in cycling stability and high rate performance without Ti modification. With Ti addition, the reversibility (ΔE) is found to be improved, but no observable enhancement on cycling and rate performance in Ti modification with this procedure is found. Further discussion will be carried out when more data are collected, including longer cycling stability and repeating of the present data.

4.4.2 MG MODIFICATION ON CHUNKY-LIKE HEMATITE

4.4.2.1 MATERIAL CHARACTERIZATIONS

Figure 4.38 shows the XRD pattern obtained for samples with 4 ml NaOH as pH monitor. Both Mg contained, and non-contained sample have shown a pure and well-crystalline phase of hematite (standard JCPDS card no. 330664).

Figure 4.38. XRD pattern for hematite with 10% Mg adding levels synthesized with 4ml NaOH

Table 4.12. Lattice parameters obtained from Rietveld refinement of XRD data for hematite with 10% Mg adding levels with 4ml NaOH

Sample	a(Å)	c(Å)	Cell volume(Å ³)
4ml NaOH	5.030(2)	13.749(7)	301.2
4ml NaOH with Mg	5.029(5)	13.746(4)	301.2

The lattice parameter is found to almost consistent for both samples. Such observation provides a strong indication that Mg content is not present in the system.

To further confirm the Mg content, EDX Spectron is carried out to semi-quantitatively examine the elemental content in the sample.

Table 4.13. Mg composition measured by EDX in hematite with 10% Mg addition

Element	Weight%	Atomic%
O K	31.77	61.91
Mg K	0.01	0.01
Fe K	68.22	38.08
Totals	100.00	100.00

*Please note the 0.01 is the limit of instrument, so the weight and atomic % of Mg is not an accurate number.

The reflection from Mg is negligible from the data, which confirms the conclusion that Mg is not in the system for this approach.

Figure 4.39 shows XRD pattern from Mg modified sample synthesized with addition of 12 ml NaOH (N12Mg1, N12Mg5 and N12Mg10).

Figure4.39. XRD pattern for hematite with different Mg adding levels synthesized with 12ml NaOH

It could be observed that pure hematite (standard JCPDS card no. 330664) with good crystallinity was obtained for until 5% Mg addition level, when 10% of Mg is

added into the system, a 2nd phase of Mg(OH)₂ is observed (standard JCPDS card no. 0070239), suggesting an over-saturation of Mg in the system. The lattice parameters and cell volumes were also obtained through Rietveld refinement. The lattice parameter is found to be increasing, when comparing with 1% and 5% Mg content added, 10% Mg modified sample has shown similar lattice parameter compared to 5%, which is in good agreement of XRD pattern, since at higher Mg addition level, the extra Mg ions are forming Mg(OH)₂ phase instead of incorporated into hematite lattice.

Table 4.14. Lattice parameters obtained from Rietveld refinement of XRD data for hematite with different Mg adding levels synthesized with 12ml NaOH

Sample	a(Å)	c(Å)	Cell volume(Å ³)
Unmodified	5.031(4)	13.747(6)	301.3
1% Mg	5.032(9)	13.748(4)	301.4
5% Mg	5.043(1)	13.769(3)	303.2
10% Mg	5.042(5)	13.765(8)	303.0

FESEM in the secondary electron imaging mode was applied to examine the morphology of the Mg modified products, as shown in figure 4.40. Only samples synthesized with addition of 12 ml NaOH were present, as based on previous analysis, only this series contained Mg content in the system.

Figure 4.40. FESEM image for hematite with different Mg modification levels synthesized with 12 ml NaOH.

It could be observed that the chunky-like morphology is gradually transformed into cube-like morphology, which is in consistency with previous report that Mg ion in hematite in this system tend to transfer into a cube-like morphology. But the overall morphology remains similar for all the samples. Thus. Mg modified sample up to 5% is then tested for electrochemical performance test to justify the effectiveness of Mg modification.

4.4.2.2 ELECTROCHEMICAL PERFORMANCES

The electrochemical performance test is carried out for different Mg modified samples synthesized with addition of 12 ml NaOH. Figure 4.41a below shows the 1st and 2nd cycle of galvanostatic curve for Mg modified samples.

Figure 4.41. a) galvanostatic curve, b) cycling, c) rate and d) ΔE value for hematite with Mg modified sample synthesized with 12 ml NaOH

Similar lithiation process is observed compare to unmodified samples, suggesting a consistent reaction mechanism. Mg ions is supposed to be inert during reaction, as formation of metallic Mg is not thermal dynamically favored.

Figure 4.41b indicates that the cycling stability for Mg modified sample remain unchanged up to 50 cycles. Reversible capacity around 700 mAh g^{-1} after 50 cycles at current density of 0.1 C is obtained for all the tested samples, no observable enhancement of decay is present for both Mg modified samples.

Capacity retaining ability under gradual increasing current density is studied using rate test. Figure 4.41c shows the delithiation capacity of samples with different modification levels under different delithiation current densities. All the samples show a similar delithiation capacity. No improvement is observed along with Mg modification.

Further analysis on ΔE value is investigated as shown in figure 4.41d. It is noticed that for 5% Mg adding level, an obvious decay in first 10 cycle ΔE value is observed compared to other 2 samples, suggesting an enhanced reaction kinetic compared to unmodified and 1% Mg added sample. Such result is in good agreement with previous data in Mg modified nanorod samples.

4.5 LITHIUM ADDITION

4.5.1 COATING OF HEMATITE WITH LITHIUM OXALATE

4.5.1.1 MATERIAL CHARACTERIZATIONS

For coating strategy in lithium addition approach, XRD is applied to examine the presence of lithium oxalate, which is the target coating material in this strategy. Figure 4.42 shows the obtained XRD pattern.

Figure 4.42. XRD pattern for lithium oxalate contained hematite.

From above data, it could be observed that in both samples, lithium oxalate (JCPDS card no. 0173166) is present in the system. Further analysis and evaluation is presented in the subsequent sections about this strategy.

Figure 4.43 below shows the FESEM image for lithium oxalate coated hematite particles.

Figure 4.43. FESEM image of lithium oxalate coated hematite particle.

From the above image, it could be firstly noted that micro-size iron oxide particles are clearly retained in this procedure, and no 2nd morphology is observed in C1, while some small particles are also observed in C2, which could very possibly be lithium oxalate phase. This, it could be concluded that no separate lithium oxalate phase could be recognized in C1, but in C2, a 2nd morphology implies the presence lithium oxalate aggregates. Such observation is in good agreement of experimental setups. As in C2, the amount of lithium oxalate presented is much more than that of in C1, thus, the excess lithium oxalate might form aggregates when coating is saturated.

4.5.1.2 ELECTROCHEMICAL PERFORMANCE

No incensement in 1st cycle efficiency is observed as shown also in repeated data in table 24. It is found that all samples, including the original uncoated hematite microsphere, generate similar 1st cycle efficiency around 70%. Thus, this coating strategy is considered unsuccessful and no further investigation is implemented.

Table 4.15 Lithiation\delithiation capacity for repeated cell for C1 and C2.

	Cell 1			Cell 2			Cell 3		
	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency
Uncoated	1013.061	716.197	70.7%	1150.490	841.336	73.1%	1114.155	806.120	72.4%
C1	1062.331	757.988	71.4%	1117.161	819.199	73.3%	1137.271	812.500	71.4%
C2	937.425	663.864	70.8%	953.054	668.046	70.9%	872.298	653.806	74.9%

4.5.2 TWO-STEP SYNTHESIS OF LITHIUM INCORPORATED IRON OXIDE

4.5.2.1 MATERIAL CHARACTERIZATIONS

Figure 4.44 below shows the XRD pattern for L1Ar and L2Ar. In general, magnetite (JCPDS card no. 0190629) is obtained for both samples, while a 2nd phase of Li₅Fe₅O₈ (JCPDS card no. 0400943) is presented for L1Ar.

Figure 4.44. XRD pattern for two-step synthesized lithium incorporated iron oxide.

Such results meet with the expectation as L2Ar is the comparing group with no lithium content present. It also suggested that through this two-step strategy,

lithium containing iron oxide phase with partially Fe^{2+} could be successfully synthesized.

Figure 4.45 below shows the FESEM image obtained from two-step synthesis procedure.

Figure 4.45. FESEM image of a) lithium incorporated iron oxide (L1Ar) and b) comparison sample (L2Ar).

From above image, it could be noticed that both samples are composed of nano-sized primary particles with diameter around 30-50nm. For sample L1Ar, the primary particles do not form a clear secondary morphology, while for sample L2Ar, micro-meter sized spherical morphology is observed as secondary morphology. Such morphology difference presents another variable when comparing electrochemical performance of L1Ar and L2Ar, which is not favored for a systematic comparison.

4.5.2.2 ELECTROCHEMICAL PERFORMANCE

The electrochemical performance for L1Ar and L2Ar is investigated to study the potential benefit from pre-lithiation. Figure 4.46 below shows the corresponding electrochemical data from L1Ar and L2Ar.

It is noted that the lithium containing sample (L1Ar) suffers from a dramatical capacity decay after 30 cycles under current density of 0.1C, which is seen in

previous literature of iron oxide, and explained as contact loss of pulverized iron oxide particle under effect of continuous irreversible SEI formation. [143]

L2Ar, has shown a stable cycling capacity of around 800 mAh g⁻¹ after 50 cycles under same current density. The high rate response for L2Ar is also slightly better than L1Ar, which is around 530mAh g⁻¹ and 460mAh g⁻¹ respectively at current density of 3C. This is very possibly due to the morphology difference, as L2Ar forms a secondary microsphere particle, which shows effectiveness on structure retaining abilities.

Figure 4.46. a) Cycling and b) rate test for two-step synthesized lithium incorporated iron oxide.

However, L1Ar shows an improved 1st cycle efficiency of around 81% compared to around 72% for L2Ar, evidenced by the repeated cell data from table 4.16 below.

Table 4.16 Lithiation\delithiation capacity for repeated cell for L1Ar and L2Ar.

	Cell 1			Cell 2			Cell 3		
	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency
L1Ar	1109.059	800.875	72.2%	1143.739	825.193	72.1%	1215.678	893.255	73.5%
L2Ar	1043.020	848.203	81.3%	1124.928	907.886	80.7%	941.673	758.207	80.5%

The above lithium incorporation strategy is proving effective on 1st cycle efficiency improvement. However, the morphology change brings another variable in the comparison, which is not favored as morphology might act as another parameter to affect the result. Thus, a three-step synthesis is proposed to minimize the morphology change as discussed in experimental section (3.1.2.3).

4.5.3 THREE-STEP SYNTHESIS OF LITHIUM INCORPORATED IRON OXIDE

4.5.3.1 MATERIAL CHARACTERIZATIONS

Figure 4.47 below shows the XRD pattern for synthesized iron oxide the the subsequent lithiated product. Magnetite (JCPDS card no. 0190629) is obtained for sample L3, while a 2nd phase of Li₅Fe₅O₈ (JCPDS card no. 0400943) is presented after incorporation of lithium source (L4Ar), as shown in figure 50 below.

Figure 4.47. XRD pattern for three-step synthesized lithium incorporated iron oxide.

Such results meet with the expectation as L3 is the comparing group with no lithium content present. It also suggested that through this two-step strategy, lithium containing iron oxide phase with partially Fe^{2+} could be successfully synthesized.

Figure 4.48 below shows the FESEM image from hydrothermal synthesized magnetite (L3), and subsequent lithiated product (L4Ar) through dispersing and annealing.

Figure . 4.48 FESEM image of hydrothermally synthesized magnetite (L3) and lithium incorporated products (L4Ar).

From above image, it could be observed that nano-sized particles with diameter around 300 nm are successfully obtained for hydrothermally synthesized magnetite.

After lithiation process, the surface roughness is observed to increase (L4Ar), which suggesting that reaction of lithium incorporation happens from the surface of material. Combined with information from XRD analysis that L4Ar is composed of magnetite and $\text{Li}_5\text{Fe}_5\text{O}_8$, it could be concluded that L4Ar may have a “coating” structure, where post-formed $\text{Li}_5\text{Fe}_5\text{O}_8$ is coated on original magnetite particles.

4.5.3.2 Electrochemical performance

Similar electrochemical test is also applied for L3 and L4Ar respectively. As shown in figure 4.49 below.

Figure 4.49. a) Cycling and b) rate test for three-step synthesized lithium incorporated iron oxide.

It is discovered that both sample have generated relatively stable cycling capacity up to 50 cycles. Pure magnetite sample have shown a reversible capacity of around 500 mAh g⁻¹ after 50 cycles under current density of 0.1 C, while for lithiated sample, a reversible capacity of around 800 mAh g⁻¹ under similar condition.

For the rate test in figure 4.49b, the lithiated sample also shows an enhanced capacity of around 550 mAh g⁻¹ at current density of 3 C, compared to around 400 mAh g⁻¹ for pure magnetite under same condition. Such behavior could be attribute to the present of Li₅Fe₅O₈ phase, as this is the only variable in the system. The presence of lithiated phase may act like a passivation layer coated on magnetite, leading to an improved structural retaining ability and more stable SEI formation.

The 1st cycle efficiency is also noted to improved, as shown in the repeated data from table 4.17 below. The 1st cycle efficiency has improved from around 68% for pure magnetite to around 80% for the lithiated product.

Table 4.17 Lithiation\delithiation capacity for repeated cell for L3 and L4Ar.

	Cell 1			Cell 2			Cell 3		
	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency	Lithiation capacity (mAh g ⁻¹)	Delithiation capacity (mAh g ⁻¹)	Efficiency
L3	1064.996	728.025	68.4%	1079.327	740.737	68.6%	1050.362	711.076	67.7%
L4Ar	997.893	789.672	79.1%	961.364	811.145	84.4%	910.556	723.748	79.5%

In conclusion, the above three-step procedure have proven that the 1st cycle efficiency could be improved by incorporating lithium ion into magnetite to form a lithiated phase. Furthermore, such pre-lithiation strategy also helps to improve the long term reversible capacity and high rate response capacity as well.

5. DISCUSSION

5.1 EFFECT OF NANOROD SIZE ON HEMATITE

A two-step transformation process is generally presented in the diamine assisted hydrothermal synthesis procedure of hematite, which could be concluded as $\text{Fe}(\text{OH})_3 \rightarrow \text{FeOOH} \rightarrow \alpha\text{-Fe}_2\text{O}_3$. The $\text{p}K_b$ is decreased in the presence of diamines, which accelerates the conversion of FeOOH to $\alpha\text{-Fe}_2\text{O}_3$. [109] In addition, the crystal growth direction of iron oxide polymorphs like FeOOH , Fe_2O_3 or Fe_3O_4 is controlled by diamines. Among other synthesis parameters (concentration, reaction time, temperature and solvents), [108, 110, 144] the shape controlling ability can be adjusted by substituents located at the reactive diamine unit that affects electronic density (+M effect) and steric interactions, which is found by results of our test series. Diamines are typical chelate ligands that interact with appropriate coordination-centers according to the proposed mechanism illustrated in Figure . First, octahedral shaped complexes are formed, described as $(\text{Fe}[\text{C}_2\text{N}_2\text{R}_1\text{R}_2]_3)^{3+}$ in previous literature. [110] Diamine derivatives, in which the two amine groups are located at adjacent C atoms (vicinal position) are assumed to be supportive, since a thermodynamically favored 5-membered ring could be formed. This might also explain the superior shape controlling ability of DIP over DAB. Besides shape controlling, the complex formation has a second effect: the free iron concentration in solution is reduced, which separates the nucleation from the growth process and supports high quality crystallization. [108]

Figure 5.1: Schematic illustration of the $\alpha\text{-FeOOH}$ nanorod formation process assisted by diamine derivatives as SCA according to literature. [110]

It is expected that during synthesis the complex stability decreases with increasing temperature and pressure, until the Fe^{3+} in complex-formation can be successfully attacked by OH^- . This will result in the gradually loss of diamine ligands leading to complexes with two OH^- groups and two diamines that form a quasi-square-plane perpendicular to the OH^- direction (figure 5.1). The following hydrolysis process is therefore inhibited in planar direction, but favored in normal direction supporting the growth of FeOOH along the $[110]$ direction.[102, 110] The growth direction of $\alpha\text{-Fe}_2\text{O}_3$ is also dictated, since diamines do not only interact with free iron ions in solution, but also coordinate directly to the lattice ferric and the complexes are released into solution.[109] The diamine adsorption capacity of $\alpha\text{-Fe}_2\text{O}_3$ surfaces varies for different indexed crystal facets depending on their loading with singly, doubly, triply or germinal coordinated hydroxyl groups (refers to the number of underlying Fe atoms the hydroxyl groups are coordinated to, Figure).[145]

Figure 5.2: Different hydroxyl groups found on surfaces of iron oxides according to literature.[145]

It is assumed that only singly coordinated hydroxyl groups are involved in the interaction with the diamines. [146] According to Barón et al., singly coordinated hydroxyl groups are located at the $[1\ 0\ 0]$, $[1\ 1\ 0]$, $[0\ 1\ 2]$, $[1\ 0\ 4]$ and $[1\ 1\ 3]$ facets of natural and artificial $\alpha\text{-Fe}_2\text{O}_3$, [147] hence the crystal growth in these direction is minimized, leading to $\alpha\text{-Fe}_2\text{O}_3$ products with small-ranged elongated shapes along the $[0\ 0\ 1]$ direction.

From Result section, it could be concluded that DIP has the most enhanced shape controlling ability, DAB and EDA are at middle, while NMD has shown no such ability in this procedure. The explanation is mainly from 2 factors that affect the shape controlling ability of diamines with side methyl group, namely increased

electron density (+M effect) and steric hindrance. On one hand, the electron-donating side methyl group help to improve the electron density at -NH₂ group, which in turn improve its reactivity. On the other hand, the side methyl group also brings steric hindrance to NH₂ group, which might decrease the chelating activity of diamine molecules. Thus, in the case of DIP, +M effect dominated, which makes it a better SCA compared to the primary molecule (EDA), while products with further addition of methyl group at adjacent C leads to a cancelation effect of both factors, since they are equality dominating. When side methyl group is directly attached on N atom (NMD), the steric hindrance will dominate, leading to a decreased shape controlling ability.

The intermediate sized nanorod have shown superior electrochemical performance compared to nano-sphere particles obtained under similar condition. This can be attributed to the specific 1D-nano-dimensions of the material, which improves the rate of lithium insertion and removal during galvanostatic cycling. The time constant t according to $t = L^2/D$ (L : Diffusion length, D : Diffusion constant), is minimized by the reduced L of nanostructures.[90]

Furthermore, electrochemical performance test has revealed that intermediated sized nanorod is also more preferred for lithium ion battery application, in terms of both cycling stability and high rate performance. Post-cycling analysis is carried out to study such effect.

Figure 5.3 shows FESEM images taken from cells with different morphology after 50 cycles under current density of 0.1C.

Figure 5.3. Post-cycling FESEM images.

It could be noted that only nanorod with intermediated size could still be observed from the image, although sever distortion is present. No rod-like shape could possibly be identified for the longer nanorod (~400 nm and aspect ratio of 5). Such observation could explain the obtained electrochemical performance perfectly. The intermediated nanorod has proven to be better in structural retaining abilities, the volumetric instability could be accommodated by intermediate sized nanorod without pulverize the particle.

Further experiments were carried out to confirm the relationship between electrochemical performance and structural retaining ability.

The intermediate sized nanorod electrode were further cycled until 100 cycles, until sever decay is observed.

Figure 5.4. Cycling performance of intermediate sized nanorod electrode (E1.5) with hematite as active material (active material ratio is 40%)

Then, the coin cell is opened in glove box after 1, 40, and 100 electrochemical cycles at 0.1C, the electrode is rinsed inside glovebox, and then examined with FESEM, to check the preservation of hematite structure, as shown in figure 5.5 below.

Figure 5.5. FESEM of electrode from hematite nanorod as active material (40%)

After 1 cycle, a rod-like morphology can be easily recognized from the electrode. After 40 cycles, nanorod can also be observed (red circles in figure 5.5), although the whole electrode has crumbled. Further increase to 100 cycles leads to total disappearance of the rod-like morphology, which indicates that the rod-like shape is no longer retained from this point. This observation is in good agreement with the cycling data at figure 5.4. After 40 cycles, lithiation capacity is still retained above 1000 mAh g^{-1} , while after 100 cycles, the capacity has drop to $\sim 600 \text{ mAh g}^{-1}$. Such relationship confirms that the structural retaining ability is of great importance for the long-term cycling stability of hematite electrode, which is also in good agreement with previous literature that structural retaining ability is one of the key benefit for special designed nano-structure.[64, 97]

It should be mentioned that capacity profiles for all samples show an increase after a minimum at ~ 25 cycles (figure 4.10a). Especially for the shorter $\alpha\text{-Fe}_2\text{O}_3$

nanorods (~240 nm up to ~280 nm) the capacity even reaches values beyond the theoretical value of 1007 mAh g⁻¹ (based on the classical conversion reaction) over the monitored area. Such additional capacity occurrences and/or capacity raise phenomena in the reversible capacity regime were reported for several iron oxide based electrodes, including porous α -Fe₂O₃ nanorods [57], macroporous α -Fe₂O₃ submicron spheres [148], and 1D hollow α -Fe₂O₃ electrospun nanofibers [149], however its origin remains speculative. Several hypotheses are stated in literature, among others, an interfacial lithium accommodation along with charge separation at phase boundaries proposed by Jamnik and Maier [150]. After conversion of α -Fe₂O₃ resulting in Fe finely dispersed in a Li₂O matrix, additional lithium is supposed to be accommodated on the Li₂O surfaces, whereas the e⁻ are transferred to the metal surface. [151] This mechanism strongly depends on the particle size and becomes significant in the nanometer regime. [150] Further explanations include processes related to interfacial film formations, for instance the possible gradual release of excessive Li⁺, previously captured by an initially inhomogeneous SEI that had sequentially developed and evolved towards a steady state over repetitive charge/discharge. [152]

5.2 ELEMENTAL MODIFICATION ON HEMATITE NANOROD

Ti and Mg modified hematite is the main study focus in this thesis, as they have shown better electrochemical performance in preliminary test. Both element could be confirmed to incorporate into hematite lattice, proven by lattice parameter shift and composition analysis by EDX/XRF. The band gap estimated from UV-vis measurement has suggested that the band gap is shift negatively along with additive element for both Mg and Ti modified sample. It is worth noting that Mg modified samples has related larger band gap deduction effect compared to Ti modification, which is in good agreement with rate test data that Mg is working

more effectively than Ti. Thus, a more detailed study of post-cycling behavior is carried out for Mg modified hematite nanorod to confirm the effectiveness of Mg.

Post-cycling analysis is also carried out to examine the status of Mg during galvanostatic cycling. One of the most important issue is to confirm if Mg is still dispersing in iron oxide. Figure 5.6 below shows the ex-situ XRD measurement of unmodified cells and cell with 5% Mg adding level respectively.

Figure 5.6. XRD pattern of fresh electrode and electrode after 1 cycle.

It could be observed that after 1 galvanostatic cycle, no Fe or Mg related reflection could be identified for both tested electrodes. The presence of $\text{LiOH} \cdot \text{H}_2\text{O}$ is most

likely due to absorption of water during sample preparation and operation process, which take several hours.

In conclusion, the XRD pattern is not conclusive as both Mg and Fe content appears to be amorphous.

Subsequently, TEM EDX mapping is applied to examine the distribution of Mg and Fe, as shown in figure 5.7 below.

Figure 5.7. EDX mapping using TEM of 5% Mg added nanorod after 10 cycles.

It could be observed that Mg and Fe reflections are coincide with each other, although the signal-to-noise ratio is lower for Mg due to the much less content in the system. Mg is evenly dispersed in the remaining nanorod structure, no “Mg rich” spot could be notified. This observation could be a strong proof that Mg is still dispersed in iron oxide, although it is no longer crystalized from XRD pattern. Combine with the fact that ΔE value shows a general deduction trend, suggesting the polarization is improved during lithiation-delithiation process, which could indirectly proof that Mg remain active and contribute to the enhancement of electrochemical performance in Mg modified nanorod case.

The effectiveness of Mg could be attributed to several reasons. Firstly, the crystal ionic radius of Mg^{2+} is larger than the value of Fe^{3+} (1s) is (85nm and 69nm respectively), hence the unit cell volume increased along with Mg modification, which could also be confirmed by previous XRD refinement. Thus, a supportive effect on the Li^+ diffusion might be present [126], [135], [153]. In general, Mg modification of hematite has already be proven to be effective to enhance the conductivity. [154, 155] Hu et al. has also observed a conductivity improvement

from around $10^{-7} \text{ S cm}^{-1}$ to $10^{-4} \text{ S cm}^{-1}$ when 4% Mg is added into Cr_2O_3 . [71] The initial conductivity of Mg modified hematite nanorod also proven to increase from the reduced band gap of as mentioned series (section 4.2.2.1). Although it has been proven that hematite lattice no longer exist after 1st cycle, the benefit in conductivity from Mg modification still remains, supported by the fact the Mg and iron overlapped in iron phase in TEM EDX mapping. It is very possible that Mg is still dispersed in small iron oxide grains, forming a p-type semiconductor, which contribute to the overall conductivity of electrodes.

5.3 ELECTROCHEMICAL PERFORMANCE COMPARISON FROM MICROPARTICLE, NANOPARTICLE AND CHUNKY-LIKE PARTICLE

A superior electrochemical performance has been obtained by hydrothermally synthesized hematite microsphere and chunky-like particle with assistance of NaOH solution. It is controversy that nanospheres synthesized in similar conditions has shown a sever decay in electrochemical performance compared to other 2 samples. The modification of Mg, Ti and Si on those particles have shown a clear improvement in ΔE value of the electrode, but no enhancement on cycling and rate performance could be observed. Such observation strongly indicated that except for morphology aspect, there is another intrinsic factor that dominated the electrochemical performance of hematite as anode material of LIB. This unidentified factor may also have great influence on the effective of elemental modification on hematite as well. To the best of my knowledge, such potential factor still remains unclear in previous literatures. Thus, it is highly recommended to implement further intensive research effort to identify this potential factor.

5.4 LITHIUM ADDITION

Lithium addition experiments have been applied to solve the general problem of low 1st cycle efficiency of TMOs, specifically iron oxide. The idea is to use extra lithium ion in anode side to compensate the lithium ion loss during SEI formation. Various approaches have been taken, and lithium incorporation has successfully proven beneficial to improve 1st cycle efficiency. Magnetite is selected as base material instead of hematite, since iron state in hematite (all 3⁺) is seen as a limitation to achieve compensation effect, as analyzed in section 2.3.3. Thus, the overall reaction process for the first cycle of Li₅Fe₅O₈ is assumed to be as follow:

The excess lithium in iron oxide could be released as free lithium ion on the 1st delithiation process, which could compensate for those lithium ions consumed during the formation of irreversible SEI layer one 1st lithiation cycle. The result of improved 1st cycle efficiency for lithiated products (L4Ar) in section 4.5.3.2 is in good alignment with above illustration, which confirms the effectiveness of such treatment.

6. CONCLUSION

This thesis provided a systematic study on modification strategies of iron oxide. In general, both intrinsic and extrinsic strategies are applied to improve the electrochemical property as anode material of lithium ion battery.

In the first part, the shape controlling effect of various vicinal diamine derivatives including EDA, DIP, DAB, and NMD was systematically studied on hydrothermally synthesized hematite. DIP is found to have the most enhanced shape controlling ability, which leading to a nanorod formation with ~390nm in length and aspect ratios of ~5.0 (1.5M Fe^{3+} concentration). However, electrochemical investigation of hematite nanorods as anode materials in LIBs suggests that intermediate rod lengths in the range of 240 to 280nm show superior electrochemical performance over longer rods and nanospheres with diameter around 150nm. Post cycle analysis has shown that this is majorly due to enhanced structural retaining ability, supported by the fact that intermediate sized nanorod is preserved after 50 cycle, while the longer rod is not. Highest electrochemical performance within the current test series was achieved by the samples synthesized with 1,2-diaminopropane/0.5M Fe^{3+} ($\alpha\text{-Fe}_2\text{O}_3\text{-D0.5}$), resulting in rod length and aspect ratio of ~240 nm/~2.6. Obtained reversible capacities at 0.1C are 1086mAh g^{-1} for $\alpha\text{-Fe}_2\text{O}_3\text{-D0.5}$, at 50 cycles and also at higher current rate of 3C this sample shows very high capacity of 770 mAh g^{-1} , when 40% of active material is used in the electrode.

Further experiment is applied on elemental modification of above mentioned nanorod. Mg and Ti modified samples are found to have potential enhancement on the electrochemical performance. In the case of Mg, nanorod morphology is preserved until 3.7% of Mg in the system (5% Mg adding level). A morphology transformation from nanorod to hollow nanocubes (~200 nm) is observed when further Mg is added in the system. A pure hematite crystal phase could be preserved until the real Mg amount of 6.8% (10% Mg adding level), further Mg intake led to the appearance of a second MgO phase. In the case of Ti, nanorod morphology is

generally preserved until 10% Ti addition level, with the exception at 1% Ti adding level, where an elongated nanowire forms. A 2nd morphology of micro-sized rigid rod is noted starting from 7% Ti adding level. UV-vis measurement is applied to both Mg and Ti modified samples to determine the band gap, a continuous decrease of band gap is observed the higher the Mg and Ti modification level, which is associated with an increased electronic conductivity. Both Mg and Ti materials showed an improved electrochemical performance vs. Li/Li⁺. When 60% active material ratio is used for electrode preparation, samples with 7% Mg exhibit a capacity of 556 mAh g⁻¹ at a current rate of 3C, which is 5 about times higher than for Mg-free hematite. At 10% Mg modification level, a discharge capacity of 650mAh g⁻¹ is obtained after 50 cycles at a current rate of 0.1 C, which is about 3 times higher than for Mg-free hematite. Similarly, 10% Ti modified sample have shown a reversible capacity of 548 mAh g⁻¹ after 50 cycles at 0.1C. A capacity of 370 mAh g⁻¹ is also achieved at current density of 3 C fort 10% Ti modified sample. This improvement is attributed to preservation of enhanced electronic conductivity, evidenced by TEM EDX mapping of Mg added sample after 5 cycles, where Mg is still dispersed in iron oxide, suggesting Mg is still incorporated in amorphous iron oxide to contribute to conductivity.

Comparing synthesis is also carried out with hydrothermal procedures synthesized with NaOH solution in replacement of SCAs. Microsphere and chunky-like morphology with diameter around 400nm could be obtained by varying NaOH concentration. Nanoparticles around 150nm could also be obtained by changing the precursors. A surprising superior electrochemical property is obtained with this procedure for microsphere and chunky-like particles. With electrode composed of 60% active material, the reversible capacity could achieve 775 mAh g⁻¹ after 50 cycles at 0.1C. The capacity at 3 C current density could also achieve 438mAh g⁻¹. It is also noted that incorporation of Mg and Ti in those samples has clearly shown a reduced ΔE value, proving incorporated elements remains active. However, both cycling and rate test has revealed that Mg and Ti does not help to improve the cycling stability and high rate capacity, which is controversy of previous experiments. Thus, combined with the unexpected superior performance from

chunky-like particles, it is highly possible that there is another factor except morphology that is dominating the electrochemical performance of hematite, as discussed in previous section.

Pre-lithiation experiment is also carried out as another extrinsic strategy, which could improve the 1st cycle efficiency. It has been confirmed that by chemically incorporating lithium ion into magnetite to form a new lithiated iron oxide phase, the 1st cycle efficiency could improve from around 68% to 80%, with a positive side effect in improving the cycling and rate capacities. The pre-lithiation strategy stated has proving to be an effective methodology to solving the 1st cycle efficiency problem of iron oxide.

6.1 SCIENTIFIC CONTRIBUTION

- Tuning of morphology of size of hematite nanorod using shape controlling agents.
- Successfully incorporated several of element into hematite nanorod with 1 step hydrothermal synthesis.
- Systematic study of Mg and Ti modified hematite nanorod, and achieved their corresponding optimized electrochemical performance.
- Identified another potential intrinsic parameter that might greatly influence the electrochemical property of hematite.
- Achieved an improvement on 1st cycle efficiency of iron oxide by chemically pre-lithated the material to form a separated lithiated phase.

6.2 TECHNOLOGICAL CONTRIBUTION

- Identified elemental modification as a cost effective way to enhance capacity and reduce voltage gap of iron oxide.
- Discovered coating strategy, which have the potential to solve 1st cycle efficiency of iron oxide.

6.3 FUTURE WORK

6.3.1 ELECTROCHEMICAL PROPERTY OF HEMATITE

As stated a few times in previous sections, the experiment around hematite microsphere and chunky-like particles and their corresponding elemental modification experiment has revealed another unidentified factor that affect the electrochemical performance of hematite. Thus, it is highly recommended to apply further research on this topic. It is suggested to examine intrinsic properties of different hematite such as defects density, oxygen vacancy etc. to identify this factor, which may potentially change current understanding of hematite behavior as anode material of lithium ion battery.

6.3.2 PRE-LITHIATION

In current study, a mixture phase of magnetite and $\text{Li}_5\text{Fe}_5\text{O}_8$ have successfully synthesized, with confirmed positive effect on 1st cycle efficiency enhancement. Thus, it is recommended to have follow up experiment on this topic to have a more detailed study. The potential recommended future research direction could be summarized as follow:

- Synthesis of pure lithiated iron oxide phase such as $\text{Li}_5\text{Fe}_5\text{O}_8$ to determine if it could achieve the highest 1st cycle efficiency.
- Broaden the experiment on other TMO material such as Co_3O_4 , Mn_3O_4 and so on to justify if it is a universal strategy for TMOs on 1st cycle efficiency improvement.

6.3.3 LONGTERM DEVELOPMENT

In general, iron oxide based material still suffers from several limitations before becoming a potential candidate for next generation lithium ion battery anode. In this thesis, a lot of studies were applied on improving the structural stability, conductivity and 1st cycle efficiency. However, it is well understood that further

improvement need to be implemented to enhance on iron oxide so that it could be competitive in real commercial world.

Specifically, from battery cell point of view, a lot of major modifications towards better electrochemical property are still needed to be improved. The proposed property and respective possible solution are shared below:

- Cycle life: For an anode material possible for future industrial application. Cycle life of the material should at least be reaching 500 cycles, and preferably reaching 2000 cycles. The current state is still far from the target. Thus, further improvement should be focused on further improving the volumetric stability and conductivity, such as using carbon composite or further surface modification with mechanical or chemical strategies.
- 1st cycle efficiency: The 1st cycle efficiency of the material is directly linked to energy density of the full battery; thus it is of great importance to bring the 1st cycle efficiency of iron oxide to the similar level of graphite, which could be as high as 93%. In this thesis, pre-lithiation strategies have increased the efficiency ~80%, but the need for further improvement is still needed. Strategies include completed lithiation with $\text{Li}_5\text{Fe}_5\text{O}_8$ as stated in section 6.3.2, further surface treatment with passive layers and introducing additives in the electrolyte for compensation should be considered to reach industrial standard.
- Reaction voltage: Iron oxide has a lithiation voltage around 1.6V, which strongly limited the discharge energy density when implemented in full battery. A lithiation voltage below 1V is strongly preferred for anode material to have competitive energy density compare to graphite. Elemental modification is the main strategy to overcome this limitation. Except for doping, construction of ternary oxides and modification with N atoms are also effective solutions to this issue.

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