STRATEGIES TO IMPROVE THE ELECTROCHEMICAL PERFORMANCE OF ELECTRODES FOR LI-ION BATTERIES

By

MING-CHE YANG

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To my lovely dad and mom
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<td>BET</td>
<td>brunauer, emmett and teller</td>
</tr>
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<td>EDS</td>
<td>energy dispersive spectroscopy</td>
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<tr>
<td>FIB</td>
<td>focus ion beam</td>
</tr>
<tr>
<td>ICP</td>
<td>induced coupled plasma</td>
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<tr>
<td>LEAP</td>
<td>local electrode atom probe</td>
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<td>LIPON</td>
<td>lithium phosphorous oxynitride</td>
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<td>LVSO</td>
<td>Li$_2$O-SiO$_2$-V$_2$O$_5$</td>
</tr>
<tr>
<td>PLD</td>
<td>pulsed laser deposition</td>
</tr>
<tr>
<td>PITT</td>
<td>potentiostatic intermittent titration technique</td>
</tr>
<tr>
<td>PVDF</td>
<td>polyvinylidene fluoride</td>
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<tr>
<td>SAD</td>
<td>select area diffraction</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SPM</td>
<td>scanning probe microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TG-DTA</td>
<td>thermogravimentic differential thermal analysis</td>
</tr>
<tr>
<td>VASP</td>
<td>vienna ab initio simulation package</td>
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<tr>
<td>XANES</td>
<td>x-ray absorption near edge structure</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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<td>XRD</td>
<td>x-ray diffraction pattern</td>
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Lithium-ion batteries are widely used in consumer market because of their lightweight and rechargeable property. However, for the application as power sources of hybrid electric vehicles (HEVs), which need excellent cycling performance, high energy density, high power density, capacity, and low cost, new materials still need to be developed to meet the demands.

In this dissertation work, three different strategies were developed to improve the properties of the electrode of lithium batteries. First, the voltage profile and lithium diffusion barrier of LiM_{1/2}Mn_{3/2}O_4 (M=Ti, V, Cr, Fe, Co, Ni and Cu) were predicted by first principles theory. The computation results suggest that doping with Co or Cu can potentially lower Li diffusion barrier compared with Ni doping. Our experimental research has focused on LiNi_{x}Cu_{y}Mn_{2-x-y}O_4 (0<x<0.5, 0<y<0.5) and we found that the amount of Cu will affect the lattice parameters, the cation disorder in the spinel lattice, the particle morphology, as well as the electrochemical properties. With detailed electrochemical measurements and in situ XAS experiments of LiNi_{0.25}Cu_{0.25}Mn_{1.50}O_4, the proposed explanation of the voltage profile by the first principles computation was
proven, a second plateau at 4.2V originates from the oxidation of Cu$^{2+}$ to Cu$^{3+}$ and the plateau at 4.95V originates from extra electrons provided by oxygen ions. Although the reversible discharge capacity decreases with increasing the Cu amount, optimized composition such as LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ exhibits high capacities at high rates.

Second, titanium dioxide flakes have been synthesized through a simple spreading method that is easily scalable. The calcined titanium dioxide flakes exhibit larger reversible charge/discharge capacity, better rate capability and excellent cycling stability compared to anatase titanium dioxide nanoparticles. The smaller grain size in the flakes most likely enables the formation of the new LiTiO$_2$ phase during the lithiation process attributing to the improved reversible charge/discharge capacity. The larger surface area of the flakes leads to a larger contact area between electrode and electrolyte, shorter diffusion lengths for the transfer of ions and electrons results in the better rate capability. The cycling performance was significantly improved by the porous structure of the calcined titanium dioxide flakes.

Finally, the all-solid state thin film batteries were deposited by pulsed laser deposition method to explore the intrinsic properties of electrode itself. The cathode of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ thin film was fabricated at 300mtorr 600°C on SiO$_2$/Si and show good electrochemical properties. The thin film electrodes offer the ability to probe the surface of the material without the need of a conductive agent and polymer binder, typically used in composite electrodes. The results suggest that neither oxidation of PF$_6$ to POF$_5$ nor the decomposition of ethylene carbonate or dimethylene carbonate occurs on the surface of the spinel material. These results confirm the enhanced cycling stability and rate capability associated with the high voltage spinel material and suggests that the
SEI layer forms due to the extra electrochemically inactive components in the composite electrode.

LVSO ceramic was chosen as the solid electrolyte and deposited by PLD technique. The analysis results show the LVSO thin film exhibit uniform element distribution with exact stoichiometry and amorphous phase that is suitable for the application of all-solid state thin film batteries.

Finally, two different thin films were fabricated as the anodes for all solid state thin film batteries. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ thin film/Au deposited at 700°C shows excellent electrochemical properties but high temperature deposition limits its application because there are differences in thermal expansion coefficients along with inter-layer diffusion during the final layer deposition process. The $\text{TiO}_2$ thin film deposited at 350-450°C show high capacity coupled with excellent cycling performance. The smaller grain size in the thin films most likely enables the formation of the new $\text{LiTiO}_2$ phase during the lithiation process. The porous thin film deposited at 350°C leads to a larger electrode/electrolyte contact area results in the better rate capability. Finally, the all solid state thin film battery with $\text{TiO}_2/\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{L}_{3.4}\text{V}_{0.6}\text{S}_{0.4}\text{O}_4/\text{SiO}_2/\text{Si}$ stack was fabricated successfully only by PLD process.
CHAPTER 1
INTRODUCTION

1.1 Challenges and Motivation

Approximately 68% of today’s electrical energy is supplied from fossil fuels. Recent increases in the demand for oil, associated with the price increases and environmental issues continue to exert pressure on an already stretched world energy infrastructure. Significant efforts have been made in the development of renewable energy technologies such as solar cells, fuel cells and biofuels. Electrochemical energy production is also considered as a different energy source, such as the lithium-ion battery system [1-4]. Lithium-ion batteries are widely used in consumer market because of its light-weight and rechargeable property that is a suitable energy source for the laptop and camera application. Recently, this system also has been considered as the power sources for hybrid electric vehicles (HEVs).

Hybrid Electric Vehicles (HEVs) are a combination of a typical Internal Combustion Engine (ICE) vehicle and a Battery Electric Vehicle (BEV) with an electric motor capable of supplying auxiliary power to the drive train. The combination provides better gas mileage compared to an ICE vehicle. The gasoline consumption of Hybrid Electric Vehicles can diminish about 30% compare to usual vehicle.

Plug-in Hybrid Electric Vehicles (PHEVs)[5] take this concept one step further by adding additional batteries to the design. This allows the vehicle to be charged at night and be powered solely from stored electric energy during the day. By using Plug-in Hybrid Electric Vehicles, the various energy sources can be used. Li-Ion battery has a higher energy density than a Ni Metal hydride system as shown in Figure1-1 that maybe an excellent candidate for the storage system of PHEV. However, for the commercial
application, the battery system need to supply 4000 deep discharge cycles. The 4000 discharge cycles only can reach if the batteries discharge around 50% depth of discharge as shown in Figure 1-2. Moreover, energy density, power density (rate capability), operating voltage, capacity, cost of materials, and safety issues of the lithium ion battery system still limits its commercial application. In this research, three different strategies were developed to improve the electrochemical performance of electrodes for Li-ion batteries.

1.2 Research Objectives

The hypotheses of this study are set as follows.

In order to improve the rate capability of the high voltage spinel material, the electronic, structural and electrochemical properties of LiM_{1/2}Mn_{3/2}O_4 (M=Ti, V, Cr, Fe, Co, Ni and Cu) was predicted by first principles theory first. A series of bi-doped spinel oxides of LiNi_xCu_yMn_{2-x-y}O_4 (0<x<0.5, 0<y<0.5) have been synthesized because of the lower lithium diffusion barrier of LiCu_{1/2}Mn_{3/2}O_4 predicted by first principles theory.

A novel TiO_2 flakes were synthesized by spreading method and the electrochemical performance of electrodes should be improved.

Thin film cathode, anode and solid electrolyte were deposited through pulsed laser deposition and thin film electrodes with high electrochemical performance were developed. All solid state thin film battery was also deposited.

The following specific objectives are set in this dissertation to verify the hypotheses.

The crystal structure, the voltage profile, capacities and the rate capabilities of LiNi_xCu_yMn_{2-x-y}O_4 particles that synthesized by sol-gel method were studies by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray absorption spectroscopy.
(XAS) and electrochemical measurements including potentiostatic intermittent titration technique (PITT) and compare with the computation results.

The crystal structure, surface area, pore size, electronic properties and electrochemical properties are compared for flakes and nanoparticles. Nano size effects of flakes are discussed, including the true size effects, which involve changes of actual materials, including the change of structure and phase stability, electronic band gap and intrinsic diffusivity and the trivial size effects, which effect is largely relied on the surface-to-volume ratio, the shape and the pores of the nanomaterials.

The electrochemical properties and the surface stability after cycling of LiMn$_2$. $x$Ni$_{1-x}$O$_{4.5}$ ($x=0.5, 0.45$) thin film and composite electrodes are compared. The thin film electrodes offer the ability to probe the surface of the material without the need of a conductive agent and polymer binder.

Solid state electrolytes have been also fabricated by PLD.

The influence of deposition conditions on the microstructure, surface morphology and the electrochemical properties of the of TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ thin film electrodes have been investigated.

1.3 Organization of the Dissertation

This dissertation consists of night chapters

In Chapter 1, the problem and motivation of this research is addressed.

Chapter 2 begins with the fundamental aspects of lithium ion batteries, and advances with the criteria for the commercial application. The materials used for lithium ion batteries are also introduced.
Chapter 3 focuses on the theory of sol-gel method, principles of PLD, the setup of the PLD system and the electrochemical measure methods.

In Chapter 4, the electronic, structural and electrochemical properties of \( \text{LiM}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) \( (M=\text{Ti, V, Cr, Fe, Co, Ni and Cu}) \) was predicted by first principles theory. Experimental research has focused on \( \text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4 \) \( (0<x<0.5, 0<y<0.5) \). The crystal structure, the voltage profile, capacities of and the rate capabilities of \( \text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4 \) are studied.

In Chapter 5, the electrochemical properties of \( \text{TiO}_2 \) flakes will be shown and discussed. The origins of the excellent electrochemical of calcined flakes materials will be explored.

Chapter 6, 7, 8 focus on the fabrication of thin film electrodes and solid electrolyte by pulsed laser deposition (PLD).

Chapter 6 begins with the introduction of the capacity fade mechanism of high voltage spinel material. The electrochemical performance and surface features of thin film and composite high voltage spinel \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) are investigated and compared. A new capacity fading mechanism was proposed.

Chapter 7 focuses on the preparation and characterization of the solid electrolyte.

Chapter 8 the achievement in the preparation of the \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) and \( \text{TiO}_2 \) thin film electrodes is shown and the relationship between deposition conditions and the electrochemical properties of the films has been investigated.

The dissertation is summarized in Chapter 9 and the proposed future work is presented.
Figure 1-1. Comparison of the different battery technologies in terms of volumetric and gravimetric energy density[4]

Figure 1-2. Cycle life characteristics of energy storage technologies[5]
CHAPTER 2
BACKGROUND

The purpose of this chapter is to provide readers with essential background knowledge of lithium ion batteries. Hence an overview of the principles of Li-ion batteries and the materials used for Lithium batteries are presented. The chapter begins with the fundamental aspects of Lithium ion batteries, and advances with the criteria for lithium ion batteries for the commercial application. Since this research involved the cathode, solid electrolyte and anodes, the various materials used for different part was also introduced.

2.1 Principles of Li-Ion Batteries

Batteries are systems for electrochemical energy storage and conversion. In batteries, electrical energy is generated by conversion of chemical energy by redox reactions at the anode and cathode. Because the reactions occur at anode usually take place at lower potentials than at the cathode, the terms negative and positive electrodes are used. Batteries are closed systems that energy storage and conversion occur at the same compartment that means the electrodes are not only the charge-transfer medium but also an active element. Various batteries were developed, such as Lead-acid, Ni-Cd, Ni-metal hydride and Lithium ion batteries. Among all batteries systems, Li-Ion batteries can supply higher energy density because Lithium is the most electropositive (-3.04V v. s. standard hydrogen electrode) and lightest metal (M=6.94 g/mole)[4]. An electrochemical cell of batteries is composed of three parts, an anode (negative), a cathode (positive) and an electrolyte. During charge and discharge process, Li ions transfer across an electrolyte between the anode and cathode with oxidation and reduction occurring at the two electrodes as shown in Figure 2-1. The majority of Li-ion
batteries use liquid electrolytes containing a lithium salt, such as LiPF$_6$, LiBF$_4$, LiClO$_4$, LiBC$_4$O$_8$, which dissolves in a mixture of organic alkyl carbonate solvents like ethylene(EC), dimethyl(DMC), diethyl(DEC) and ethylmethyl(EMC) carbonate that has high electronic and ionic conductivity. The two electrodes usually are separated by a porous plastic film (separator) to prevent the contact of electrode.

The Li-ion technologies started with the finding of intercalation compounds, such as Li$_x$MO$_2$ that proposed by Goodenough[6]:

In 1991, Sony commercialize the LiC$_6$/Li$_{1-x}$CoO$_2$[4] cells

The energy storage in the cells can be expressed by following reaction:

Anode: $Li_xC_6 \xrightarrow{\text{discharge}} xLi^+ + xe^- + C_6$  \hspace{1cm} (2-1)

Cathode: $Li_{1-x}CoO_2 + xLi^+ \xrightarrow{\text{discharge}} LiCoO_2$  \hspace{1cm} (2-2)

Cell reaction: $Li_xC_6 + CoO_2 \xrightarrow{\text{discharge}} C_6 + LiCoO_2$  \hspace{1cm} (2-3)

The li-ion cells operate with 3.7 V with a capacity with 150mAh/g.

The basic thermodynamic equations for a reversible electrochemical transformation are given as equation (2-4):

$$\Delta G = -nFE$$  \hspace{1cm} (2-4)

Where n is the number of electrons transferred, F is Faraday constant and E is the voltage of the cell.

so the voltage of a lithium ion cell can be decided by equation (2-5):

$$E = -\frac{\mu^{\text{cathode}} - \mu^{\text{anode}}}{nF}$$  \hspace{1cm} (2-5)
For the commercial Li-ion battery, the materials and reaction of the cell need to satisfy following criteria[2]:

- **Mechanical and Chemical Stability**: the electrode must keep their mechanical properties and their chemical composition, structure and surface over time and temperature in operation environment. Mechanical and chemical stability limitations come from reaction of electrolyte, phase change, corrosion and poor conductivity of materials in the discharge state.

- **High Energy Density**: the voltage of the cell should achieve the maximum amount by selecting the anodes with the high lithium chemical potential or the cathodes with the low lithium chemical potential. Moreover, the electrode material should allow a large amount of lithium to insert and maximize the capacity.

- **High power density**: the electrode should have high electronic conductivity and ionic conductivity in order to support high current density.

- **Temperature range of operation**: the operation temperature of battery is between -50 to 80°C for automotive and military applications. For a general application, the range is between 0°C to 40°C. In the hot summer or cold winter, the performance of batteries will face the challenge. The organic electrolyte and interface formed at interface limited the performance of battery operated at extreme condition.

- **Shape of the discharge curve**: for operation of an electronic device, a flat voltage plateau is necessary. A sloping curve is preferred for applications when determining the state of charge is important. The shape of curve is determined by the one(slopping) or two-phase reactions (plateau).

- **Cost**: the cost of battery is determined by the materials used and the manufacturing and assembling process. The cheaper Fe, Ni and Mn materials are preferred to replace the Co based material with high price.

- **Safety**: all consumer and commercial batteries must be safe in the normal operating environment or the mild abuse conditions. The battery should not leak, vent hazardous materials or explode.

- **Cycle life**: for the commercial application, the battery system need to supply 4000 deep discharge cycles. This requires a very robust system and reversible electrode reactions. There should be minimal side reactions and structure transformation during the charge/discharge process.

### 2.2 Materials of Cathode Electrodes

Li intercalation compounds are ideal electrode that can accommodate lithium over large concentration ranges. Good cathode electrode should have low lithium
diffusion barrier, high electronic conductivity, low lithium chemical potential, high capacity, good structure stability that can prevent significant structural change after charge/discharge process. The lithium transition metal oxides own above advantages that are widely used in Li-ion Battery field [3]

2.2.1 Layered LiCoO\textsubscript{2}

Layered lithium transition metal oxides: LiMO\textsubscript{2}(M=Co,Ni or Mn) are intercalation compounds that have been widely studies as cathodes for lithium ion batteries. LiCoO\textsubscript{2} [6]has the NaFeO\textsubscript{2} structure with the oxygen in cubic closed-packed arrangement. A typical layered structure of transition metal oxides can be expressed as Figure 2-2. The lithium and cobalt ions occupy octahedral sites in alternating layer. On complete removal of the lithium, the oxygen layers rearrange themselves to give hexagonal close packing of the oxygen in CoO\textsubscript{2}[7]. The theoretical capacity of LiCoO\textsubscript{2} is 272mAh/g but several phase transition happen when the cell is charged above 4.2V which are accompanied significant structure change[7, 8]. For the commercial application, the capacity of LiCoO\textsubscript{2} is 140mAh/g when cell charge to 4.2V that only extract about 0.5 mole lithium. Although the LiCoO\textsubscript{2} cathode dominates the rechargeable lithium battery market now, there is a limited of cobalt. The high price of the cobalt and safety issue make the material only can be used for small cells. For application of the large scale, such as plug-in hybrid car, an alternative cathode development is necessary.

2.2.2 Spinel LiMn\textsubscript{2}O\textsubscript{4}

Thackeray et al[9] proposed the spinel cathode LiMn\textsubscript{2}O\textsubscript{4} first and the materials has been extensively developed by Bellcore[10, 11] labs. LiMn\textsubscript{2}O\textsubscript{4} adopt the spinel structure with space group Fd3-m as shown in Figure 2-3. The edge-shaped octahedral Mn\textsubscript{2}O\textsubscript{4} structure supply the stability and possesses a series of intersecting tunnels,
formed by the face-sharing of tetrahedral lithium (8a) sites and empty octahedral (16c) sites, When Li ions diffuse in this structure, it first moves from 8a site to the neighboring 16c site, and then to the next 8a site in such a way that enables three dimensional lithium diffusion.

The discharge of LiMn$_2$O$_4$ proceeds in two steps, one around 4V and one around 3V. To avoid Jahn-Teller distortion, only the 4V plateau was used with a capacity about 120mAh/g. However, LiMn$_2$O$_4$ tends to exhibit capacity fade even in the 4V region, particularly at elevated temperatures. Factors such as Mn dissolution[12] into the electrolyte and the development of micro-strains[13] during cycling have been suggested to be the main sources of capacity fading. The poor cycling performance could be improved by partial substitution of Mn with other metals, an approach of making the LiM$_x$Mn$_{2-x}$O$_4$ (M = Co, Mg, Cr, Ni, Fe, Al, Ti, Cu, Zn etc.) electrode material[14-16]. It has been found that a higher voltage plateau (> 4V) accompanies some transition metal doping.

**2.2.3 Olivine LiFePO$_4$**

In 1997, Padhi et al[17] discover the excellent electrochemical properties of the olivine phase. This is the first cathode material with low, abundant amount and also environment friendly. The crystal structure of LiFePO$_4$ composed of LiO$_6$ and FeO$_6$ octahedral and PO$_4$ tetrahedral as described in the space group Pmna with the orthorhombic unit cell. LiO$_6$ octahedral share edges in order to form LiO$_6$ chains running parallel to (111) direction, where the one-dimensional lithium ion mobility in this framework is high as shown in Figure 2-4. The discharge plateau of LiFePO$_4$ is about 3.4V with capacity about 170 mAh/g and owns excellent cycling performance. The low intrinsic electrical conductivity of the material lead the theoretical capacity only can be
achieved at low rate capability[18], or a high temperature[19]. The electrochemical properties of the material can be improved by the carbon coating though enhanced electrical conductivity [20]. Chiang et al[21] get excellent electrochemical behavior when the LiFePO$_4$ doped with different elements, such as niobium, which increased the conductivity by orders of magnitude. Malik et al[22] prove the diffusion constant will increase with the decreasing of particle size for LiFePO$_4$. The existence of defects in the diffusion path blocks the diffusion of the lithium ion in bulk material while smaller particles with small amount defects facilitate the migration of lithium ions. Critical to the use of LiFePO$_4$ is its reactivity and thermal stability[19]. For its charged product, FePO$_4$ will transfer to spinel phase under high pressure.

2.3 Materials of Anode Electrodes

Good anode electrode should have low lithium diffusion barrier, high lithium chemical potential, high electronic conductivity, high capacity, and good structure stability that can prevent significant structural change after charge/discharge process. The graphite was used as anode for lithium battery now because its low cost and the low operation voltage. The formation of LiC$_6$ produces a maximum capacity about 372mAh/g. However, the chemical potential of graphite is closed to 0V versus lithium, which causes serious safety issue. Diverse anodes were developed to solve the problem.

2.3.1 Spinel Li$_4$Ti$_5$O$_{12}$

Spinel Li$_4$Ti$_5$O$_{12}$ has been investigate as a promoting anode material for lithium ion batteries because of the extremely flat discharge and charge plateaus at 1.55V, excellent cyclability, zero strain insertion and stable in moisture environment.
Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ has a defect spinel framework structure (Fd3-m; a=8.36Å). For conventional spinel material, such as LiMn$_2$O$_4$ cathode materials, extra lithium can be intercalated into the spinel LiMn$_2$O$_4$ up to a maximum composition Li$_2$Mn$_2$O$_4$ with the cubic to tetragonal phase transformation. The cubic to tetragonal transition, often referred as Jahn-Teller distortion, is accompanied by 6.5% increase in the unit cell volume, which is too severe for the electrodes to maintain structural reliability during charge/discharge cycling and will result in rapid capacity fading. However, for Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ materials, X-ray diffraction measurements indicate that the lattice dimension did not change during the reaction and capacity fading due to the damage to the matrix material was not observed after 100 cycles. Ohzuku et al proposed a mechanism for this zero-strain material[23].

\[ \text{Li[Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4 + xe^- + xLi^+ \rightarrow +Li_{1+x}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4 \quad (0 < x < 1) \quad (2-6) \]

\[ \text{8(a) 16(d) 32(e) } \quad \text{8(a) 16(c) 16(d) 32(e) } \quad \text{8(a) 16(c) 16(d) 32(e) } \]

\[ \rightarrow Li_2[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4 \quad (2-7) \]

The other advantage of Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ is its higher voltage compared to lithium metal. It could be interesting to shift the voltage window from 0-4V to 1-5V range with some of the high voltage cathode materials (>4.5V).

The zero strain during cycling, stable in moisture environment and flat discharge and charge plateaus at 1.55V make Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ a good anode candidate for thin film battery.
2.3.2 Anatase and Rutile TiO₂

For TiO₂, eight polymorphs are recognized but only three structures were discussed for their electrochemical performance: anatase(I₄₁/amd) as shown in Figure 2-5, rutile(space group P42/mmm) as shown in Figure 2-6, and TiO₂ B(bronze, C2/m). Rutile are recognized as the most thermodynamic stable structure of eight polymorphs but only anatase[24] and TiO₂(B)[25, 26]exhibit theoretical capacity. Due to the safety against overcharging and stable voltage plateau at 1.78V that corresponds to the occurrence of the two phase equilibrium of Lithium-poor (Li₀.₀₁TiO₂) and Lithium-rich (Li₀.₆TiO₂) domains[27], anatase titanium dioxide is a promising negative electrode material. The theoretical capacity of anatase is 168mAh/g that corresponding to insert half amount lithium. However, various nanostructures had also fabricated and the improvement on electrochemical properties has been shown[28, 29]. The smaller grain size in the anatase TiO₂ most likely enables the formation of the new LiTiO₂ phase during the lithiation process attributing to the improved reversible charge/discharge[30]. Similar results were shown in nanosized rutile. Hu et al[31]proved that the capacity can been improved with the decreasing of the particle size. The short diffusion length for both electrons and ions lead to the improved capacity.

2.3.3 Nanoalloys

Lithium metal alloy have the ability to storage large amounts of lithium because it low molecular weight. Such alloys have capacity that exceed than graphite anode, such as Li₄.₄Sn(993 mAh/g)and Li₄.₄Si(4200 mAh/g)[32]. However, the large volume expansion cause cracking and pulverization of the metal particles during the alloy formation inducing the deterioration of the electrode and limit the cycling performance.
There have been many attempts to overcome the problem. First, tin-based, SnO$_x$[33] amorphous oxide was proposed: a irreversible reaction happen as follows[34]:

$$SnO_2 + 4Li \rightarrow Sn+2Li_2O$$  \hspace{1cm} (2-8)

the fine Sn particles were well-dispersed in the Li$_2$O medium. Second, the reversible mechanism was proposed

$$Sn + 4.4Li \leftrightarrow Li_{4.4}Sn$$  \hspace{1cm} (2-9)

The free degree supplied by the Li$_2$O medium provides accommodation of the stresses formed during the alloying process. Nanowire anodes also facilitate the strain relaxation and maintain good electrical connections both maximize the capacity with excellent cycling performance. The Si[36] and Ge[37] nanowires were synthesized by Chan et al with capacity 3000 and 1141mAh/g after twenty cycles. The major properties of the cathodes and anodes used in this research are summarized in Table 2-1 and the voltage profiles of the materials are shown in Figure 2-7.

### 2.4 Solid-State Electrolyte

An proper solid electrolyte material must satisfy following requirements[38]:

- High lithium ionic conductivity of the solid-state electrolyte
- Low electrical conductivity
- No chemical reaction between anode, cathode materials and solid state electrolyte.
- High electrochemical voltage window
- Easily fabricated and high stability.

In order to investigate the electrode/electrolyte interface by TEM ex-situ or in ex-situ, some extra condition must be satisfied.
• Dense structure
• Stable in the electrolyte beam
• Stable in the ion beam (in the cutting process of Focus Ion Beam (FIB))

Solid electrolytes can be divided into sulphide based and oxide based compound, or amorphous and crystalline structure. Although the ionic conductivity of the sulphide glass is higher than oxide glass, the less hygroscopic properties of oxide glass and high stability in moisture make oxide glass get more attention. Moreover, the amorphous electrolyte can supply isotropic lithium transportation path. [39]

. Only limited literatures have been reported for the solid electrolyte films. Recent research has focused on two: Li$_2$O-SiO$_2$-V$_2$O$_5$ (LVSO) and Li$_2$O-P$_2$O$_5$+N$_2$ (LiPON) because of their high ionic conductivity and easily preparation.

2.4.1 LiPON Electrolyte

Bates et al [40] deposited LiPON by Li$_3$PO$_4$ with N$_2$ atmosphere using sputtering system. The Lithium Phosphorus Oxy-Nitride (LiPON) films are widely used in solid-state lithium batteries now because of its low reactivity with lithium metal [41] and the high voltage window make it is possible to use various anode electrode. However, the lower conductivity and unstable under the electron beam and ion beam exposure limit its application. Moreover, the low deposition rate hinder the commercial application if the film fabricated by sputtering. PLD with high energy can deposit the films with high rate [42]. However, rough surface morphology and high fluence 15 J/cm$^2$ requirement, also make it is impossible to fabricate the films by PLD.

2.4.2 LVSO electrolyte

Other candidate is the Lithium Vanadium Silicon Oxide (LVSO) [43]. This compound has relatively higher ionic conductivity and dense morphology. In order to increase the ionic conductivity of solid electrolyte Li$_4$XO$_4$ (X = Si, Ge), γ- tetrahedral
structures such as Li$_3$PO$_4$, Li$_3$AsO$_4$, Li$_3$VO$_4$ and Li$_2$ZnGeO$_4$ (LISICON) were added to Li$_4$XO$_4$ to form a solid solution. The conductivity can be improved by formation of lithium vacancies or interstitials. The conductivity data were shown as following plot (Figure 2-8)[43] with different composition. The experiment result shows 0.4Li$_4$SiO$_4$ - 0.6Li$_3$VO$_4$ has a maximum conductivity. The facile explanation for the increase of the conductivity can be expressed as follows:

The substitution reaction Li$^{+}+$ Si$^{4+}$ ----V$^{5+}$ will induce extra lithium vacancy. The concentration of lithium vacancies is small in Li$_4$SiO$_4$ compound. By adding the Li$_3$VO$_4$ to form a solid solution, lithium vacancies will increase. Structural differences between Li$_4$SiO$_4$ and Li(P, As, V) are also considered to be unimportant because both structure have a similar oxide packing and should supply same 3-dimensional ionic transportation path.

The mechanism of conduction can be expressed in terms of the following equation

$$\sigma = N\chi(1-c)\rho^2\omega^2k^{-1} \exp(-\Delta G/\kappa T)$$  \hspace{1cm} (2-10)

$\sigma$, $\alpha$, $\gamma$, $\omega$, $\kappa$, $T$ and $G$ are, the ionic jump distance, a constant depending on the number of possible jumps available to a particular ion, the vibrational frequency of the mobile ions, Boltzmann’s constant, and the free energy of activation for migration. $N$ is the number of equivalent sites and $c$ is the concentration of lithium ions on these sites if $c = 1/2$, the product has a maximum value.

The activation energy for conduction decreases to a minimum at intermediate solid solution compositions. The reasons for this are not known. Possibly, cooperative interactions between the mobile Li$^+$ ions could act to reduce the activation energy for
migration. Second, the Arrhenius pre-exponential factor (c(l - c)), passes through a maximum at intermediate compositions. This is attributed to a variation with composition in the number of mobile Li+ ions.

LVSO thin films were first deposited by Hideaki[44] by using rf-sputtering method, it is partially crystallized even deposited at room temperature and display high ionic conductivity and low electronic conductivity. Zhao et al [45] also deposited the LVSO thin film by PLD successfully. The LVSO thin film deposited by PLD shows amorphous state even deposited at 300 °C, exhibiting relatively lower ionic conductivity and lower electronic conductivity compared to the thin films deposited by sputtering. Electrolyte decomposition were not observed in the potential range of −1.75 to +1.75V, suggesting that this electrolyte thin film exhibits a electrochemical window at least more than 3.5V. The electrochemical window of Li–V–Si–O thin film electrolyte seems to be narrow comparing with the LIPON electrolyte.
<table>
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<tr>
<th></th>
<th>LiCoO$_2$</th>
<th>LiFePO$_4$</th>
<th>LiMn$_2$O$_4$</th>
<th>LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</th>
<th>Li$_4$Ti$<em>5$O$</em>{12}$</th>
<th>TiO$_2$</th>
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<td>4V</td>
<td>4.7V</td>
<td>1.5V</td>
<td>1.75V</td>
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<td>Good</td>
<td>Excellent</td>
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<td>Spinel</td>
<td>Spinel</td>
<td>Spinel</td>
<td>Anatase, Rutile</td>
</tr>
</tbody>
</table>

Figure 2-1. Schematics of a typical Lithium-ion cell
Figure 2-2. The crystal structure of Layered structure (Blue: transition metal ions; Red Li ions)

Figure 2-3. The crystal structure of Spinel structure (Blue: transition metal ions; Red Li ions)
Figure 2-4. The crystal structure of Olive structure (Green: transition metal ions; Orange: P ions; Red: Li ions)
Figure 2-5. The crystal structure of anatase TiO$_2$ (Green: transition metal ions; Blue Li ions)

Figure 2-6. The crystal structure of rutile TiO$_2$ (Green: transition metal ions; Blue Li ions)
Figure 2-7. The voltage profiles of various electrode materials

Figure 2-8. Conductivity of Li$_4$SiO$_4$-Li$_3$VO$_4$ solid solution. Numbers refer to % Li$_4$SiO$_4$ content[43]
CHAPTER 3
EXPERIMENT PROCEDURES

This chapter focuses on the principles of experiment method and experiment procedures, especially focus on the theory of sol-gel method, principles of PLD, the design of the PLD system in UF and the electrochemical measure methods that will be used in this research. The sol-gel theory has been expressed first, four different steps were used to fabricate ceramic. The mechanism of laser ablation will be also described, and the set-up of PLD system and the deposition procedure are introduced. Finally, the electrochemical measurement method and electrochemical measurement system are given.

3.1 Principles of Sol-Gel Synthesis Method[46]

Attention for the sol-gel process start as mid-1800s with Ebelman and Grahams[47]. A sol is composed of a suspension of colloidal particles in a liquid, a gel is a semi-rigid mass formed if colloidal particles are linked to form a network or the polymer molecules are cross-linked. The sol-gel process is a method to ceramic fabricating. There are two type sol-gel processes, including the colloidal gel route and polymeric route. The precursors for the sol-gel process consist of inorganic salt or metal-organic compounds but people focus on the metal alkoxides. The precursor composition, the concentration of reactants, pH value and the temperature will affect the conversion of the sol-gel process. After gelation process, a large amount of liquids still exist in the interconnected channels, the drying process must be performed to remove to water, including the conventional drying and the supercritical drying process. Finally, sintering process was performed to get final product. The whole sol-gel process can be divided into following steps[46, 48, 49] as Figure 3-1:
3.1.1 Selection of Precursor

The physical properties of metal alkoxides major depend on the properties of the metal, such as the valence, the electronegativity and atomic radius. The alkyl group will also affect the volatility of the precursor, with the increasing of the number of methyl groups, the size of atom will decrease and the precursors will become sublimable solids or volatile liquids. The wide range properties can be achieved depend on the alkyl group and metal. Many metal alkoxides are sensitive to the moisture and need to be careful for handling or storage. The use of dry atmosphere or dehydrated solvents is necessary.

3.1.2 Conversion of Sol to Gel

The basic reaction process sol-gel process can be described as follows by using tetramethoxysilane(TMOS) as a precursor in limited water and alcohol solvent

The overall reaction of Si(OCH₃)₄ are described as follows

\[
\text{Si(OCH₃)₄} + \text{H₂O} \rightarrow \text{Si(OH)(OCH₃)₃} + \text{ROH} \quad (3-1)
\]

\[
\text{Si} – \text{OH} + \text{Si} – \text{OCH₃} \rightarrow \text{Si} – \text{O} – \text{Si} + \text{ROH} \quad (3-2)
\]

\[
\text{Si} – \text{OH} + \text{Si} – \text{OH} \rightarrow \text{Si} – \text{O} – \text{Si} + \text{H₂O} \quad (3-3)
\]

Hydrolysis in excess water commonly leads to the insoluble hydroxides or hydrated oxides. However, if the limited amount of water was added, partial hydrolysis reaction happen and yield soluble species that will take part in polymerization and form a by-product.

An acid (HCl) or a base(NH₃) usually used as a catalyst. Under conditions of acid catalysis and low H₂O/Si precursor mole ratio, the sol composed of weakly branch polymers. With base catalysis and high H₂O/Si precursor mole ratio, condensed particulate sols will form. Structural evolution of sol-gel silicates has been investigated.
on different length scales using different techniques. On the scale of 1 to 299nm, the structures are not uniform, a tenuous fractal structure will form. These objects have an interesting property, they are invariant under a change of magnification and can be characterized by fractal number

\[ M \sim R^D \] (3-4)

Where \( M \) is the mass of the object, \( R \) is the radius of the object and \( D \) is the fractal dimension. The fractal dimension is a useful morphological descriptor. A lower value of \( D \) indicates a more open structure. A fractal object has interesting properties that object decrease as the fractal size increases. The density of a fractal tend zero as the object increase in size.

3.1.3 Drying of gels[50]

Gels are composed of a weak amorphous solid structure containing an interconnected network of very fine pores filled with liquid. The gel must be dried before the final sintering process. The conventional drying involved to remove the water by evaporation in the air or in a drying chamber and the gel produced by conventional drying process is referred as a xerogel. The gel produced by supercritical drying is referred as an aerogel.

Conventional drying involves the interaction of three independent process, evaporation, shrinkage and fluid flow in the pores and can be expressed as two steps: a constant-rate evaporation period (CPR) and a falling rate period as shown in Figure 3-2.

During the CPR, the liquid–vapor meniscus remains at the surface of the gel and the evaporation occurs at a rate close to a free liquid surface. In this stage, the amount of gel decreases is same as the amount of liquid take out. The shrinkage occurs with the liquid evaporation. The driving force of shrinkage comes from the decrease of the
interfacial energy. The process can be described by the following process. When evaporation occurs and a solid interface appear, the solid-vapor boundary will be substituted by the solid-liquid boundary as shown in Figure 3-3 to decrease the surface energy if the contact angle $<90^\circ(\gamma_{SV} > \gamma_{SL})$ where $\gamma_{SV}$, $\gamma_{SL}$, $\gamma_{LV}$ are the specific surface energy of the solid-vapor, solid-liquid and liquid-vapor interfaces. The capillary tension in the liquid can be expressed as

$$P = -\frac{2\gamma_{LV}}{r}$$  \hspace{1cm} (3-5)$$

$P$ is the capillary pressure, $r$ is the radius of curvature.

If the radius of curvature is same as the pore, the maximum pressure will take place. For solution with cylindrical shape and a radius $a$, the $r$ can be expressed as

$$r = -\frac{a}{\cos \theta}$$  \hspace{1cm} (3-6)$$

The maximum tension is

$$P = \frac{2\gamma_{LV} \cos \theta}{r}$$  \hspace{1cm} (3-7)$$

liquid imposes a compressive stress on the solid phase causing contraction of the gel.

Osmotic pressure that produced by concentration gradient also can cause the shrinkage of the gel. For example, gel prepared by the hydrolysis of metal alkoxides contains a solution of liquids that has different volatility. Evaporation creates a composition gradient and liquid diffuses to reduce the gradient. If pores are large, a counterflow of liquid occurs and no stress will be developed. On the other hand, if the pores are small enough to inhibit the flow, diffusion away from the interior can produce a tension in liquid.
When shrinkage stops, evaporation forces the liquid meniscus into the pores and the evaporation rate decrease. This stage is called the falling-rate period. During the FRP, the liquid recedes into the gel as shown in Figure 3-2(c).

During drying, the structure of gel will change. Polymeric gels will collapse and cross-link. When the structure becomes stiff enough to resist the capillary stress, residual porosity will be formed. Silica gels prepared by acid catalyzed reactions own the porosities as 35-40% compared to base-catalyzed that has the porosities as 60 to 70%. For particulate gels, the structure will fold under the action of the capillary stresses. Neck formation or an increase in the coordination number of the gel will continue until the structure is strong enough to resist the capillary stress. Because the particulate structure of the gel can better withstand the smaller capillary stresses arising from the large pores, the shrinkage will be much smaller than the polymer gels. The porosity is typical in the range of 70-80%.

In supercritical drying, the liquid in the pores is removed above the critical temperature, $T_c$ and the critical pressure $P_c$. In this situation, there is no difference between the liquid and vapor phases. There is no capillary pressure and no stresses formed during drying process. The aerogel with little shrinkage and high porosity can be fabricated. The critical temperature and pressure of ethanol are 243°C and 6.4MPa. An autoclave needed for such high temperature and pressure makes the process time-consuming, dangerous and expensive. Carbon dioxide has lower critical point means the process can be performed in ambient temperature. Moreover, the cheap price makes it possible to use in commercial application.
3.1.4 Gel Densification During Sintering

The structure of xerogel has a high free energy that can act as a powerful driving source for sintering. The surface area of the solid-vapor interface was the main source, the reduced cross-link density and the free volume of the solid skeletal phase are also expected to provide a contribution to the free energy. The particulate gel shrink only at elevated temperatures and the behavior is similar to the porous metal glass. For polymeric gel, the mechanisms contribute to the densification depend on the porosity, pore size and skeletal density as well as the heating rate and thermal history. A borosilicate gel that heated at a constant rate 0.5°C/min was used as an example here: the whole processes can be divided into three regions:

- Region I: weight loss with a small shrinkage 25-150°C: the desorption of water and alcohol contributed to a small loss of weight. The small shrinkage was due to energy increase contributed by the desorption process of liquid.

- Region II: weight loss with concurrent shrinkage 150-525°C: the weight loss was attributed by two processes, the removal of the water and the oxidation of carbonate. The shrinkage in region II was attributed by polymerization reaction, which leads to a higher cross-link density of polymer chain and structural relaxation of the polymeric network as the structure approach the configuration of the melt-glass.

- Region III: shrinkage without weight loss (>525°C): the large and fast shrinkage was contributed by viscous flow. The pores in the gel will be removed in this stage. The driving force of densification is the decreasing the solid-vapor surface tension formed by pores. Densification also involves transport of matter and it is limited by the kinetics of the process, for example, the rate of heating have a significant effect for densification. High heat rate reduces the amount of viscous flow that can occur in a given temperature interval and decrease the amount of cross-link and structure relaxation.

3.2 Principles of Pulsed Laser Deposition

Pulsed laser deposition is a simple, but versatile method that can fabricate diverse range of materials. In 1962, Breech and Cross[51] used ruby laser to vaporize and ablate material from a solid(or liquid) target. In 1965 Smith and Turner[52] used
ruby laser to deposit thin films. However, the availability of the types of laser, stability and low laser repetition rate limits it application. With the rapid progress of the laser technology such as the development of nanosecond pulsed Nd-YAG, excimer lasers and the availability of intense pico-and femto-second pulses, high-temperature $T_c$ superconducting material was synthesized successfully[53]. Laser used in PLD process, including CO$_2$ laser (10.6um), Nd-YAG laser (1064nm and 532nm), excimer laser (XeCL 308nm, KrF 248nm ArF(193nm)157nm(F2). The KrF excimer laser was used in this research.

There are many advantages for PLD process. The laser system is outside of the chamber that make the highly freedom for design of the deposition system. The targets used in PLD are smaller than conventional sputtering method. Moreover, the all-solid state thin film battery with multi-layers can be fabricated only by this technique. In addition, the stoichiometry of material can be keep since the extremely high heating rate supply by the laser. This deposition method was already used for different field, including film deposition, patterning polymers and wide band gap materials or removal of biological tissue and surface clean.

3.2.1 Mechanism of Pulsed Laser Deposition

The mechanism of the PLD process can be expressed in three steps[54-56] as shown in Figure 3-4:

3.2.1.1 The interaction of the laser beam and target

Electronic excitation, thermal conduction in solids and the removal of material (macroscopic sputtering) will be induced by the interaction of laser beam and target;
their relative importance depend on the nature of the target material and the excitation wavelength and the pulse duration[54-56].

When a laser beam interacts with material, electrons are excited by the absorption of photons. The electrons are heated to high temperature by absorbing laser energy through collisions. For materials such as metals, the band structure allows absorption of most low to moderate energy photons. For semiconductor or insulator, the band structure make the photon energy cannot be absorbed by linear process. The photon absorption will happen by accompanying with one of two processes: electron avalanche [57]and strong multiphoton absorption. Electrons at defects sites, which have intermediate energies can be excited by single photon absorption. Moreover, small amounts of multiphoton absorption can lead to a small number of electrons enter to the conduction band. Collisions of these excited electrons with bound electrons lead to avalanche ionization.

For thermal conduction in solids, the effects including electron-lattice energy coupling, thermal conduction and phase transition . For femtosecond pulsed, there is insufficient time for energy transfer to the lattice and can be considered as direct solid-vapor transition make the thermal damage is minimal[58].

For long-pulsed lasers, ablation of materials occurs through melt expulsion driven by the vapor pressure and the recoil pressure of light. The melt layer is resolidified, resulting in geometric change of the holes. With ultrashort pulse, the deposited energy is limited to a smaller depth and the absorbed energy heats the material very quickly past the melt to the vapor phase. The material is removed by direct vaporization away from the surface without formation a recast layer.
3.2.1.2 Plume formation and propagation\[55\]

Extensive experiments have been performed to study the plume propagation using optical absorption and emission spectroscopy. Neutral atoms, ions and the electrons travel at different velocities and strong interaction between the species of plasma and background gas are observed. The plasma plume expands like a pulsed jet from a nozzle at supersonic velocities in the direction of the target normal. The emitted light and the color of the plume are caused by fluorescence and recombination processes in the plasma. The pressure and the laser fluence both have significant effect on the shape, size of the plume.

3.2.1.3 Nucleation and growth [55]

The quality of the film was established by this step. Different reactions happen in this stage, including atom deposition on the substrate, atom re-evaporation from substrates, atom diffusion over substrate, and clusters dissociation.

If the real vapor pressure of the arriving particle is larger than its equilibrium value, film will grow on the substrate. The total change of free energy for the nucleation of a cluster on a substrate can be expressed as

\[
\Delta G = a_1 r^2 \gamma_f + a_2 r^2 r_i - a_2 r^2 r_s + a_3 r^3 \Delta G_V
\]

(3-8)

and show in Figure 3-5 where the \( a_i \) is the shape factor, \( r \) is the radius of the cluster, \( \gamma_f \) is the surface energy of the film per unit area, \( \gamma_s \) is the surface energy of the substrate per unit of area, \( \gamma_i \) is the interface energy between the film and the substrate per unit area, and \( \Delta G_V \) is the change of volume free energy.

The cluster is stable and will start to grow if the derivative of the change in the total free energy to the number of atoms is negative.
The critical size of the nucleus can be derived from Eq. 3-8 as following equation[59]

\[ r^* = \frac{(a_1\gamma_f - a_2\gamma_l - a_1\gamma_s)}{3a_2\Delta\gamma} \]  

(3-9)

If the free energy is negative and the total surface free energy is positive, the cluster will continue growing until reaching the critical size of the nucleus. Three growth modes developed depend on the surface energy[60, 61]:

In the island (Volmer-Weber) mode, small clusters are nucleated directly on the substrate surface and then grow into islands of the condensed phase. This happens when the atoms of the deposit are more strongly bound to each other than to the substrate \((a_1\gamma_f + a_2\gamma_l - a_1\gamma_s > 0)\).

The layer (Frank-van der Merwe) mode displays the opposite characteristics. Because the atoms are more strongly bound to the substrate than to each other \((a_1\gamma_f + a_2\gamma_l - a_1\gamma_s < 0)\), the first atoms to condense form a complete monolayer on the surface, which becomes covered with a somewhat less tightly bound second layer.

The layer plus island (Stranski-Krastaov) mode is an interesting intermediate case. After forming the first monolayer, or a few monolayers, subsequent layer growth is unfavorable and islands are formed on top of this monolayer. The reason is an increase with increasing thickness in the stress due to the lattice mismatch[62].

For the PLD process, because of the short laser pulsed duration (ns) and the small temporal spread (<10µm/s) of the ablated materials. The layer mode is preferred and smooth film can be fabricated. Moreover, the energetic ablation species lead to a lower deposition temperature for crystalline the film.
3.3 Set-up of Pulsed Laser Deposition System

The PLD system was built in University of Florida. The system is composed of a laser, a deposition chamber, several optic lenses and a vacuum system. The laser source is Lambda Physic LPX300 as shown in Figure 3-6. Because KrF is the highest gain system for electrically discharged pumped excimer laser system, the KrF excimer laser with wavelength 248nm was used in this research. The pulse energy of laser system can be controlled between 200 to 550mJ and the repetition rate can be controlled between 1 and 50 Hz with pulsed width 25ns. Four different gases were used including Kr, F₂, Ne, O₂.

The deposition chamber was brought from Excel Instruments, Mumbai and was composed 5 parts

- 12" dia SS vacuum chamber as shown in Figure 3-7
- 2” hot zone Cylindrical flat plate heater capable of working at 850°C
- Programmable controller can index the targets as well as rotate them in front of the laser beam. The number of targets is 6 which means multi-layer deposition is possible
- Gas flow assembly for controlling the ambient gas as well as venting the chamber
- Lens holder attachment for X,Y, Z movement of lens in order to focus the laser beam.

The Vacuum system was brought from Pfeiffer Vacuum, including TMU 261P Turbo molecular Drag Pump with TC 600, XtraDry 150-2, Dry Piston pump with solenoid actuated angle valve compact full range Pirani/Cold Cathode Gauge (Measurement range 1000 to 5x10⁻⁹mbar) and DCU 200 Display Control Unit for gauge with power supply. The series design was used for the vacuum system as shown in Figure 3-8.
3.4 Experiment Procedure for PLD

Several different substrates were used for the experiment, including Stainless Steel 304 foil, gold foil, SiO$_2$/Si and Pt/Ti/SiO$_2$/Si substrate. The SiO$_2$/Si substrate was supplied by National Nano Device Laboratory in Taiwan and the oxide with 150nm was fabricated by wet oxidation method. The Pt/Ti with 150nm and 20nm was prepared by sputtering deposition in Nano Facility in University of Florida. For metal substrate, the substrates were polished with 3, 1 and 0.3 um alumina suspension. Then, three steps were performed to clean the contaminants. First, the acetone solvent was used by to remove organic contaminations by ultrasonic cleaner for 10 minutes. Then ultrasonic bath in alcohol was carried out for rinsing contaminated acetone as well as removing particles from surfaces. Finally, de-ionized water was used for the final cleaning.

Before the deposition process, the sample must be pasted on the sample holder by silver paste. After waiting two minutes, the substrate was heated to 60 °C to remove the solvent of the silver paste. The chamber was evacuated to $10^{-5}$ torr by starting the rotary and turbo pump. After the base pressure arrived, the thermal controller was turn on to heat the substrate to desired temperature. After the specific temperature was reached, oxygen gas was introduced into the chamber and kept at a specific pressure during the deposition.

3.5 Electrochemical Measurements

3.5.1 Configuration of Cells

Two types of cells were used for electrochemical measurements, including coin cell 2016 and Swagelok cell as shown in Figure 3-9(a)(b). For the powder or the flakes samples, the coin cell 2016 was used. For the thin film samples, the Swagelok cell was used.
The 2016 coin cell and Swagelok cell were consisting of metallic lithium as an anode and an electrolyte comprised of 1M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with 1:1 volume ratio. Celgard model C480 separator (Celgard Inc. USA) was used as separator. Cathode films for coin cell were prepared from slurries of powders or flakes with suitable polyvinylidene fluoride (PVDF) and acetylene carbon black dissolved in N-methyl-2-pyrrolidinone (NMP). The mixtures were cast onto Al foil using a doctor blade and dried at 100°C overnight. Electrode discs were cut into cathodes containing 2-3 mg of active materials before storing them in an argon filled glove box (H$_2$O level<1.6ppm). The Swagelok Cells for thin films samples were similar configuration compared to coin cell but there is no carbon black or PVDF necessary for testing. The cells were assembled in an argon filled glove box and tested using an Arbin BT2000 instrument in galvanostatic mode as shown in Figure 3-10(a)(b).

### 3.5.2 Potentiostatic Intermittent Titration Technique (PITT) method[63, 64]

The potentiostatic intermittent titration technique (PITT) was used to abstract the lithium chemical diffusion coefficient. This technique applied a constant voltage step to the cell and measure the current drop with time. A new voltage is applied when the current drops to a very small value.

The PITT measurements were based on the Fick’s second law with one dimension

\[
\frac{\partial C_{Li}}{\partial t} = \widetilde{D}_{Li} \frac{\partial^2 C_{Li}}{\partial x^2}
\]

(3-10)

where \(x\) is the distance into the solid film from the electrolyte/electrode interface, \(C_{Li}\) is the Li concentration at \(x\) and time \(t\), and \(\widetilde{D}_{Li}\) is the chemical diffusion coefficient.

We can assume the electrode initially has a uniform lithium concentration \(C_0\). A new concentration \(C_S\) is imposed on the electrode surface by applying a voltage step.
Lithium must be continuously supplied by transport through the electrolyte in order to keep the surface concentration constant at the imposed $C_S$, until the electrode reaches the composition $C_S$ everywhere. The boundary conditions of the PITT can be expressed as following equation

$$C_{Li} = C_0 \text{ at } 0 \ll x \ll L \text{ and } t = 0 \quad (3-11)$$

$$C_{Li} = C_s \text{ at } x = 0 \text{ and } t > 0 \quad (3-12)$$

$$\frac{\partial C}{\partial x} = 0 \text{ at } x = L \text{ and } t \gg 0 \quad (3-13)$$

Where the $L$ is the diffusion length, $C_s$ is the surface concentration of lithium.

By solving the Fick’s second law, the concentration of Li can be expressed as [63]

$$C_{Li(x,t)} = C_S - (C_S - C_0) \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \left( \frac{(2n+1)\pi x}{2L} \right) \exp \left( -\frac{(2n+1)^2\pi^2 D_{Li}t}{4L^2} \right) \quad (3-14)$$

The current formed by the voltage step depend on the concentration gradient and can be expressed as following equation

$$I(t) = -2z Fa D_{Li} \frac{\partial C}{\partial x} \big|_{x=0} \quad (3-15)$$

$$I(t) = \frac{2z Fa (C_S - C_0) D_{Li}}{L} \sum_{n=0}^{\infty} \exp \left( -\frac{(2n+1)^2\pi^2 D_{Li}t}{4L^2} \right) \quad (3-16)$$

where $a$ is the area of the interface, $z$ is charge number, $F$ is the Faraday constant,.

Moreover, by using following relationship

$$dx = V_M (C_S - C_0) = \frac{Q}{2F n_B} \quad (3-17)$$

$$\frac{V_M n_B}{S} = L \quad (3-18)$$

where $V_M$ is the molar volume, $Q$ is the charge transferred number and $n_B$ molar number

$$I(t) = \frac{2Q D_{Li}}{L^2} \sum_{n=0}^{\infty} \exp \left( -\frac{(2n+1)^2\pi^2 D_{Li}t}{4L^2} \right) \quad (3-19)$$

For a long time, the current can be expressed by a reasonable approximation

$$I(t) = \frac{2Q D_{Li}}{L^2} \exp \left( -\frac{\pi^2 D_{Li}t}{4L^2} \right) \quad (3-20)$$
Finally, the chemical diffusion coefficient can be abstracted by following equation.

\[
\text{\( D_{\text{Li}} \)} = \frac{d \ln (I)}{dt} \frac{4L^5}{\pi^2}
\]  

(3-21)

PITT can be avoided the two phase reaction during measurement when the voltage steps are well controlled and the relationship between the current and time more directly and exactly reflect the diffusion property of Li although the results were obtained under a slight deviation from the equilibrium conditions,
Figure 3-1. The routes that indicate the process of sol-gel [48]

Figure 3-2. Stage of drying [50]
Figure 3-3. Schematic illustration of shrinkage of the gel

Figure 3-4. Mechanism of PLD[55]
Figure 3-5. Schematic illustration of nucleation of a cluster on a substrate surface

Figure 3-6. Lambda physic LPX300. Photo(s) courtesy of Ming-Che Yang.
Figure 3-7. Chamber design of the in house PLD system

Figure 3-8. The design of vacuum system
Figure 3-9. The cells for electrochemical measurement (a) coin cell 2016 (b) Swagelok Cell. Photo(s) courtesy of Ming-Che Yang.

Figure 3-10. The equipment for electrochemical measurement (a) Arbin machine and (b) glove box. Photo(s) courtesy of Ming-Che Yang.
CHAPTER 4
ELECTRONIC, STRUCTURAL AND ELECTROCHEMICAL PROPERTIES OF LiNi_xCu_yMn_{2-x-y}O_4 (0<x<0.5, 0<y<0.5) HIGH-VOLTAGE SPINEL MATERIALS

4.1 Introduction

LiMn_2O_4 spinel is an attractive compound as a cathode material in lithium-ion batteries, due to its economical, environment and safety advantages over LiCoO_2. LiMn_2O_4 adopts the spinel structure with the space group Fd-3m, in which the Li and Mn occupy the 8a tetrahedral and 16d octahedral sites of the cubic close-packed oxygen ions framework, respectively. However, LiMn_2O_4 tends to exhibit capacity fade in the 4V region, particularly at elevated temperatures. Factors such as Mn dissolution into the electrolyte and the development of micro-strains[12, 65] during cycling have been suggested to be the main sources of capacity fade. The poor cycling performance could be improved by partial substitution of Mn with other metals, an approach of making the LiM_{x}Mn_{2-x}O_4 (M = Co, Mg, Cr, Ni, Fe, Al, Ti, Cu, Zn etc.) electrode material[13-15]. It has been found that a higher voltage plateau (> 4V) accompanies some transition metal doping[13]. Among all LiM_{x}Mn_{2-x}O_4 materials, LiNi_{0.5}Mn_{1.5}O_4 is an attractive high voltage cathode material since it offers a flat voltage plateau at 4.7 V and demonstrates a reversible capacity >135mAh/g[66, 67]. Several strategies were developed to improve the rate capability of LiNi_{0.5}Mn_{1.5}O_4. J. C. Arrebola et al. obtained excellent rate properties by homogeneously mixing nano and micro size LiNi_{0.5}Mn_{1.5}O_4 powders[68], or by adding polyethylene glycol(PEG) to increase the crystallinity and decrease the strain[67]. The rate capability was also affected by the atomistic structure of the spinel material, as proposed by M. Kunduraci et al[69]. It is found that nonstoichiometric LiNi_{0.5}Mn_{1.5}O_{4-δ} (Fd-3m) as shown in Figure 4-1 exhibited better structural reversibility at high rate compared with stoichiometric LiNi_{0.5}Mn_{1.5}O_4 (P4_332). The oxygen deficiency
leads to the presence of a small amount of Mn$^{3+}$ in the pristine materials, which leads to better electronic conductivities in the material. The Cu doped spinel materials were investigated by a few research groups[70-73]. Although the Cu-rich spinel electrodes provide lower discharge capacity than Ni-rich spinel electrodes, it is more stable during electrochemical cycling. Moreover, LiCu$_{x}$Mn$_{2-x}$O$_{4}$ has a higher electronic conductivity than other spinel LiM$_{x}$Mn$_{2-x}$O$_{4}$ materials (Cr, Fe, Co, Ni) [74], because Cu can participate in the charge transport process. All the previous work focused mainly on the electronic conductivity in the doped spinel LiM$_{x}$Mn$_{2-x}$O$_{4}$ materials. Little has been explored to enhance the lithium ionic diffusivity in this family of materials. Using ab initio computational modeling, it is possible to rapidly screen the effect of different doping elements on the lithium diffusion activation barrier, as well as the redox potentials in the spinel structure. Ab initio computational method was firstly used by Van der Ven et al. to determine the energy barrier of Li diffusion in layered transition metal oxides[75]. Kang et al. also used this method to identify the factors that limits Li$^{+}$-ion hopping in layered oxide and successfully synthesize an optimized layered material with superior rate capability [76].

Many researchers have already shown that the cycling performance of LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$ can be improved by doped with different transition metal ions[77-80]. However, a systematic understanding on the effects of co-doped elements is still lacking. In this work, first principles computation, based on density functional theory (DFT), is used to examine the voltage profile and electronic structures of the LiM$_{x}$Mn$_{2-x}$O$_{4}$ (M = Ti, V, Cr, Fe, Co, Ni, Cu$^{+}$). The Li diffusion activation barriers in each material are calculated and compared. Based on the computational pre-screening, our
experimental research focuses on LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ (0<x<0.5, 0<y<0.5) which have the potential to achieve high voltage, high rate and good cycling performance, while keeping relatively high capacity. The materials with different Cu/Ni concentrations are synthesized by using the sol-gel process. Their crystal structures, electronic structures and electrochemical properties are then characterized and studied.

4.2 Experimental Methods

4.2.1 Computational Methods

The computation work was performed with Mrs. Bo Xu in my group. In this work, a supercell composed of eight formula units of Li$_x$M$_{1/2}$Mn$_{3/2}$O$_4$ (M= Ti, V, Cr, Fe, Co, Ni and Cu) is used. The doped spinel with ordered cation arrangement belongs to the space group $P4_332$. O ions occupy the 8$c$ and 24$e$ sites, forming a close-packed fcc lattice. Mn ions occupy the 12$d$ octahedral sites while M ions occupy the 4$b$ octahedral sites. The 8$c$ tetrahedral sites are filled with Li ions. For Li$_x$Cu$_{1/2}$Mn$_{3/2}$O$_4$, an additional model of Cu ions exchanging sites with half of the Li ions was built and investigated. Calculations were performed using density functional theory (DFT) in the spin-polarized generalized gradient approximation (GGA) and in the GGA with Hubbard U correction (GGA+U). Core electron states were represented by the projector augmented-wave method[81] as implemented in the Vienna ab initio simulation package (VASP) [82-84]. The Perdew-Burke-Ernzerhof exchange correlation[85] and a plane wave representation for the wave function with a cutoff energy of 370eV were used. The Brillouin zone was sampled with a 5x5x5 mesh by Gamma packing. The atomic positions and cell parameters are fully relaxed to obtain total energy and optimized cell structure. To obtain the accurate electronic density of states (DOS), a static self-consistent calculation was run, followed by a non-self-consistent calculation using the
calculated charge densities from the first step. The cell volume was fixed with internal relaxation of the ions in the second step calculation. A supercell with one vacancy out of eight Li sites (Li$_7$M$_4$Mn$_{12}$O$_{32}$) was used to calculate the Li diffusion activation barriers in the Li-rich phase with GGA approximation. The Hubbard U correction was introduced to describe the effect of localized $d$ electrons of transition metal ions when investigating the valence states and electronic structures of the ions. Previous work has shown that the U values can be calculated in a self-consistent way and the U values of Mn and Ni ions in the spinel structure are well established [86-88]. These values are taken as the references. In the doped spinel system, the same transition metal ions with different valence states may co-exist; therefore, small adjustments are made to the reference U values, so that each transition metal ion has a unique effective U value applied in the rotationally invariant LSDA+U approach[89]. In this work, the applied effective U value given to Mn ions is 5eV, to Ni ions is 5.96eV, and to Cu ions is 7eV.

4.2.2 Synthesis Methods

Sample Preparation: Six samples were synthesized using the sol-gel method:

LiNi$_{0.5}$Mn$_{1.5}$O$_4$, LiNi$_{0.45}$Mn$_{1.55}$O$_4$, LiCu$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$, LiCu$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$, LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ and LiCu$_{0.5}$Mn$_{1.5}$O$_4$. The sol solutions were prepared from the stoichiometric mixtures of Li(CH$_3$COO)-2H$_2$O (Fisher), Ni(CH$_3$COO)$_2$-4H$_2$O (Fisher), Cu(CH$_3$COO)$_2$·H$_2$O (Fisher) and Mn(CH$_3$COO)$_2$·4H$_2$O (Fisher) in distilled water. Then the solution was added drop-wise to a solution of citric acid which was used as a chelating agent. Ph value was adjusted to 6.5 by adding ammonium hydroxide. A gel was obtained by heated at 75 °C overnight. The gel were calcined at 450 °C for 10 hours to remove the carbonate in air and calcined at 800 °C for 10 hours.
4.2.3 Characterizations

Powder diffractions of all samples were collected using a high-resolution synchrotron powder X-ray diffractometer at beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory (USA). The conditions for the data collection were: continuous scanning of a detector covering an angular range from 0.5° to 40 with a step size of 0.0001° and wavelengths of $\lambda=0.413964\text{Å}$. The diffraction patterns were analyzed by the Rietveld refinement software, FullProf. The Ex-Situ XRD after electrochemical testing were collected by a laboratory x-ray diffractometer equipped with a curved position sensitive detector (Inel CPS120, detection range 0-120°), a Cu X-ray tube source and a Gobel mirror on the incident beam. The collection time for each XRD spectrum was 20 minutes. The samples for ex-situ XRD were recovered by disassembling cycled batteries in an argon-filled glove box and the powder mixture was scraped from the aluminum disks. The chemical compositions of the samples were analyzed by inductive coupled plasma atomic emission spectroscopy (ICP-AES Perkin Elmer Plasma 3200). The instrument was initially calibrated using commercial LiCoO$_2$ and LiFePO$_4$ powders. Field emission secondary electron microscopy (FEG-SEM, JEOL JSM-6335F) was carried out to investigate the particle size and morphologies. Images were collected with an accelerating voltage of 15kV. X-Ray absorption spectroscopy (XAS) at the Ni, Mn and Cu K-edges were obtained in transmission mode at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan to observe the changes in Nickel, Manganese and Copper oxidation states for LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ during the charging process. A Si (111) double crystal monochromator was employed for energy selection. The coin cell 2016 was charged to target voltage (4.1 to 5V) and rested for 40min (10minutes to reach equilibrium, 30
minutes to get spectrum) to get the spectroscopy. The spectrum was collected every 0.1V.

### 4.2.4 Electrochemistry

The electrochemical properties of all cathode electrodes were measured using 2016 coin cells consisting of metallic lithium as an anode and an electrolyte comprised of 1M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with 1:1 volume ratio. Celgard model C480 separator (Celgard Inc. USA) was used as separator. Cathode films were prepared from slurries of LiCu$_y$Ni$_x$Mn$_{2-x}$O$_4$ with 7.5% polyvinylidene fluoride (PVDF) and 7.5% acetylene carbon black dissolved in N-methyl-2-pyrrolidinone (NMP). The mixtures were cast onto Al foil using a doctor blade and dried at 100°C overnight. Electrode discs were cut into cathodes containing 5-10mg of active materials before storing them in an argon filled glove box (H$_2$O level<2ppm). The coin-cells were assembled in an argon filled glove box and tested using an Arbin BT2000 instrument in galvanostatic mode. The tests were conducted between 3.0V and 5.0V at a constant current rate of C/20, C/10, C/5 and C/2. The samples for ex-situ XRD were recovered by disassembling charged batteries and washed using acetonitrile to remove residual electrolyte in an argon-filled glove box. The potentiostatic intermittent titration technique (PITT) was performed by applying a voltage step of 10mV to measure the chemical diffusion coefficient. When the current decrease below 3x10µA (which is equivalent to C/200 rate), the next voltage step will be applied. The voltage window was set from 4.5V-4.9V.
4.3 Results and Discussion

4.3.1 Computation Results

Previous research has shown that, when Li ions diffuse in the un-doped LiMn$_2$O$_4$ spinel structure, the diffusion activation barriers are reached when Li ions occupy the intermediate 16c sites which are surrounded by six Mn ions forming a Mn ring [88]. A similar situation occurs in the doped spinel Li$_x$M$_{1/2}$Mn$_{3/2}$O$_4$ (M= Ti, V, Cr, Fe, Co, Ni and Cu); however, the rings are now composed of two types of metal ions - Mn and the doped transition metal ion M. In the supercell used for this work, for each dopant, two distinct local environments of transition metal ion rings can be found. One is composed of three doped M ions and three Mn ions alternatively arranged (Figure 4-2(a)). The other one is composed of one doped M ions and five Mn ions (Figure 4-2(b)). The corresponding Li diffusion barriers with different dopants (M= Ti, V, Cr, Fe, Co, Ni and Cu) are calculated using GGA method (Figure 4-3). The Li diffusion barrier in un-doped Mn spinel[88] is also provided as the reference. Comparing to the un-doped Mn spinel material, the average Li diffusion barrier remains largely unchanged when Ni and Fe ions are present. The average diffusion barrier increases with Ti, V, Cr doping and decreases with Co and Cu doping. Specifically when only one Cu or three Co ions appears in the ring, the Li diffusion barrier can be reduced to as low as 256 meV, respectively.

As shown in previous work[88], the introduction of the Hubbard U correction accurately captures the charge/discharge voltages of the Li-intercalation spinel materials. More importantly different valence states of the same transition metal ions can be distinguished. Calculations using GGA+U method are performed on LiCu$_{1/2}$Mn$_{3/2}$O$_4$ spinel with different Li concentrations. In the first model, where Cu ions
occupy 4b octahedral sites and Li ions occupy 8c tetrahedral sites, the calculated average voltage of \( \text{Li}_x\text{Cu}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) (0.5< \( x < 1 \)) is 4.44V, which is 7% higher than the experimental low voltage plateau. In addition, the calculated average voltage of \( \text{Li}_x\text{Cu}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) (0 < \( x < 0.5 \)) is 5.36V, which is 9% higher than the experimental high voltage plateau. The projected electronic density of states (DOS) of Cu 3d orbitals in \( \text{Li}_x\text{Cu}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) (x=1, 1/2, 0) are calculated and presented in Figure 4-4(a), Figure 4-4(b) and Figure 4-4(c), respectively. In the proposed spinel model, the octahedral crystal field splits the Cu 3d orbitals into two parts. \( d_{xy}, d_{yz} \), and \( d_{xy} \) orbitals belong to the \( t_{2g} \) orbitals with lower energy levels while \( d_{z}^2 \) and \( d_{x^2 - y^2} \) belong to the \( e_g \) orbitals with a higher energy level[90]. Figure 4-4(a) shows the projected DOS of Cu ions in the fully-lithiated phase \( \text{LiCu}_{1/2}\text{Mn}_{3/2}\text{O}_4 \). Both spin-up and spin-down states of the three \( t_{2g} \) orbitals are below the Fermi energy, which means the \( t_{2g} \) orbitals are completely occupied. For \( e_g \) orbitals, the \( d_{z}^2 \) orbital is occupied, but the spin-up state of the \( d_{x^2 - y^2} \) orbital is above the Fermi energy indicating that the \( d_{x^2 - y^2} \) orbital is half empty. The DOS plot is consistent with the \( t_{2g}^6 e_g^3 \) electron configuration of Cu\(^{2+} \) ions. The projected DOS of Cu ions in the half-delithiated phase \( \text{Li}_{1/2}\text{Cu}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) (Figure 4-4(b)) and in the fully-delithiated phase \( \text{Cu}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) (Figure 4-4(c)) are generally the same minus trivial differences in shape. It suggests that Cu ions are in the same valence state in the two compositions. The spin-up states of the \( e_g \) orbitals are completely empty while all of the other electronic states are occupied. The DOS plots indicate the electron configuration of \( t_{2g}^6 e_g^2 \) consistent with Cu\(^{3+} \) ions. Based on these results from first-principles calculation, the Cu valence in doped spinel \( \text{LiCu}_{1/2}\text{Mn}_{3/2}\text{O}_4 \), is Cu\(^{2+} \) at fully lithiated state. The Cu\(^{2+} \) ions can be oxidized to Cu\(^{3+} \) ions when half of the Li ions are extracted.
Valence higher than 3+ cannot be obtained and the calculated voltage of the Cu$^{2+}$/Cu$^{3+}$ redox couple is 4.44V. When more than half of the Li ions are extracted, the charge densities of oxygen ions change significantly, suggesting that the extra electrons may be provided by oxygen ions.

If one exchanges the sites of Cu ions with half of the Li ions, a defect spinel model can be created with tetrahedral Cu and octahedral Li included. For the defect spinel system, its total energy is 493 meV per formula higher than the perfect spinel system and therefore the structure should be thermodynamically less stable. However, the experimental synthesis is often conducted at relatively high temperatures (>700ºC) and a certain amount of transition metal and lithium ion site mixing occurs. The change of Cu valence versus Li concentration is investigated using a similar method as described above. Tetrahedral Cu$^{2+}$ can also be oxidized to Cu$^{3+}$ but no higher valence can be obtained. In the defect spinel model, Li ions in octahedral sites are preferred to be extracted first and the calculated voltage is 4.58V. The calculated voltage step for removing the remaining tetrahedral Li is 4.99V, a surprisingly high value.

Compared to the NiMn spinel LiNi$_{1/2}$Mn$_{3/2}$O$_4$, in which Ni$^{2+}$ can be oxidized to Ni$^{4+}$ providing two electrons per ion, the reversible capacity of Cu doped spinel may be reduced as Cu ions can only provide one electron per ion. However, when doped with a small amount of Cu, it is possible to lower the Li diffusion activation barriers so that better rate capability can be obtained. To further understand the crystal structure, electronic structure and electrochemical properties in a new series of bi-dopant spinel materials, we successfully synthesized and studied the LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ with different amount of dopants ($x=0$, 0.05, 0.10, 0.25 and 0.5).
4.3.2 Experimental Results

The atomic compositions of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ electrode materials calcinated at 800°C obtained from ICP-AES analysis. Although a Nickel oxide and a Copper oxide impurity phase appear respectively in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiCu$_{0.5}$Mn$_{1.5}$O$_4$ samples, the molar ratio of Li, Ni and Mn are in good agreement with the theoretical ratio of all samples.

X-ray diffraction patterns for LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ are depicted in Figure 4-5. Detailed Rietveld Refinement Fitting Results of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ were shown in 4-6(a)(b)(c). The spinel structure with space group $Fd-3m$ can be identified according to the indexed major peaks. In some samples, small amounts of impurities are present, such as nickel oxide in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and copper oxide in LiCu$_{0.5}$Mn$_{1.5}$O$_4$ as shown in an inset in Figure 4-5. The impurities may be tied with the solubility limit of nickel or copper in the spinel LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ as nickel or copper approach 0.5 which supports the findings of other research groups[72, 91] It is also consistent with previous reports that oxygen deficiency is usually found in LiCu$_{0.5}$Mn$_{1.5}$O$_4$. The results show that the impurity phase can be eliminated by slightly changing the Ni-Mn stoichiometry (LiNi$_{0.45}$Mn$_{1.55}$O$_4$, Figure 4-(a)) or by doping Cu into the NiMn spinel (Figure 4-5(c)(d)(e)).

According to Ohzuku et al., the integrated intensity ratios of the (400)/(311) peaks in spinel structure represents the extent of occupancy of the substituent ions on the tetrahedral site ($8a$)[92, 93]. From Table 4-2, the integrated intensity ratio of (400)/(311) peaks generally decreases with the increase of Cu content. Exceptions are found in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiCu$_{0.5}$Mn$_{1.5}$O$_4$ where the oxide impurities are involved and may affect the related peak intensities. The decrease of the integrated intensity ratio of
(400)/(311) peaks indicates that the occupancy of the substituent Cu in the tetrahedral sites (8a) increases when the Cu amount increases.

For LiNi$_{0.5-y}$Cu$_y$Mn$_{1.5}$O$_4$ samples, refinements are performed and Rietveld fitting results of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ are shown in Table 4-3 and the trend of lattice parameters change with respect to $y$ is depicted in Figure 4-7. From the plot, the lattice parameter decreases from $y=0$ to $y=0.05$, and then increases with the increase of $y$. The trend generally agrees with the results reported in previous literature. The site refinements also suggest that some Cu ions occupy the 8a tetrahedral sites instead of the 16d octahedral sites.

SEM was performed to examine the particle size and morphologies of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ after 800°C calcination. Figure 4-8 (a), (b) and (c) show that in samples with no Cu or small amounts of Cu doping, spherical particles with 100nm diameter were formed. It is also noted that when the amount of doped Cu increases (Figure 4-8(d), (e) and (f)), the particle size increases and the shape of the particles becomes more faceted. For the LiCu$_{0.5}$Mn$_{1.5}$O$_4$ sample, the particle size is in the range of 300nm - 500nm, while the particle size for NiMn spinel sample is in the range of 50-100nm.

The electrochemical properties of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ (0<x<0.5, 0<y<0.5) were investigated in lithium half-cells. The charge/discharge profiles between 3.0 and 5.0V are shown in Figure 4-9(a) and Figure 4-9(b). The cells were tested with a constant current 0.1mA/cm$^2$ applied to the cells. The LiNi$_{0.45}$Mn$_{1.55}$O$_4$ example exhibits the highest reversible capacity of 139.8 mAh/g, which is about 10mAh/g higher than that of LiNi$_{0.5}$Mn$_{1.5}$O$_4$. The small capacity reduction in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ sample is attributed to the presence of NiO impurity. These two cells both have two distinct voltage plateaus.
around 4.7V, which corresponds to the Ni$^{2+}$-Ni$^{4+}$ redox potential. A relatively small plateau can be found in the region around 4.0V. This is attributed to the Mn$^{3+}$-Mn$^{4+}$ redox couple. Previous work has shown that calcination temperature may cause oxygen loss and can lower the average oxidation state of Mn and introduce Mn$^{3+}$ ions [69]. For the LiNi$_{0.45}$Mn$_{1.55}$O$_4$ sample, the average oxidation state of manganese decreases further due to the decrease of Ni/Mn ratio, therefore the capacity of the LiNi$_{0.45}$Mn$_{1.5}$O$_4$ sample at the 4.0V region is larger than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ sample. When Cu ions are doped, the voltage plateau shifts from 4.7V to 4.95V and a new plateau appears between 4.2V to 4.6V. When the doped Cu amount increases, the total capacity decreases while the capacity between 4.0V and 4.6V increases. Capacities contributed by the plateau around 4.0V and by the plateau between 4.2V to 4.6V in different materials are listed respectively in Table 4-4.

To study the rate capability of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ (0<x<0.5, 0<y<0.5), electrodes were made with similar loading of active materials in each cell (about 20mg active material/cm$^2$). For each material, the cells were charged to 5.0V at constant low current rate (C/20) and discharged to 3.0V at various current rates (C/20 C/10, C/5, and C/2). The measured discharge capacities are shown in Figure 4-10. For LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ and LiCu$_{0.5}$Mn$_{1.5}$O$_4$, the discharge capacities are highly retained when tested at a high discharge rate, while for LiNi$_{0.45}$Mn$_{1.55}$O$_4$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$, and LiCu$_{0.05}$Ni$_{0.25}$Mn$_{1.5}$O$_4$, the discharge capacity drops significantly at a high discharge rate. Discrepancy of the discharge capacity after cycling shows little capacity fading for each sample as shown in Figure 4-11.
X-ray Absorption Near Edge Structure (XANES) measurements was performed on the LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ cathode material to study the active redox couple(s) in different voltage range. Figure 4-12 shows the charge curve for a LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ half cell that is used for *in situ* XAS experiment. The Cu, Ni, and Mn K-edge XANES spectra of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ measured as a function of voltage are shown in Figure 4-13, Figure 4-14 and Figure 4-15. In each figure, (a) is the original spectra and its second order derivative is shown in (b) to investigate the distinct energy shifts. The spectra of related oxides are also provided as references for comparison. The pre-peak region of K-edge absorption peak of pristine sample is in the same position as the pre-edge peak for the CuO reference. This indicates that the oxidation states of Cu in the two materials are the same, thus Cu is +2 in the pristine LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$. During the charging process, the position of Cu K-edge absorption peak remains unchanged until the voltage reaches 4.2V. After that, the peak begins to shift to the higher energy side. The shift stops at around 4.7V and no significant energy shift can be observed at high voltage region between 4.7 V to 5.0V. The Cu spectra shows that the Cu valence only changes between 4.2V and 4.7V. Similar methodology was applied on Ni and Mn spectra. Ni is Ni$^{2+}$ in the pristine sample and it starts to be oxidized from 4.7V and the K-edge energy shift continues until 4.9V is reached. The Mn valence is +4 in the pristine sample and it remains unchanged during the entire charging process.

X-ray photoelectron spectroscopy was used to examine surface features on the LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ cathode. Figure 4-16(a)(b)(c) shows the spectra observed for the Cu2p, Ni2p and Mn2p regions for pristine cathode. The binding energy of the Cu2p and Ni2p shown in Figure 4-16(a)(b) indicate the oxidation states of Cu and Ni are two. De-
The convolution of the Mn2p spectra reveals two peaks, a minor peak at 641.5 eV (Mn$^{3+}$) and major peak at 642.5 eV (Mn$^{4+}$) confirming the presence of a small amount Mn$^{3+}$ that is similar to previous electrochemical measurement results.

*Ex-situ* XRD patterns for LiNi$_{0.25}$Cu$_{0.25}$Mn$_{1.5}$O$_4$ at different state of charge were measured between 4.2V to 5.0V, in order to investigate the possible phase transition during Li de-intercalation. Figure 4-17(a) shows the XRD patterns of the LiNi$_{0.25}$Cu$_{0.25}$Mn$_{1.5}$O$_4$ sample at different charged voltages during the second charging process. At low voltages between 4.2V to 4.6V, the diffraction peaks shift to higher angles with increasing voltage, indicating that the lattice parameters are decreasing. However, at high voltage, no shifts in the diffraction peaks were observed, indicating the lattice parameters remain mostly constant. Although the amount and direction of shift may change with state-of-charge, no additional peaks appear during the entire charging process, suggesting the reaction remains single phase throughout the charging.

The potentiostatic intermittent titration technique[94] was performed to identify the lithium diffusion coefficient associated with the high voltage plateau observed in the second charging cycle of the electrochemical curve. Figure 4-18(a) shows the PITT profile for LiNi$_{0.25}$Cu$_{0.25}$Mn$_{1.5}$O$_4$ sample between 4.5V and 4.9V. Within this region, the current decays quickly at first, then takes seven hours to reach the limit value. The trends are consistent when different sets of samples are tested. Figure 4-18(b) shows the variation of chemical diffusion coefficients of Li ions in LiNi$_{0.45}$Mn$_{1.55}$O$_4$, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$. The lithium diffusion coefficient is determined from the following equation where $I$ is the current and $L$ is the particle size. $L$ is estimated from SEM images (Figure 4-8).
\[ \dot{D}_{Li} = -\frac{d\ln(t)}{dt} \frac{4L^2}{\pi^2} \] (4-1)

D_{Li} changes with the lithium content. This trend shown in Figure 4-18(b) is similar to previous literature but the values of the diffusion coefficient from our results are smaller than results acquired by Xia et al.\[95\]. The main source of discrepancy may come from the errors in estimation of the diffusion length for powered composite electrode as opposed to thin film electrode. The minimum of D_{Li} appears between 4.7V and 4.8V. These coincide with the oxidation of Ni^{2+} to Ni^{4+}. Among the three samples, D_{Li} of LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_{4} is one order of magnitude higher than that of LiNi_{0.5}Mn_{1.5}O_{4} and LiNi_{0.45}Mn_{1.55}O_{4}.

4.3.3 Discussion

4.3.3.1 The crystal structure of LiNi_{x}Cu_{y}Mn_{2-x-y}O_{4}

Although the results from first principles calculations performed at 0K suggest that tetrahedral Cu is energetically less favored, results from XRD indicate that Cu ions do occupy tetrahedral sites in materials synthesized at high temperature. According to Shannon et al., the effective ionic radii of Cu^{2+} (0.57 Å) is slightly smaller than that of Li^{+} (0.59 Å) if the atoms are tetrahedrally coordinated\[96\]. When a small amount of Cu ions are doped into the NiMn spinel materials, most of the Cu^{2+} ions may occupy the tetrahedral sites, leading to a smaller lattice parameter than undoped materials. However, when more Cu ions are doped, Cu^{2+} will also occupy the octahedral sites that were originally occupied by Ni^{2+} ions. Because the effective ionic radii of octahedral Cu^{2+} (0.73 Å) is larger than that of octahedral Ni^{2+} (0.69 Å)\[96\], the decrease of lattice parameter is gradually compensated, and the lattice parameters will finally increase with the increase of doped Cu amount.
4.3.3.2 The voltage profile and capacities of LiNi\textsubscript{x}Cu\textsubscript{y}Mn\textsubscript{2-x-y}O\textsubscript{4}

Although in previous research\cite{71,73}, the high voltage plateau of 4.95V were attributed to the oxidization of Cu\textsuperscript{2+} to Cu\textsuperscript{3+}, our results show that this may not be true. The calculated voltage corresponding to the oxidization from Cu\textsuperscript{2+} to Cu\textsuperscript{3+} in non-defect spinel LiCu\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} is only 4.44V, much lower than the experimentally measured high voltage plateau at around 4.95V but quite close to the low voltage step at around 4.2V. Cu\textsuperscript{3+} ions cannot be further oxidized to higher valences and the extra electrons needed in the high voltage may be provided by oxygen densities. This conclusion is also supported by our XANES results obtained from LiNi\textsubscript{0.25}Cu\textsubscript{0.25}Mn\textsubscript{1.5}O\textsubscript{4}, in which Cu ions are only oxidized at low voltages between 4.2V and 4.7V. Mn ions are inactive and the high voltage plateau is caused by the Ni\textsuperscript{2+} oxidization, together with possible oxygen charge-loss mechanism as suggested by first principles computation in this work, but cannot be detected by XANES.

In regards to the electrochemical charge-discharge results of LiNi\textsubscript{x}Cu\textsubscript{y}Mn\textsubscript{2-x-y}O\textsubscript{4}, the capacity contributed by the second plateau between 4.2 to 4.6V increases with the increase of doped Cu amount (Table 4-4). This trend is consistent with the above conclusion, as more Cu\textsuperscript{2+} ions are present and oxidized to Cu\textsuperscript{3+} ions. However, when more Cu ions are doped, the total capacity of LiNi\textsubscript{x}Cu\textsubscript{y}Mn\textsubscript{2-x-y}O\textsubscript{4} keeps on decreasing. The capacity of LiCu\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} is just slightly higher than half of the capacities of undoped NiMn spinel materials. It suggests that in Cu doped NiMn spinel, not all Li ions can be electrochemically extracted. Two reasons may be attributed to this phenomenon. 1) As Cu ions can only provide one electron per atom, extra electron sources are not absolutely confirmed from experiments. Calculation results suggest a possibility that extra electrons may be extracted from oxygen ions, though further investigation is
necessary to confirm the exact electron sources. 2) The first principles calculations show that when tetrahedral Cu ions are presented, Li in octahedral sites prefer to be extracted first. However, with tetrahedral Li and Cu ions blocking the diffusion paths, some octahedral Li ions may never be extracted. On the other hand, it is possible that voltage plateaus higher than 5V may exist but cannot be obtained due to cut off voltage limit imposed by the electrolyte de-composition.

4.3.3.3 Rate capabilities of LiNi\textsubscript{x}Cu\textsubscript{y}Mn\textsubscript{2-x-y}O\textsubscript{4}

Although the reversible capacity is partially affected, a suitable amount of Cu doping in NiMn spinel may significantly improve the rate capability of the materials. As shown in figure 4-10, LiCu\textsubscript{0.25}Ni\textsubscript{0.25}Mn\textsubscript{1.5}O\textsubscript{4} shows the best rate performance among all the materials. The discharge capacity of LiNi\textsubscript{0.25}Cu\textsubscript{0.25}Mn\textsubscript{1.5}O\textsubscript{4} at C/20 is around 95 mAh/g and 97% of them can be retained at C/2. In the other hand, the discharge capacity of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} at C/20 is 122mAh/g, but it drops to 76mAh/g at C/2. The improvement of rate performance of LiNi\textsubscript{0.25}Cu\textsubscript{0.25}Mn\textsubscript{1.5}O\textsubscript{4} may come from two major sources. 1) The ionic conductivity of the materials is improved by the enhancement of Li mobility. As shown in Figure 4-18(b), the measured lithium diffusion coefficient of LiCu\textsubscript{0.25}Ni\textsubscript{0.25}Mn\textsubscript{1.5}O\textsubscript{4} is significantly larger than that of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} or LiNi\textsubscript{0.45}Mn\textsubscript{1.55}O\textsubscript{4}. A possible reason is that the cation distribution of LiNi\textsubscript{x}Cu\textsubscript{y}Mn\textsubscript{2-x-y}O\textsubscript{4} varies with the change of cation composition. When the amount of Cu doping is in a certain range, the corresponding cation arrangements can provide more local environments that are similar to Figure 4-2(b), therefore may significantly reduce the Li diffusion barriers and improve the overall Li mobility. 2) The LiCu\textsubscript{0.25}Ni\textsubscript{0.25}Mn\textsubscript{1.5}O\textsubscript{4} system experiences smaller strains during the Li-extraction than the non-doped NiMn spinel. For LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} and LiMn\textsubscript{2}O\textsubscript{4}, a second or third cubic phase will form during the charging stage[97]. As the
co-existence of two phases usually causes lattice mismatch as shown in Figure 4-17(b), high stress and strain may be introduced into the non-doped NiMn spinel and affect the stabilities of the systems, especially at high rate. For LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$, however, the ex-situ XRD results (Figure 4-17(a)) shown that, only single cubic phase is present during the charging stage. No phase transition occurs inside the materials, the experienced strains are much less and the system is therefore more stable at high rate. Besides the above two sources, the effect of electrical conductivity may also play a role. It was already reported by M. Kunduraci et al[69] that cation ordered $P4_332$ spinel exhibits less capacity retention than disordered spinel at fast discharge rates. This phenomenon is attributed to the higher electronic conductivity of the disordered spinel. J.Molenda et al.[74] also showed that the electrical conductivity of LiCu$_x$Mn$_{2-x}$O$_4$ would increase with the Cu amount. There are factors that may negatively affect the rate capability of the materials as well, such as the increased particle sizes for Cu doped NiMn spinel and the presence of unmovable tetrahedral Cu that may block the Li diffusion channels. From the experimental results obtained in this work, however, these factors can be compensated by the positive effects discussed previously.

4.4 Summary

In this work, a series of bi-doped spinel oxides of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ ($0<x<0.5$, $0<y<0.5$) have been studied. Their crystal structure, electronic structure and electrochemical properties are compared. A new explanation of the voltage profile for LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ is proposed, supported by the results from first principles computation, and confirmed by electrochemical property measurement and in situ XAS experiment. We have shown that Ni, Cu and Mn are 2+, 2+ and 4+ respectively in the pristine sample and. Cu cannot be further oxidized to Cu$^{4+}$ and the plateau at 4.95V originates
from extra electrons provided by oxygen ions. Li diffusion activation barriers of
$LiM_{1/2}Mn_{3/2}O_4$ ($M=$ Ti, V, Cr, Fe, Co, Ni and Cu) are calculated. The results show that
different dopants can have significant effects on the Li diffusion barriers. Although the
capacity of the doped spinel materials decreases with the increasing doped Cu amount,
$LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ spinel oxideexhibits higher capacity than undoped $LiNi_{0.5}Mn_{1.5}O_4$
spinel at high rates. The good rate capability of $LiCu_{0.25}Ni_{0.25}Mn_{1.5}O_4$ spinel oxideis
attributed to the single phase transformation during charging, the lower Li diffusion
barrier induced by Cu doping, and possibly higher electronic conductivity contributed by
Cu doping.
Table 4-1. Chemical composition of LiNi<sub>x</sub>Cu<sub>y</sub>Mn<sub>2-x-y</sub>O<sub>4</sub>

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Li:Ni:Cu:Mn Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi&lt;sub&gt;0.45&lt;/sub&gt;Mn&lt;sub&gt;1.55&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.02:0.45:0.00:1.55</td>
</tr>
<tr>
<td>LiNi&lt;sub&gt;0.5&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.00:0.51:0.00:1.49</td>
</tr>
<tr>
<td>LiCu&lt;sub&gt;0.05&lt;/sub&gt;Ni&lt;sub&gt;0.45&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.96:0.45:0.05:1.50</td>
</tr>
<tr>
<td>LiCu&lt;sub&gt;0.1&lt;/sub&gt;Ni&lt;sub&gt;0.40&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.97:0.39:0.10:1.51</td>
</tr>
<tr>
<td>LiCu&lt;sub&gt;0.25&lt;/sub&gt;Ni&lt;sub&gt;0.25&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.97:0.25:0.26:1.49</td>
</tr>
<tr>
<td>LiCu&lt;sub&gt;0.5&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.96:0.00:0.49:1.51</td>
</tr>
</tbody>
</table>

Table 4-2. I(400)/(311) Integrated intensity ratios of XRD spectrum of LiNi<sub>x</sub>Cu<sub>y</sub>Mn<sub>2-x-y</sub>O<sub>4</sub>

<p>| LiNi&lt;sub&gt;0.45&lt;/sub&gt;Mn&lt;sub&gt;1.55&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; | 1.354 |
| LiNi&lt;sub&gt;0.5&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; | 1.278 |
| LiCu&lt;sub&gt;0.05&lt;/sub&gt;Ni&lt;sub&gt;0.45&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; | 1.294 |
| LiCu&lt;sub&gt;0.1&lt;/sub&gt;Ni&lt;sub&gt;0.40&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; | 1.121 |
| LiCu&lt;sub&gt;0.25&lt;/sub&gt;Ni&lt;sub&gt;0.25&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; | 0.854 |
| LiCu&lt;sub&gt;0.5&lt;/sub&gt;Mn&lt;sub&gt;1.5&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; | 0.983 |</p>
<table>
<thead>
<tr>
<th>Materials</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>a=8.1809±0.0001</td>
</tr>
<tr>
<td></td>
<td>Z(O)= 0.2625±0.0001</td>
</tr>
<tr>
<td></td>
<td>Rwp =6.35 RB= 2.32</td>
</tr>
<tr>
<td>NiO</td>
<td>a=4.1517±0.0001</td>
</tr>
<tr>
<td></td>
<td>Rwp =5.15 RB= 4.25</td>
</tr>
<tr>
<td>LiNi$<em>{0.45}$Mn$</em>{1.55}$O$_4$</td>
<td>a=8.1739±0.0001</td>
</tr>
<tr>
<td></td>
<td>Z(O)= 0.2623±0.0001</td>
</tr>
<tr>
<td></td>
<td>Rwp =4.62 RB= 4.87</td>
</tr>
<tr>
<td>LiCu$<em>{0.05}$ Ni$</em>{0.45}$ Mn$_{1.5}$ O$_4$</td>
<td>a=8.1693±0.0001</td>
</tr>
<tr>
<td></td>
<td>Z(O)= 0.2618±0.0001</td>
</tr>
<tr>
<td></td>
<td>n Cu(in Li site)= 0.012±0.001</td>
</tr>
<tr>
<td></td>
<td>Rwp =5.02 RB= 4.44</td>
</tr>
<tr>
<td>LiCu$<em>{0.1}$ Ni$</em>{0.40}$ Mn$_{1.5}$ O$_4$</td>
<td>a=8.1795±0.0001</td>
</tr>
<tr>
<td></td>
<td>Z(O)= 0.2621±0.0001</td>
</tr>
<tr>
<td></td>
<td>n Cu(in Li site)= 0.040±0.001</td>
</tr>
<tr>
<td></td>
<td>Rwp = 8.03 RB= 4.08</td>
</tr>
<tr>
<td>LiCu$<em>{0.25}$ Ni$</em>{0.25}$ Mn$_{1.5}$ O$_4$</td>
<td>a= 8.1991± 0.0001</td>
</tr>
<tr>
<td></td>
<td>Z(O)= 0.2633±0.0001</td>
</tr>
<tr>
<td></td>
<td>n Cu(in Li site)= 0.133±0.010</td>
</tr>
<tr>
<td></td>
<td>Rwp = 8.56 RB= 4.10</td>
</tr>
<tr>
<td>LiCu$<em>{0.5}$ Mn$</em>{1.5}$ O$_4$</td>
<td>a=8.2131± 0.0001</td>
</tr>
<tr>
<td></td>
<td>Z(O)= 0.2646±0.0001</td>
</tr>
<tr>
<td></td>
<td>n Cu(in Li site)= 0.112±0.010</td>
</tr>
<tr>
<td></td>
<td>Rwp =7.24 RB= 5.62</td>
</tr>
</tbody>
</table>
Table 4-4. Charge capacity (mAh/g) of \( \text{LiNi}_{x}\text{Cu}_{y}\text{Mn}_{2-x-y}\text{O}_4 \) at low voltage range

<table>
<thead>
<tr>
<th></th>
<th>Capacity (mAh/g) of 4V</th>
<th>Capacity (mAh/g) from 4.2V-4.6V</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi(<em>{0.45})Mn(</em>{1.55})O(_4)</td>
<td>23.18</td>
<td>0</td>
</tr>
<tr>
<td>LiNi(<em>{0.5})Mn(</em>{1.5})O(_4)</td>
<td>17.63</td>
<td>0</td>
</tr>
<tr>
<td>LiCu(<em>{0.05})Ni(</em>{0.45})Mn(_{1.5})</td>
<td>21.27</td>
<td>0</td>
</tr>
<tr>
<td>LiCu(<em>{0.1})Ni(</em>{0.40})Mn(_{1.5})O(_4)</td>
<td>21.31</td>
<td>10.54</td>
</tr>
<tr>
<td>LiCu(<em>{0.25})Ni(</em>{0.25})Mn(_{1.5})O(_4)</td>
<td>23.12</td>
<td>20.83</td>
</tr>
<tr>
<td>LiCu(<em>{0.5})Mn(</em>{1.5})O(_4)</td>
<td>23.14</td>
<td>28.46</td>
</tr>
</tbody>
</table>

Figure 4-1. Structure of LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\)
Figure 4-2. Local environments of transition metal ion rings (a) Three M ions in the ring; (b) One M ion in the ring

Figure 4-3. Li diffusion barriers in LiM_{0.5}Mn_{1.5}O_{4} (M= Cr, Fe, Co, Ni, Cu, Mn) calculated by GGA
Figure 4-4. Calculated DOS of Cu in LiₓCu₁/₂Mn₃/₂O₄ (a) x=1 (b) x=1/2 (c) x=0)
Figure 4-4. Continued

Figure 4-5. X-ray diffraction patterns of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$
Figure 4-6. Refinement Results of (a) LiNi$_{0.45}$Mn$_{1.55}$O$_4$ (b) LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (c) LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$
Figure 4-6. Continued

Figure 4-7. Lattice parameters of LiNi$_{0.5-x}$Cu$_x$Mn$_{1.5}$O$_4$ (x=0,0.05,0.1,0.25,0.5)
Figure 4-8. FESEM images of $\text{LiNi}_x\text{Cu}_y\text{Mn}_{2-x-y}\text{O}_4$ (a) $\text{LiNi}_{0.45}\text{Mn}_{1.55}\text{O}_4$ (b) $\text{LiNi}_{0.9}\text{Mn}_{1.5}\text{O}_4$ (c) $\text{LiNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{1.5}\text{O}_4$ (d) $\text{LiNi}_{0.4}\text{Cu}_{0.1}\text{Mn}_{1.5}\text{O}_4$ (e) $\text{LiNi}_{0.25}\text{Cu}_{0.25}\text{Mn}_{1.5}\text{O}_4$ (f) $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$
Figure 4-9. (a) Charge Curves of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ (b) Discharge Curves of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$. Voltage window of 5.0-3.0V were used.
Figure 4-10. Rate Capability of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$

Figure 4-11. The cycling performance of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$
Figure 4-12. Charge curve of LiNi$_{0.25}$Cu$_{0.25}$Mn$_{1.5}$O$_4$ for XANES experiment
Figure 4-13. (a) The Cu K-XANES spectra of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ measured as a function of voltage (b) 2nd order derivative of Cu K-edge XANES spectra of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ measured as a function of voltage
Figure 4-14. (a) The Ni K-XANES spectra of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ measured as a function of voltage.(b) 2nd order derivative of Ni K-edge XANES spectra of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ measured as a function of voltage
Figure 4.15. (a) The Mn K-XANES spectra of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_{4}$ measured as a function of voltage (b) 2nd order derivative of Mn K-edge XANES spectra of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_{4}$measured as a function of voltage
Figure 4-16. XPS plots of the Cu2p, Ni2p and Mn2p region scans for LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ (a) Cu(b)Ni(c)Mn
Figure 4-16. Continued
Figure 4-17. (a) The XRD pattern of the LiNi$_{0.25}$Cu$_{0.25}$Mn$_{1.5}$O$_4$ sample at different voltage during the second charge process (b) The XRD pattern of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ sample at different voltage during the second charge process[97]
Figure 4-18. (a) PITT profile for LiNi_{0.25}Cu_{0.25}Mn_{1.5}O_4 sample (b) Diffusion Coefficient of LiNi_{0.45}Mn_{1.55}O_4, LiNi_{0.5}Mn_{1.5}O_4 and LiNi_{0.25}Cu_{0.25}Mn_{1.5}O_4.
CHAPTER 5
TIO₂ FLAKES AS ANODE MATERIALS FOR LI-ION-BATTERIES

5.1 Introduction

Anatase titanium dioxide is a promising negative electrode material for Li-ion batteries due to its safety against overcharging and stable voltage plateau at 1.78 V, which made it possible to be paired with high voltage (5 V) cathode materials such as LiNi₀.₅Mn₁.₅O₄.[13, 67, 98]. However, the low electrical conductivity, poor rate capability and poor cycling performance caused by the structural changes during the lithiation process have limited its applications.

Several different methods have been developed to address these issues. Wagemaker [99] investigated the dependence of insertion reactions to titanium dioxide particle sizes and revealed progressively increasing Li capacity and Li-ion solubility with decreasing particle sizes. This result was also confirmed by other groups[100-102]. Besides the nanosized particle samples, various of titanium dioxide with different phases had been fabricated by several groups. Bruce et al [98, 103-105] synthesized TiO₂-B nanowires by a hydrothermal reaction to increase the discharge capacity and improve the cycling performance. Hu et al [106] proved that difference occurs in the Li-incorporation amount between bulk and nanosized TiO₂ with rutile phase. Nevertheless, the difficulty of fabricating the nano-sized rutile TiO₂ limits its validity. Moreover, various of nanostructures had also been fabricated, such as nanofibers[107], nanorods[108], nanotubes[109-111], mesoporous films[112, 113], laminar TiO₂[114] and hollow ribbon nano-network structures[115], which were characterized with different surface areas, porosities and shapes that can significantly enhance the kinetics and improve electrochemical properties[116-118]. Using these low dimensional nanostructures as
the building blocks, new electron and ion transportation pathways can be established as a new strategy.

Although many different synthesis methods were developed, these processes are complex, time-consuming and difficult to be applied in large-scale synthesis. To reduce the complexity and the price of precursors of conventional synthesis process, such as non-ionic surfactant template method and sol-gel method[119, 120], a simple spreading method was used in this paper to make novel TiO$_2$ flakes. In particular, the porous TiO$_2$ flakes exhibit larger reversible charge/discharge capacity, better rate capability and excellent cycling stability compared to anatase titanium dioxide nanoparticles. The thermal reaction process of the flakes was investigated by thermogravimetric-differential thermal analysis (TG/DTA). The phase, structure, morphology and size distribution were examined by X-ray diffraction (XRD), high-resolution transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The surface area and pore sizes were monitored by physisorption measurements. The relations between crystal structure, surface area, pore volume and electrochemical properties of anatase TiO$_2$ flakes were examined. The nano-sized grains of TiO$_2$ flakes, the pore volume and the surface area are all key factors contributing to the enhanced electrochemical properties.

5.2 Experimental Methods

5.2.1 Sample Preparation

Titanium dioxide flakes (F-TiO$_2$) were fabricated by spreading a mixture of stearic acid (Fisher, 99%), low surface tension hydrocarbon (Fisher, 97%) and titanium $n$-butoxide (Aldrich, 97%) on the surface of high purity water (Barnstead Nanopure Infinity, 18 MΩ/cm$^{-1}$). Stearic acid and the hydrocarbon were used to decrease the
viscosity of titanium dioxide precursor and enhance the spreadability of the mixture.

Typically, a ratio of 1:8 of titanium $n$-butoxide to hydrocarbon was used to produce titanium dioxide flakes with thickness about 40 nm. The resulting slurry was washed with Nanopure water and then centrifuged (Begman BH-2) at 3000 rpm for 15 minutes to concentrate the slurry. The precursor was then suspended in isopropanol and centrifuged to remove further impurities. This process was repeated for a total of five times. After solvent exchanging with isopropanol alcohol ($(\text{CH}_3)_2\text{CHOH}$), the flakes were dried by a supercritical fluid drying process [121]. The 400°C heat treatments were applied using a programmable electric furnace with a desired heating rate of 1 °C/min for two hours in the air to make the calcined flakes (CF-TiO$_2$).

5.2.2 Characterization

Differential thermal analysis-thermogravimetry TG/DTA measurements were carried out by a Pyris diamond TG/DTA at a heating rate of 20 °C/min with a 200 ml/min flow rate in $\text{N}_2$ to understand the thermal reaction process such as weight loss and phase formation temperature of the F-TiO$_2$. X-ray powder diffractions of all samples were taken using XRD Philips APD 3720 using a Cu Kalpha radiation source operated at 45 kV and 20 mA. The scan speed was 3 sec/step with a step size of 0.02 degree in two theta. A Quantachrome NOVA 1200 was used to perform the physisorption measurements. Surface area and average pore size can be determined based on the measurement. Field emission scanning electron microscopy (FEG-SEM, JEOL JSM-6335F) was carried out to investigate the particle sizes and morphologies. Images were collected with an accelerating voltage of 10 kV. The sizes of the flakes distribution were examined by Particle Size Analyzer Coulter LS13320. The flakes were suspended on a copper grid with lacey carbon and investigated by using a field emission gun JEOL.
2010F high-resolution transmission electron microscopy (TEM) with an accelerating voltage of 200 kV. The band gap of the titania samples were estimated by UV-visible diffuse reflectance spectroscopy using a Perkin-Elmer Lambda 800 UV/Vis spectrometer in the wavelength range of 250-500 nm.

5.2.3 Electrochemical Testing

The electrochemical properties of anatase TiO$_2$ particles (Fisher, 99.9%, average size 50 nm diameter seen by SEM), F-TiO$_2$ and CF-TiO$_2$ electrodes were measured using 2016 coin cells consisting of metallic lithium as an anode and an electrolyte comprised of 1M LiPF$_6$ ethylene carbonate (EC)/dimethyl carbonate (DMC) with 1:1 volume ratio. A Celgard model C480 separator (Celgard Inc.USA) was used. Anode films were prepared from slurries of TiO$_2$ nanomaterials with 20 % polyvinylidene fluoride (PVDF) and 20 % acetylene carbon black dissolved in N-methyl-2-pyrrolidinone (NMP). The mixtures were cast onto Al foil using a doctor blade and dried at 100 °C overnight. The cast film was cut into cathode discs containing 2-3 mg of active materials before storing them in argon filled glove box (H$_2$O level<1.6 ppm). The coin-cells were assembled in the glove box and tested using an Arbin BT2000 instrument in galvanostatic mode. The tests were conducted between 3.5 V and 1 V at a constant current rate of C/20, C/10, C/5, C/2 C and 2C. For cycling performance, tests were conducted with a voltage window between 3.5 V and 1 V at a constant current rate of C/20.

5.3 Results and Discussion

5.3.1 Materials Characterization

Figure 5-1 shows the TG-DTA curves for the F-TiO$_2$ with a weight loss of about 9 % at the temperature range from room temperature to 400 °C, which was resulted
from either the desorption of water and isopropanol or the decomposition of organic compounds. According to the DTA data, a broad endothermic peak around 150 °C is present and is attributed to the loss of water and the organic residues absorbed at the surface of the flakes. There is a relatively small exothermic peak at 255 °C that was contributed to the decomposition of titanium n-butoxide in the pristine F-TiO$_2$. The observed peaks shown at 400 °C and 600 °C were contributed by the phase transformations from amorphous to crystalline anatase phase, and from anatase phase to the rutile phase, respectively.

Crystalline structural changes of the F-TiO$_2$, CF-TiO$_2$ and particles (Fisher, average 50 nm diameter) were monitored by XRD. As shown in Figure 5-2, the F-TiO$_2$ shows broadened and weak Bragg peaks, which indicate that the flakes are partially amorphous with presence of the crystalline anatase phase. After a 2 hr heat treatment at 400 °C, the expected phase transformation from the amorphous to crystalline anatase titanium dioxide was confirmed by the seven distinct characteristic diffraction peaks. The XRD results were identical to the TG-DTA results confirming that the heat treated flakes were converted to a pure crystalline anatase phase. There is no indication of any rutile phase by XRD. Compared to the powder sample, the diffraction peaks of the flakes are broadening and overlap with each other due to the smaller grain size. The average crystal grain size can be calculated by the Scherrer equation

$$d = \frac{k\lambda}{B\cos\theta_B}$$  (5-1)

Where $d$ is the calculated grain size, $\lambda$ is the wavelength of X-ray (Cu Kα 1.54 Å), $B$ is the full-width at half-maximum intensity, and $\theta_B$ is the Bragg diffraction angle. The grain sizes of F-TiO$_2$ and CF-TiO$_2$ are 4 nm and 9 nm respectively.
SEM was performed to examine the particle size and morphologies of TiO$_2$ flakes. The surface morphology of F-TiO$_2$, and the thickness are shown in Figure 5-3(a)-(d). The lateral dimension of the F-TiO$_2$ was found to be in the order of 20-30 μm (Figure 5-3(a)), and the thickness of these flakes is approximately 40 nm (Figure 5-3(c)). The apparent thin-sheet morphology was explored and the aspect ratio of the lateral dimension to thickness ranged from 250:1 to 500:1. The flakes were further treated by calcination at 400 °C in air for 2 hrs. Aggregation was not apparent when comparing the CF-TiO$_2$(Figure 5-3(b)) with the F-TiO$_2$(Figure 5-3(a)). Moreover, the thickness of the CF-TiO$_2$ did not change by the heat treatment, as shown in Figure 5-3(d).

A comparison of the measured particle size distribution of F-TiO$_2$ and CF-TiO$_2$ by laser diffraction is shown in Figure 5-4. With the differential volume distribution of flakes that moved in turbulence and passed the laser beam, the maximum diameter was measured through the average random orientation of the flakes. The lateral dimension of flakes were estimated by dispersing both flakes in deionized water with liquid modules and were fairly close to the results taken from the SEM images (Figure 5-3(a) and (b)). The D10, D50, D90, mean and standard deviation values for the particle size distributions are shown in Table 5-1. F-TiO$_2$ has a broad size distribution spanning from 1-100 μm while the D50 for the F-TiO$_2$ and CF-TiO$_2$ are of 39.1 and 23.5 μm, respectively. It is evident that some larger flakes broke or cracked during dehydration and crystallization.

The crystalline structure of the flakes was further investigated under HR-TEM. The images show that the F-TiO$_2$, and CF-TiO$_2$ were comprised of crystalline platelets
of about 5 and 8 nm in diameter (Figure 5-5(a)(b)), respectively. The interference lattice fringes can be seen in the TEM images and has a separation distance of 0.35 nm, corresponding to the interplanar spacing of the (101) planes for anatase [122]. Random orientation of individual grains over both F-TiO$_2$ and CF-TiO$_2$ samples is observed from the concentric diffraction rings in the selected area diffraction mode and consistent with the anatase (101), (004), (200), (105) diffraction planes (the insets of Figure 5-5(a) and (b)). On a closer inspection, an amorphous layer can be seen surrounding the smaller crystallites in the F-TiO$_2$ sample. An overall dense structure was seen in the F-TiO$_2$, as shown in Figure 5-5(c). After the calcination process, pores with an average size of 7 nm were developed, as shown in Figure 5-5(d), due to local rearrangement caused by the growth of crystal grains and by removing the residual solvent. Consequently, it is considered that the CF-TiO$_2$ are polycrystalline consisting of fine nano-grains and nano-size pores.

In order to investigate the change of surface area and porosity after the calcination treatments, the nitrogen absorption isotherms were used. Higher specific surface areas of anode materials can increase the electrode and electrolyte contact area. Compared to a commercial TiO$_2$ nanoparticles, the surface area of F-TiO$_2$ was 15 times higher (in Table 5-2), while the surface area of the CF-TiO$_2$ was still 7.5 times higher than that of TiO$_2$ nanoparticles. The BET measurements also show that the pore size of the calcined flakes is about 7.2nm, which is consistent with the TEM observation.

Figure 5-6 shows the typical UV-visible diffuse reflectance spectra in the wavelength range of 250-500 nm for the F-TiO$_2$ and CF-TiO$_2$. The sharp decrease in the diffuse reflectance in the UV region is attributed to the fundamental light absorption of
the TiO$_2$ flakes. The spectral profile for CF-TiO$_2$ was apparently blue-shifted compared with that of the F-TiO$_2$. The general relation between the absorption coefficient and the band gap energy is given by the equation:

$$(\alpha h \nu)^m = h\nu - E_g$$

(5-2)

Where $m$ is an index depending on the nature of the electron transitions, $\alpha$ is the absorption coefficient, $h$ is the Planck constant, $\nu$ is the frequency of electromagnetic radiation, and $E_g$ is band gap energy of the semiconductor. The estimated band gap energies of the as-prepared and calcined flakes are 3.25 and 3.33 eV, respectively. Both values are higher than the band gap energies of nanoparticles (3.2 eV). The increase of the band gap is most likely due to the quantum confinement effect [122].

5.3.2 Electrochemical Properties

5.3.2.1 Charge-discharge studies

The electrochemical properties of the TiO$_2$ powder, F-TiO$_2$ and CF-TiO$_2$ were investigated using lithium half-cells with a constant current 0.1 mA/cm$^2$. The first discharge/charge profiles between 3.5 and 1.0 V are shown in Figure 5-7(a)(b). As Figure 5-7(a) shows, there is a plateau around 1.75 V for TiO$_2$ nanoparticles and CF-TiO$_2$ that corresponds to the occurrence of the two phase equilibrium of Lithium-poor (Li$_{0.01}$TiO$_2$) and Lithium-rich (Li$_{0.6}$TiO$_2$) domains[123]. However, there is no voltage plateau observed in the F-TiO$_2$. The amorphous phase of the F-TiO$_2$ seen by TEM and the smaller grain size [99] may be the contributing factors to the sloping voltage curve. The lithium intercalation/deintercalation reaction in this region can be written as

$$TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2$$

(5-3)
The amount of lithium insertion depends on the crystallinity, morphology as well as the microstructure. Generally, increasing the specific surface area or decreasing the particle size for anatase TiO$_2$ particles can increase the discharge capacity [100]. In our work, the flakes show a similar trend. The capacity, grain size and specific surface area for F-TiO$_2$, CF-TiO$_2$ and nanoparticles are (238 mAh/g, 5 nm, 309 m$^2$/g), (213 mAh/g, 8 nm, 151 m$^2$/g), and (170 mAh/g, 50 nm, 20 m$^2$/g) respectively. Although the F-TiO$_2$ have the largest 1$^{st}$ cycle discharge capacity, the first cycle charge capacity is very small, as shown in Figure 5-7(b). Apparently, the lithiation reaction was not reversible for the F-TiO$_2$. Although the surface area and the grain size are key factors to determine the electrochemical properties, the amorphous phase (Figure 5-2, Figure 5-5(a)), residual organic precursors (Figure 5-1) and denser microstructure (Figure 5-5(c)) lead to the poor electrochemical performance. The supercritical drying process during the preparation of the F-TiO$_2$ can induce a partially crystallized anatase phase and keep the largest surface area, but the enhanced electrochemical performance can be achieved only after the 400˚C post-synthetic calcination process. For the anatase TiO$_2$ nanoparticles, the discharge/charge capacity is about 170 mAh/g, corresponding to Li$_{0.5}$TiO$_2$ that is identical to the conventional anatase TiO$_2$ materials. The CF-TiO$_2$ exhibit a 1$^{st}$ cycle discharge capacity exceeding 200 mAh/g and subsequent discharge/charge capacities of 180 mAh/g. Interesting observations can be made through comparing the discharge and charge curves in Figure 5-7: The length of the biphasic region (plateau region) corresponds to the number of lithium ions inserted into the bulk lattice [100]. Therefore, the capacity in the plateau region should decrease for smaller grain sizes, as observed by others [100]. Although the grain size of the CF-
TiO₂(8 nm) is much smaller than that of the nanopowders (50 nm), the capacity of the plateau region is similar to that of nanoparticles. Obviously, the CF-TiO₂ still keep some bulk characteristics. On the other hand, the capacity of the sloping region for CF-TiO₂ is larger than that in the TiO₂ nanoparticles, thus implies that Li ions are further inserted into the surface layer[101]. Upon the first charging, a sloping region can be clearly observed at the beginning of the charge as well. Wagemaker et al have shown that anatase TiO₂ nanoparticles can completely convert to the Li₁TiO₂ phase if the particle size is smaller than 7 nm, as shown in Figure 5-8(a)[99]. The grain sizes of the flakes are between 5-8 nm which suggests the new Li₁TiO₂ phase may form during the lithiation process and lead to a larger capacity compared to that of the nanoparticles (50 nm). In theory, the bulk Li₀.₅TiO₂ and LiTiO₂ phase have distinct diffraction peaks and the extra peaks should be detected by the ex-situ XRD. However, it is difficult to differentiate the overlapping peaks of nano-sized Li₀.₅TiO₂ and LiTiO₂ because the serious peak broadening for the nano-sized materials. The XRD patterns of Li₀.₅TiO₂ and LiTiO₂ were simulated using the Crystal Diffraction software with 5 nm particle size, shown in Figure 5-8(b).The major peaks of Li₀.₅TiO₂ and LiTiO₂ overlap significantly. In practice, the peak broadening from the laboratory instrument also has to be considered. Therefore, the Li₁TiO₂ phase cannot be identified clearly by conventional laboratory XRD. High-resolution neutron diffraction experiments are necessary to identify the detailed structural change. According to Wagemaker et al[4], the neutron diffraction has identified the new LiTiO₂ phase in 7 nm TiO₂ nanoparticles.

5.3.2.2 Rate apability performance

To study the rate capability of TiO₂ nanomaterials, electrodes were made with similar loading of active materials in each cell (about 5 mg active material/cm²). For
each material, the cells were discharged to 1 V at constant rates (C/20) and charged to 3.5 V at various current rates (C/20, C/10, C/5, C/2, C and 2C). The measured 1st cycle charge capacities with different current density were shown in Figure 5-9. Clearly, CF-TiO₂ shows better rate performances than TiO₂ nanoparticles. The charge capacity of the CF-TiO₂ tested at 2C still retains 48.44 % of its capacity, compared to the capacity at C/20. On the other hand, the charge capacity of TiO₂ nanoparticles tested at 2C decreased to 26.81 %, compared to the capacity at C/20.

Nano size effects of electrochemical energy storage systems can be divided into two categories ;[117] The first is the true size effects, which involve changes of actual materials, including the change of structure and phase stability, electronic band gap and intrinsic diffusivity etc. The second is the trivial size effects, and the result of trivial size effect is largely relied on the surface-to-volume ratio, the shape and the pores of the nanomaterials.

TiO₂ is an intrinsically low electronic conductive material. The quantum confinement effects show that the band gap will increase for decreased particle size, confirmed in our UV-Vis diffuse reflectance measurement. The band gap of nanoparticles, F-TiO₂ and CF-TiO₂ are 3.20 eV, 3.25 eV and 3.33 eV respectively. This implies that the intrinsic electronic conductivity of the calcined TiO₂ flakes will decrease. Moreover, Wagemaker et al [124, 125] used static ⁷Li NMR T2 relaxation measurements to detect the Li-ion mobility of micro and nanosize anatase TiO₂. The result shows that the lithium diffusion coefficient for nanomaterials is lower than that for the microsized materials. Nevertheless, our electrochemical data clearly show that the CF-TiO₂ have superior electrochemical properties.
For the flakes, the *trivial* size effects should be the key factors that contribute to the excellent rate capability. The specific surface area of the CF-TiO₂ is 7.5 times than the nanoparticles. The large surface area can lead to larger electrode/electrolyte contact area that can improve the ionic conductivity. At the same time, nanostructured materials can supply the short Lithium ions and electron transportation distance even though the nanomaterials have intrinsically lower electronic and ionic conductivity. Considering that the diffusion length is scaled with time by \( l \propto t^2 \), the Li diffusion time may be much lower for 8 nm grains in the CF-TiO₂. Moreover, the lower specific current density of flakes can be contributed by the larger surface area of nanostructured electrodes and the excellent rate performance can be achieved by the lower specific current density. [117].

**5.3.2.3 Cycling performance**

The cycling performance of CF-TiO₂ and TiO₂ nanoparticles at a constant current density (C/20) was shown in Figure 5-10. TiO₂ nanoparticles show a fast fading with the increasing of cycle number, while there is virtually no fading for the CF-TiO₂. The F-TiO₂ have poor cycling performance due to the residual solvent or amorphous phase present. CF-TiO₂ with nano-grains and nano-porous structure show an excellent cycling performance with high capacity. This makes it become a excellent anode candidate for Li-ion batteries. The porous structure is expected to supply the space to accommodate the volume change and preventing the undesired fractures or electronic disconnects of the electrode materials during the de-lithiation and lithiation process[107]. On the other hand, the lack of a two-phase boundary in nanosize < 8 nm TiO₂ is another possible reason for the improved cycling performance. Previous work by neutron diffraction shows two different lithiated mechanisms for the bulk and nano size anatase
materials[99, 126]. For bulk materials, the Li-titanate crystal phase will grow at the cost of the crystal anatase phase and induce extra strain during the lithiation process. However, for nano-sized particles (7 nm), either the anatase or the Li-titanate phase is detected during the lithiation process. This indicates that in extremely small particles, the two phases do not coexist in the same particle during the insertion process, as shown in Figure 5-11. The unique nano-grains and nano-porous structure in CF-TiO$_2$ and the possible elimination of the phase boundary during lithiation lead to the excellent cycling performance.

The advantage of the porous structure can be tarnished by the low volumetric energy density. However in the case of flakes, it is possible to improve the volumetric energy density by packing the sheets of flakes aligned in a horizontal orientation. This methodology is in development and will be reported elsewhere.

5.4 Summary

In this work, titanium dioxide flakes were fabricated by a simple spreading method. This process is easy and scalability is high. The low surface tension hydrocarbon and titanium n-butoxide were used as the precursors and continuously added into the solution on the surface of flowing water. A supercritical drying process was performed to remove the residual water. The size of the synthesized flake is about 40nm in the lateral dimension and was composed of 5nm nanograins. After a 400 °C calcination process, the flakes transformed into a pure anatase phase that is free of any impurity. In this phase, the flakes are characterized to have 8 nm grains and the 7nm pores. The crystal structure, surface area, pore size, electronic properties and electrochemical properties are compared for flakes and nanoparticles. The electrochemical and structural properties of the flakes are significantly influenced by
subsequent heat treatment process. The CF-TiO$_2$ exhibits larger reversible charge/discharge capacity, better rate capability and excellent cycling stability. The nano-sized grains (8 nm) may lead to the absence of two-phase in single particles during lithiation, improving the cycling performance significantly. A larger interface between electrode and electrolyte, the short diffusion path of lithium ions and electron and lower specific current density of in the CF-TiO$_2$ lead to a much better rate capability.
Table 5-1. Particle diameter statistics for F-TiO\textsubscript{2} and CF-TiO\textsubscript{2}

<table>
<thead>
<tr>
<th></th>
<th>D10(µm)</th>
<th>D50(µm)</th>
<th>D90(µm)</th>
<th>Median(µm)</th>
<th>StandardDeviation(µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-TiO\textsubscript{2}</td>
<td>5.2</td>
<td>39.1</td>
<td>81.6</td>
<td>20.8</td>
<td>58.9</td>
</tr>
<tr>
<td>CF-TiO\textsubscript{2}</td>
<td>5.1</td>
<td>23.5</td>
<td>50.1</td>
<td>16.4</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Table 5-2. Surface area and pore size of TiO\textsubscript{2} particles, F-TiO\textsubscript{2} and CF-TiO\textsubscript{2}

<table>
<thead>
<tr>
<th></th>
<th>Specific surface area (m\textsuperscript{2}/g)</th>
<th>Specific pore volume (cm\textsuperscript{3}/g)</th>
<th>Average pore diameter(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-TiO\textsubscript{2}</td>
<td>309</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF-TiO\textsubscript{2}</td>
<td>151</td>
<td>0.511</td>
<td>7.2</td>
</tr>
<tr>
<td>Particles</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5-1. TG/DTA measurements of F-TiO₂

Figure 5-2. X-ray diffraction patterns of TiO₂ samples.
Figure 5-3. FESEM images of TiO₂ samples. (a) F-TiO₂ (b) CF-TiO₂ (c) edge view of F-TiO₂ (d) edge view of CF-TiO₂
Figure 5-4  Particle size distribution for F-TiO$_2$ and CF-TiO$_2$ by laser diffraction
Figure 5-5. HR-TEM images of TiO$_2$ samples (the SAD pattern as inset). (a) F-TiO$_2$ (b) CF-TiO$_2$. The diffraction rings are indexed as (1) 101 (2) 004 (3) 200 (4) 105 for anatase. (c) F-TiO$_2$ (d) CF-TiO$_2$
Figure 5-6. UV-visible diffuse reflectance spectra of F-TiO$_2$ and CF-TiO$_2$
Figure 5-7. (a) First discharge curves of TiO$_2$ samples (b) First charge curves of TiO$_2$ samples
Figure 5-8. (a) Neutron diffraction patterns of maximum lithiated LixTiO\textsubscript{2} for different particle sizes[30]. (b) The XRD patterns of Li\textsubscript{0.5}TiO\textsubscript{2}, LiTiO\textsubscript{2} simulated by Crystal Diffraction.
Figure 5-9. Rate capability comparison of CF-TiO$_2$ and TiO$_2$ particles.

Figure 5-10. The variation of specific discharge capacity with respect to the cycle number of CF-TiO$_2$ and particles.
Figure 5-11. Lithiation mechanism of bulk and nanosized material[30]
6.1 Introduction

Capacity fading does not create from single source, the fading mechanism was contributed by interaction of different processes. Since the processes happen at same timescales the understanding of fading mechanisms is limit. The major factors induce the capacity fading are summarized as follows [12, 65, 127, 128]

6.1.1 Inactive Materials

Conventional cathode electrode consisted of active material, conductive additive and polymer binder to enhance the electronic conductivity and binding the particles together. The corrosion of metal, the reaction of binder and carbon additives with electrolyte during charge/discharge process may induce capacity fade.

6.1.2 Structural Changes During Cycling(Jahn–Teller Distortion)

If an extra lithium ion is introduced into LiMn$_2$O$_4$ lattices, the valence of Mn will decrease and the injected electrons will occupy Mn-$e_g$ orbitals. The enhanced interaction of Mn-$e_g$ and O-$2p$ orbitals create the instability of the lattice. In order to decrease the repulsion force, the lattice expands and the cubic phase transfer to tetragonal structure [9]. The capacity loss on cycling at 3 V is thought to be mainly a result of Jahn- Teller distortion, which causes a 16% increase in the $c/a$ ratio of the unit cell during extraction and insertion of lithium from or into this spinel.

6.1.3 Structural Changes of Delithiated Lithium Manganese Spinel;

With the delithiation process, an ordered superstructure Li$_{0.5}$Mn$_2$O$_4$[129] will form with the double hexagonal phase[130] and lead to the structure change during
charge/discharge process. The phase transformation should be avoided in order to keep the stable structure.

6.1.4 Chemical Dissolution Reaction;

At high temperature, the metal dissolution reaction in electrolyte leads to serious capacity fading. The weight loss of manganese dissolution leads to the decreasing of capacity. Moreover, the impedance increases due to the compound formed by the side reaction, such as MnF₂ and MnCO₃. Finally the Mn³⁺ will move to anode and included in the SEI.

Manganese ions can be dissolved by two different mechanisms.

At low operating voltage, Mn³⁺ will disproportionate into Mn³⁺ and Mn²⁺ the basic chemical con be expressed as follows[131]:

\[ 2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+} \]

The Mn²⁺ ions will be dissolved into the electrolyte and lost the weight of active material. At high voltage, The hydrolysis reaction of the LiPF₆ electrolyte leads the formation of LiPF₅ and F₂. If any water present, the active material will be dissolved by the formed HF [132].

6.1.5 Oxidation of Electrolyte Components And Surface Film Formation

The increase of the impedance will induce the power loss and the high temperature and high operation voltage will accelerate the reaction. The oxidation of electrolyte components and the carbonate film formed at surface induce the surface films. Some gaseous also formed by the side reaction of the electrolyte[134].

This work aims to fabricate the high voltage LiMn₂₋ₓNiₓO₄₋₅ and explore the intrinsic surface stability in the high voltage LiMn₂₋ₓNiₓO₄₋₅ spinel-type cathode. Compare
to LiMn$_2$O$_4$ cathode, previous research indicate the oxidation of electrolyte components and the carbonate film formed at surface are the major sources inducing capacity fading of LiMn$_{2-x}$Ni$_x$O$_{4-\delta}$ cathode. However, detailed information pertaining to the electrode/electrolyte interface are still not properly investigated. A solid electrolyte interface (SEI) typically forms at the cathode and is said to originate from the decomposition products of the electrolyte at very high (>4.4V) voltages. While the SEI layer can protect the electrode if stable, it also creates a barrier for lithium diffusion during electrochemical cycling and results in an increase in cell impedance and decreases the cycling efficiency. Several groups have reported on the characterization of the SEI layer using composite electrodes containing conductive agents and polymeric binders and show that it mainly consists of lithium alkyl carbonates (ROCO$_2$-Li), phosphates, LiF, and Li$_2$CO$_3$ stemming from the electrolyte components.[135-146]. However, these results are typically not a direct representation of the surface stability in the cathode material, rather an overall composite study, as the conductive agents and polymer binders tend to react with the electrolyte at high voltages and accelerates the formation of the SEI layer. Thin film electrodes offer the ability to investigate the intrinsic activity in the cathode surface, free of polymeric binders and conductive agents, while the controlled geometry enables more accurate measurements of ionic diffusion coefficients. To adequately assess the intrinsic surface stability this work aims to compare both conventional powder composites and thin film electrodes after extended cycling.
6.2 Experiment Method

6.2.1 Synthesis of Powders

The sol solutions were prepared from the stoichiometric mixtures of Li(CH₃COO)·2H₂O (Fisher), Ni(CH₃COO)₂·4H₂O (Fisher), and Mn(CH₃COO)₂·4H₂O (Fisher) in distilled water. Then the solution was added drop-wise to a solution of citric acid which was used as a chelating agent. pH value was adjusted to 6.5 by adding ammonium hydroxide. A gel was obtained by heated at 75 °C overnight. The gel were calcined at 450 °C for 10 hours to remove the carbonate in air and calcined at 800 °C for 10 hours.

6.2.2 Synthesis of Thin Films

LiNi₀.₅Mn₁.₅O₄ target was synthesized by a solid state reaction. MnO₂, NiO and LiOH precursors were mixed by 3d ball miller for 5 hr and were cold-pressed into a pellet and calcined in air at 750°C for 24 h. Then, the pellet was grinded and re-fabricate by static press machine and calcined at 900°C for 2 h. The mole ratio of Lithium and transition was controlled at 1.3 in order to avoid the evaporation of lithium during the deposition process.

The LiNi₀.₅Mn₁.₅O₄ thin films were deposited on stainless steels (SS304) or SiO₂/Si. In the deposition process, KrF excimer laser with 248 nm was used. Laser fluence with 500 mJ and repetition rate with 5Hz was used in the process. Substrate temperature was controlled at 600 °C and in the oxygen partial pressure at 300mTorr for 40minutes and calcined with extra 20minutes in oxygen atmosphere.

6.2.3 Characterization

X-ray diffraction (XRD) data were collected using a Philips APD 3720 diffractometer using a Cu Kα radiation source operated at 45kV and 20mA. The scan
speed was 3 sec/step with a step size of 0.02 degrees two theta. SEM Images were collected using a field emission scanning electron microscopy (FEG-SEM, JEOL JSM-6335F).

X-ray photoelectron spectroscopy data were collected using a PHI 3056 spectrometer equipped with a hemispherical detector, 54.7 degrees off normal, with a Mg anode source operated at 15kV. The energy of the spectra was calibrated by the binding energy of the hydrocarbon C1s (C-H) at 284.6 eV, which corresponds mainly to the carbon black in the composite electrode and adventitious carbon. The data was analyzed using the software CasaXPS and all peaks were fit using a Shirley-type background. Powder samples and thin Film samples were disassembled in an Ar-filled glove box, washed with acetonitrile three times, then transferred to ORNL in a custom made transfer case designed to prevent atmospheric gases from reacting with the samples. The samples were subsequently transferred to XPS, from the glove box, without exposure to air.

6.2.4 Electrochemistry

The electrochemical properties of power electrodes were measured using 2016 coin cells consisting of metallic lithium as an anode and an electrolyte comprised of 1M 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with 1:1 volume ratio. Celgard type C480 (CelgardInc.USA) was used as separator. Cathode films were prepared from slurries of LiNi₀.₅Mn₁.₅O₄ powders with 7.5% polyvinylidene fluoride (PVDF) and 7.5% acetylene carbon black dissolved in N-methyl-2-pyrrolidinone (NMP). The mixtures were cast onto Al foil using a doctor blade and dried at 100°C overnight. Electrode discs were cut into cathodes containing 2-3 mg of active materials before
storing them in an argon-filled glove box (H₂O level<2 ppm). The coin-cells were assembled in an argon filled glove box and tested using an Arbin BT2000 instrument in galvanostatic mode. The tests were conducted between 5V and 3.5V at a constant current rate of C/20. The electrochemical properties of cathode thin film was measured using Swagelok type cell consisting of metallic lithium as an anode, an electrolyte comprised of 1M LiPF₆ in a 1:1 volume fraction of ethylene carbonate (EC)/dimethyl carbonate (DMC) and Celgard type C480 separator (CelgardInc.USA).

6.3 Results and Discussion

6.3.1 Characterization

SEM images of both the powder and thin film samples are shown in Figure 6-1. Formation of the spinel structure at 600°C using the PLD method shows a dense yet relatively faceted crystal morphology with well-defined grains ranging between 100-200 nm. The grains exhibited an octahedral-type morphology reflecting the cubic spinel structure. Compared to the PLD method, the sol-gel synthesis produced 100 nm particles with a pseudo-polyhedral morphology when calcined at 800°C. Figure 6-2(a) shows the XRD patterns for the NiMn spinel thin film deposited on a stainless steel at 600°C and the sol-gel synthesized powder. All diffraction peaks from the thin film electrode can be indexed to the spinel structure with an Fd-3m space group and the SS substrate. A (111) textured structure is seen for the thin film, as evidenced by the XRD pattern, resulting in larger relative intensities for the (111)/(311) and (111)/(222) peaks compared to that of the synthesized NiMn spinel powder material. Rietveld refinement on the powder material similarly shows the disordered Fd-3m space group with no NiO impurities as shown in Figure 6-2(b) [147] The refinement results show the lattice
parameter of 8.1804Å, similar to that of previously published data[13]. For the disordered (Fd-3m) structure both the Mn$^{4+}$ and Ni$^{2+}$ ions occupy the octahedral 16(d) sites.

### 6.3.2 Electrochemical Measurement

The electrochemical properties of the NiMn spinel powder and thin film were investigated in lithium half-cells. The charge/discharge profiles between 3.6 and 5.0V are shown in Figure 6-3(a) and (c). The NiMn spinel powder and thin film electrodes have a reversible capacity of ~130 mAh/g and ~125 mAh/g, respectively. In addition, both cells have two distinct voltage plateaus around 4.7V, which corresponds to the Ni$^{2+}$-Ni$^{4+}$ redox couples. A relatively smaller plateau can be found in the 4.0V region for the thin film material during the first charge cycle corresponding to the Mn$^{3+}$-Mn$^{4+}$ redox couple. The high vacuum deposition process of the PLD system may cause oxygen loss and can lower the average oxidation state of Mn and introduce more Mn$^{3+}$ surface ions. The lower deposition temperature associated with the thin film process may also be attributed to the lower reversible capacity compared to the powder electrodes. To study the rate capability of the NiMn spinel electrodes, half-cells were charged to 5.0V at a constant current density (C/20) and discharged to 3.6V at various current densities. The measured discharge capacities with the various current densities are shown in Figure 6-3(b) and (d). When the rate increases from C/20 to 2C for the thin film electrodes only a relatively small capacity loss (~15%) is shown. In contrast, capacity loss the composite electrode is ~40%. The rate capability performance for the thin film electrode in the absence of carbon black and binder indicates the intrinsically fast Li diffusion in the NiMn spinel material due to the 3D Li-ion diffusion pathway. Cycling performance tested at number at a constant current density (C/20) shows little capacity fading after 5 cycles for both composite and thin film electrodes as shown in Figure 6-4.
6.3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was used to examine surface features of the thin film and powder electrode materials after electrochemical cycling. All data was collected by Dr. Carroll in Oak Ridge National laboratory. The thin film batteries were disassembled, in the fully discharged state, in an argon-filled glove box and transferred to the XPS using a load-lock system to eliminate exposure to air. Figure 6-5 shows the spectra observed for the C1s, Ni2p, and F2p regions for pristine and cycled samples. The thin film electrodes offer the ability to probe the surface of the cathode material more accurately than that of the composite powder electrodes. This is critically important when trying to determine failure mechanisms associated with the cathode material. For example, the thin film electrodes show no significant formation of decomposed electrolyte such as the formation of carbonate species after electrochemical cycling, evident in the C1s data (Fig 6-5d). This suggests that even at the higher voltages (5V) during charging, the NiMn spinel material is intrinsically stable and does not contribute to the decomposition of the electrolyte. In contrast, the composite electrode shows several peaks, which are associated with the carbon additive and PVDF binder (Figure 6-5a). The C1s spectra can be de-convoluted into 4 peaks. The peak at ~284.6 eV (C-C, C-H) corresponds mainly to carbon black while the peaks at 285 eV (-CH2-), and 290.5 eV (CF2) correspond to the PVDF binder.[148] A peak at 287 eV (C-O) corresponds to the EC/DMC electrolyte. The powder composite electrodes shown a gradual increase in the C-O peak with increasing cycle numbers corresponding to the decomposition of the ethylene carbonate and dimethylene carbonate (EC/DMC) electrolyte solution. In addition, the O1s spectra for the composite electrodes show the gradual formation of a C-O (~533 eV) species after cycling.
consistent with the C1s spectra for the decomposition of the EC/DMC electrolyte during cycling as shown in Figure 6-6(a). In contrast, no C-O formation is seen for the thin film electrode after extended cycling as shown in Figure 6-6(b).

Changes can also be seen in the Ni2p region where a significant loss of spectral features, particularly a loss in intensity and peak shape, are present for the composite electrode (figure 6-6b). This can be attributed to a large signal from the carbon black and PVDF binder and a relatively lower stoichiometry when compared to Mn in the spinel structure, resulting in a lower percentage of surface exposed Ni. Loss of spectral intensity detracts from adequately assessing the effect cycling on the surface of the NiMn spinel material. The Ni2p region scans for the thin film, however, have a much higher signal-to-noise ratio than those of the composite electrode due to the elimination of carbon black and PVDF binder (Fig 6-6e). The Ni2p region shows a slight loss in spectral resolution and broadening of the Ni2p3/2 peak upon extended cycling. It is hypothesized that this may be contributed to a higher nickel valence (Ni$^{3+}$/Ni$^{4+}$) and suggests some irreversibility of the surface Ni species, which contributes little to the total capacity. De-convolution of the Mn 2p3/2 spectra for the thin film and composite electrodes reveals two peaks, a minor peak at 641.2 eV (Mn$^{3+}$) and major peak at 642.5 eV (Mn$^{4+}$) shows Mn$^{3+}$ appear, similar to previous reports by Shaju et al.[149, 150]

The F1s and P2p region scans offer the most contrast between the thin film and composite electrodes for the formation of the SEI layer. It has been reported for composite electrodes, LiPF$_6$ will react and form LiF and PF$_5$ as byproducts, which further reacts with water forming POF$_3$ and HF on the surface of the particles.[128]. This trend is consistent with our composite electrodes, which show the presence of
phosphates after electrochemical cycling, shown in F1s spectra (figure 6-5c). However, in the thin film XPS analysis, no phosphate formation is shown and only a small amount (<5%) of LiF after 20 cycles, which suggests minimal electrolyte decomposition on the surface of the electrode after extended cycling.

6.4 Summary

The results from this analysis implies that the surface of the NiMn spinel material is not directly contributing to the SEI formation mechanism; rather the SEI formation seen in the composite electrodes is a result of the incorporation of carbon black and PVDF. These results may also explain the enhancement seen in the rate testing for the thin film electrodes relative to the composite electrode, which enables faster Li mobility without the formation of an SEI layer and without the inactive PVDF binder.
Figure 6-1. SEM images of thin film (a,b) and powder (c,d) NiMn spinel electrode materials.
Figure 6-2. (a) XRD patterns for thin film and powder composite NiMn spinel electrodes (b) The refinement pattern of the composite powder NiMn
Figure 6-3. Charge/discharge profiles and rate testing for NiMn spinel powder (a,b) and thin film (c,d) electrodes.

Figure 6-4. Discharge capacity performance as a function of cycle number for thin film and powder electrodes.
Figure 6-5. XPS data collected using a Mg anode on pristine and post electrochemically cycled powder composite (a-c) and (d-f) thin film NiMn spinel electrodes.
Figure 6-6. XPS plots of the Mn2p and O1s region scans for the composite (a,c) and thin film (b,d) electrodes.
CHAPTER 7
SOLID ELECTROLYTE DEPOSITION BY PLD

In order to fabricate all-solid-state thin film batteries, the solid electrolyte must be prepared following the cathode electrolyte deposition. The LVSO thin films were deposited using the PLD system with different oxygen pressure. The amorphous and dense film can be prepared in the low oxygen pressure. Although the XPS results show the existence of oxygen vacancy, the EDS and LEAP analysis show exact stoichiometry and uniform distribution of each element.

7.1 Introduction

An suitable electrolyte material should follow some requirements: high ionic conductivity, no chemical reaction between electrodes and electrolyte and high electrochemical decomposition voltage[151]. Moreover, with the aim of examination the reaction of interface by TEM in-situ or ex-situ, the solid electrolyte should have dense structure and keep stable in the electron beam(TEM) and ion beam(FIB). Several methods were developed to prepare solid electrolyte, including solid state method[152], thermal evaporation[153], sputter method[154] and PLD method[155-158]. In order to fabricate the all-solid thin film batteries, the PLD deposition process was selected as the deposition method in this research because it is easier to fabricate dense film and it is possible to fabricate the all-solid state thin film batteries only by pulsed laser deposition method.

However, it is difficult to fabricate the solid electrolyte films by PLD technique,: Li$_2$O-SiO$_2$-V$_2$O$_5$ (LVSO)[157-161] and Li$_2$O-P$_2$O$_5$+N$_2$ (LiPON)[40, 41, 153, 156, 162-164] are the widely used electrolyte can be prepared by PLD technique. In this research, Li$_2$O-SiO$_2$-V$_2$O$_5$ (LVSO) was deposited by PLD process..
7.2 Experiment Method

7.2.1 Thin Films Preparation

The Li$_2$O-SiO$_2$-V$_2$O$_5$(LVSO) target was brought from Plasmaterials. Energy of the laser system and frequency were set at 300mJ, 5Hz. The films were deposited at room temperature and 5mtorr-200mtorr oxygen pressure. Stainless Steel 304 and SiO$_2$/Si substrate were used as substrate.

7.2.2 Characterization

X-ray diffraction (XRD) data were collected using a Philips APD 3720 diffractometer using a Cu Kα radiation source operated at 45kV and 20mA. The scan speed was 3 sec/step with a step size of 0.02 degrees two theta. X-ray diffraction (XRD) data of LVSO target was collected using Philips XPer MRD because of the thickness issue. Images were collected using a field emission scanning electron microscopy (FEG-SEM, JEOL JSM-6335F). The energy dispersive X-ray spectroscopy (EDS) system of JEOL SEM 6335 was also used to identify the ratio of V:Si element. X-ray photoelectron spectroscopy (XPS) Perkin-Elmer PHI 5100 System was performed using Mg Kα X-ray source to investigate the valence number of each element. The incident X-ray beam was 45° off normal to the sample while the X-ray photoelectron detector was normal to the sample. Binding energies of the photoelectron are correlated to the C 1s peak at 285 eV. A pass energy of 22.36 eV and 30 scans per region were taking with a step size of 0.100 eV. Local electrode atom probe (LEAP) facility at Alabama University, Tuscaloosa was used to get 3D compositional images: LEAP Model is LEAP-3000XSi, the laser wavelength and pulse Energy used is 532nm: 0.5 nJ separately. The experiment was performed by Dr. Santhanaqopalan in my group.
Local electrode atom probe is a unique analytical microscopy with highest spatial resolution producing 3D compositional images. A sharp specimen is used for obtaining such 3D compositional images. A high voltage is applied to the apex of the sharp specimen to create electric fields of the order of $10^{10}$ V/m or even higher. Such a high field can strip off the electrons of the atoms sitting at the tip of the specimen by the phenomena called field ionization. The ionized atoms are pulled off from the surface and accelerated by the electric field towards the counter electrode[165]. This process of pulling off of ionized atoms is called field evaporation. To produce such high electric fields for field evaporation the specimen tip radius of curvature must be about 100 nm or less and the voltage must be around kV. The field evaporated ions are detected by a large area 2D position sensitive detector to give the X-Y position of atoms. The tip apex is about 100 nm across and the detector is 100 mm across and hence, the image of atoms on the surface is projected onto the detector with a projection magnification of about one million times. At this magnification, interatomic distances of 0.2 nm are 0.2 mm on the detector, which is relatively easy to resolve. More importantly with this technique the ionization voltage is controlled in a fashion to evaporate one atom at a time, so that the sequence of evaporating events would give information about the z-position.

7.3 Results And Discussion

Figure 7-1 shows the XRD pattern of the $L_{3.4}V_{0.6}S_{0.4}O_{4}(0.6(Li_4SiO_4)-0.4(Li_3VO_4))$ target. Although there are some small peaks can’t be identified, the major peaks belong to crystalline Li$_4$SiO$_4$ and Li$_3$VO$_4$ phases that means the target is suitable for subsequent deposition process.
Figure 7-2 shows the XRD pattern of the LVSO film deposited in different pressure range, all films are amorphous that are identical with the previous literature. Figure 7-3 shows the SEM pictures of LVSO film deposited in different pressure range. When the film deposited at low pressure (5-20mTorr), the dense and smooth film will form as show in Figure 7-3(a). However, the film is discontinuous when the deposition pressure increase to 200mTorr as shown in Figure 7-3(b). The thickness of the electrolyte film deposited on low pressure is about 600-800nm. Figure 7-4 shows the EDS of LVSO thin films deposited on stainless steel deposited at 5 mTorr, Fe, Cr, Ni, V and Si were investigated by EDS, the signals of Fe, Cr, Ni are belong to substrate, the V : Si ratio is 3:2 that is identical with the theoretical values. The LEAP technique reveals the distribution of Li, V, Si and O element in the LVSO film as shown in Figure 7-5. The different color means the different amount of the element. Except the edge, all element show similar color which represent the uniform element distribution.

XPS results of LVSO thin films were shown in Figure 7-6. The binding energy of the Li 1s and V2p_{3/2} for LVSO film is 55.1 eV and 516.94 eV that is similar with the standard for Li^{1+} and V^{5+} separately. The binding energy of Si2p as shown in Figure 7-6(c) is smaller than the standard for Si^{4+} about 1.8eV that suggest oxygen deficient in the LVSO film because of the low oxygen pressure deposition condition (5mTorr).

In order to examine the effects of solid electrolyte after anode deposition process, the prepared solid electrolyte was put in vacuum chamber and heated up to 650°C 2hr in oxygen flow of 20sccm the thin film will crack after the process as show in Figure 7-7(a)(b), which sets the limitation of the subsequent deposition temperature of the anode electrode.
7.4 Summary

LVSO solid electrolyte was prepared by PLD method successfully. The low oxygen deposition condition will form the dense amorphous film that is suitable for manufacture of nano-batteries. Different analysis methods were performed to investigated the properties of LVSO film, the XPS show some oxygen vacancy exhibit in the thin film because of the low oxygen deposition pressure, the EDS of the film show the exact stoichiometry compared the theoretical value. The LEAP analysis shows the excellent uniformity of each element.
Figure 7-1. XRD pattern of LVSO target

Figure 7-2. XRD pattern of LVSO thin film deposited at different pressure
Figure 7-3. SEM of LVSO thin films deposited on different pressure (a) 5 mtorr (b) 200 mtorr

Figure 7-4. EDS of LVSO thin films/stainless steel deposited on 5 mtorr
Figure 7-5. The element distribution of LVSO investigated by LEAP
Figure 7-6. XPS results of LVSO thin films (a) Li (b) V (c) Si
Figure 7-6. Continued

Figure 7-7. SEM pictures of LVSO after 650°C
CHAPTER 8
ELECTROCHEMICAL PROPERTIES OF TiO₂ AND Li₄Ti₅O₁₂ THIN FILMS AND ALL-SOLID STATE THIN FILM BATTERIES PREPARED BY PULSED LASERDEPOSITION

8.1 Introduction

The all solid-state thin film battery is a promising micro-powder source that can be fabricated by a typical thin film deposition process[158, 167]. Different thin film cathodes, such as LiCoO₂, LiMn₂O₄, LiNi₀.₅Mn₁₅O₄ [168], V₂O₅[169] and various solid electrolytes including LVSO[170], LIPON[171] and Li₂SO₄[172] were fabricated successfully by various techniques. Compared to cathodes and solid electrolyte materials, it is more difficult to choose a suitable anode as there are differences in thermal expansion coefficients along with layer diffusion during the final layer deposition synthesis process. Several materials were selected as anode candidates for fabrication of all solid state thin film battery, such as Li-metal, Li₄Ti₅O₁₂[173], a-Si[174], SnO [33], Si-Sn[175], Si₀.₇V₀.₃[176] and Ni₃Sn₂[177]. a-Si and alloy anode has relatively higher capacity but the large volume difference between the lithiated and host induce losses of electrical contact between active material and current collector lead to the poor cycling performance. The initial irreversible capacity of SnO anode also inhibits the availability Li₄Ti₅O₁₂ has been recognized as a zero-strain anode with excellent cyclability[23]. Titanium oxide is also a promising anode electrode material for Li-ion batteries due to its safety against overcharging and stable voltage plateau at 1.78V. TiO₂ and Li₄Ti₅O₁₂ thin films already deposited successfully by various deposition methods, such as PECVD[178], sputtering [179, 180], sol-gel[181], atomic layer deposition [182] and pulsed laser deposition[183-185]. The optical, electrical properties, surface characterization and deposition parameter were explored detail in previous research[185, 186]. However, there are limited literatures that discuss the
electrochemical properties of Li$_4$Ti$_5$O$_{12}$ and TiO$_2$ thin films, this chapter uses a PLD method to fabricate TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ thin films on different substrate and temperature. The phase, structure, morphology were examined by X-ray diffraction (XRD), and scanning electron microscopy (SEM). The valence of Titanium and surface environment was investigated by X-ray photoelectron spectroscopy (XPS). The relationships between crystal structure, surface morphology and electrochemical properties of thin films were examined. The crystalline TiO$_2$ thin film can be fabricated at low temperature that make it is a powerful anode candidate for all solid state thin film batteries fabrication. Finally, the all solid state thin film battery with TiO$_2$/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ / L$_{3.4}$V$_{0.6}$S$_{0.4}$O$_4$/SiO$_2$/Si stack was fabricated successfully by PLD process for the first time.

8.2 Experimental Methods

8.2.1 Preparation of Li$_4$Ti$_5$O$_{12}$ Materials

Li$_4$Ti$_5$O$_{12}$ powder was synthesized by a typical sol–gel method. Li(CH$_3$COO)$_2$·2H$_2$O and tetrabutyl titanate [Ti(OC$_4$H$_9$)$_4$] with suitable stoichiometric amounts were dissolved in alcohol. Then, the citric acid with half amount of mole ratio compared to titanium was also dissolved in alcohol and drop-wise to precursor solution. The solution was dried at 80 °C for 6 h to form a gel and calcined at 700 °C in air for 6 h and then calcined at 850 °C for 24 h to get Li$_4$Ti$_5$O$_{12}$ powder.

Li$_4$Ti$_5$O$_{12}$ target was synthesized by a solid state reaction. The starting powders were TiO$_2$ and LiOH with proper molar ratio. The mixture was stirred by 3-D ball miller for 5 h and then calcined in oxygen at 850°C for 20 hr. After calcination, the powder was ground again and remade to a pellet. Finally, in order to densify the target, the target was calcined in oxygen at 900°C for 2 hr.
The deposition process was performed by a 248nm KrF excimer laser. The energy of the laser system and frequency were set to 500mJ, 5Hz. The films were deposited between room temperature and 800°C and the oxygen pressure was set to 300mTorr for 40 minutes on Au and SiO$_2$ substrate.

8.2.2 Preparation of TiO$_2$ Materials

TiO$_2$ target was also synthesized by a solid state reaction and starting materials anatase (50nm, Fisher) powder was ground and pressed into a pellet by cold press machine then calcined at 1000°C for 15 hrs. Thin films were deposited on stainless steel and SiO$_2$/Si after the pressure lower than 10$^{-5}$ Torr. The deposition process was performed by a 248nm KrF excimer laser. The energy of the laser system and frequency were set to 480mJ, 5Hz. The films were deposited between room temperature and 850°C and the oxygen pressure was set to 50mTorr for 40 minutes.

8.2.3 Preparation of All-Solid State Thin Film Battery

First, the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ thin films were deposited on stainless steels substrate (SS). The deposition process was performed by a 248nm KrF excimer laser. The energy of the laser system and frequency were set to 480mJ, 5Hz. The films were deposited between room temperature and 600°C and the oxygen pressure was set to 300 mTorr for 40 minutes. After the deposition process, the samples were put into chamber with extra 20 minutes in oxygen atmosphere. Second, the solid electrolyte LVSO was deposited. Laser fluence and repetition rate were controlled at 300mJ and at 5Hz. Film depositions were carried out at room temperature and in the oxygen partial pressure at 5mTorr for 30 min. Finally, the anode TiO$_2$ thin film was deposited at 450°C and in the oxygen partial pressure at 50mTorr for 40 minutes.
8.2.4 Characterization

X-ray powder diffraction of all samples were taken using XRD Philips APD 3720 using a Cu Kalpha radiation source operated at 45kV and 20mA. The scan speed was 3 sec/step and a step size of 0.02 degrees in two theta. Field emission scanning electron microscopy (FEG-SEM, JEOL JSM-6335F) was performed to investigate the thickness and morphologies. Images were collected with an accelerating voltage of 15kV. X-ray photoelectron spectroscopy data were collected using a PHI 3056 spectrometer equipped with a hemispherical detector, 54.7 degrees off normal, with a Mg source in Oak Ridge National laboratory.

8.2.5 Electrochemical Testing

The electrochemical properties of powder and thin films were measured using coin cell 2016 and swagelok consisting of metallic lithium as an anode and an an electrolyte composed of 1M 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) with 1:1 volume ratio. Celgard model C480 separator (Celgard Inc.USA) was used as separator. The swagelok cells were assembled in an argon filled glove box and tested using an Arbin BT2000 instrument in galvanostatic mode. The tests were conducted between 3.5V and 1V (TiO₂) and 2.5V and 1V(Li₄Ti₅O₁₂) at a constant current rate of C/4, C/2, C, 2C, 4C and 8C. For Cycling Performance test, the tests were conducted between 3.5V and 1V at a constant current rate of C/4.

8.3 Results and Discussion

8.3.1 Materials Characterization and Electrochemical Properties Of Li₄Ti₅O₁₂

Figure 8-1 shows the XRD diffraction patterns for the Li₄Ti₅O₁₂ powder synthesized by sol-gel method and the Li₄Ti₅O₁₂ target synthesized by solid state reaction. Although small amount anatase TiO₂ phase appears, most peaks can be
identified as the spinel structure with an Fd-3m space group, the average of cubic lattice constants of the samples are 8.381 Å, 8.373 Å, separately. Figure 8-2 shows the XRD patterns of the Li$_4$Ti$_5$O$_{12}$ thin film deposited on SiO$_2$/Si substrate from room temperature to 850°C, only thin films deposited higher than 700°C show the spinel structure. The pure spinel phase can be formed at relative lower temperature compared to chemical sol-gel method. A (111) textured structure is seen for the Li$_4$Ti$_5$O$_{12}$ thin film deposited on 700°C. However, the anatase TiO$_2$ phase appears for the sample deposited on 800°C. High temperature deposition leads to the evaporation of the Li ion in vacuum and induces the TiO$_2$ impurity.

Figure 8-3 shows SEM photos of Li$_4$Ti$_5$O$_{12}$ thin film deposited on SiO$_2$/Si substrate from 500-800 °C (a-d) and on gold substrate on 700°C (e-f). The thin films deposited at 500-600°C are composed of agglomerated particles. The films deposited at 700-800°C (b,d) show solid and flat morphology with grain size between 50 and 100nm. Figure 8-4(g-h) depicts the microstructure of the Li$_4$Ti$_5$O$_{12}$ film deposited on gold substrate at 700°C. Some pores appear and the pore sizes vary between a few nanometers to a few micrometers. The high magnification image shown in Figure 8-3(f) also indicates a unique architecture containing smaller grain size <100 nm.

The electrochemical properties of the powder and thin film spinel Li$_4$Ti$_5$O$_{12}$ were investigated in Swagelok cells. The charge/discharge profiles between 2.5 and 1V are shown in Figure 8-4(a) and (b). The powder and thin film electrodes have a reversible capacity of ~147 mAh/g and ~163 mAh/g, respectively. In addition, both cells have one distinct voltage plateaus around 1.55V. However, the sloping region of Li$_4$Ti$_5$O$_{12}$ thin film extend, the small grain size of the sample [187] or the shape of grain, size distribution...
and surface environment[188] lead to the difference of the voltage profile. With the
decreasing of the particle size, the increasing of the elastic energy penalty lead the
decreasing of the mixing Gibbs free energy at the two phase boundary that extend the
sloping region.

The Li$_4$Ti$_5$O$_{12}$ thin film with pure spinel phase can only be deposited at high
deposition temperature, which limits its application as the anode in all solid state
batteries. The differences in thermal expansion coefficients along with layer diffusion
during the final anode deposition synthesis process is the fact that prevents Li$_4$Ti$_5$O$_{12}$
thin film from being used for all-solid state thin film battery, despite its intrinsic excellent
electrochemical performance.

8.3.2 Materials Characterization of TiO$_2$ Materials

Figure 8-5 shows the XRD pattern for the TiO$_2$ target. The peaks can be identified as a rutile structure with P42/mnm space group. The TiO$_2$ thin films were fabricated on stainless steels and SiO$_2$/Si separately. Only films deposited on stainless steels can be used for electrochemical measurements. The thickness of the thin films was estimated by the samples deposited on the SiO$_2$/Si substrates and the samples also can be used for evaluating the properties when the TiO$_2$ anode deposited on amorphous solid electrolyte.

Crystalline structure changes of the TiO$_2$ thin films deposited between 25°C and 850°C and different substrate were also monitored by XRD as shown in Figure 8-6 and Figure 8-7. When the films are deposited at the temperature lower 450 °C on SiO$_2$/Si substrate, the film is of an amorphous structure. As the substrate temperature increases to 450 °C, the texture (101) anatase phase with I41/amd space group is observed. When the substrate temperature increases to 650°C, the (004) peak increases rapidly.
At 850°C deposition condition, the mixed anatase and rutile phases were formed. The average crystal grain size can be calculated by the Scherrer equation.

\[
d = \frac{k\lambda}{B \cos \theta_B}
\]  

(8-1)

Where \( d \) is the calculated grain size, \( \lambda \) is the wavelength of X-ray (Cu K\( \alpha \) 1.54Å), \( B \) is the full-width at half-maximum intensity, and \( \theta_B \) is the Bragg diffraction angle. The grain size of anatase phase is determined to be 10.3, 32.9, 57.3nm separately for 450, 650 and 850°C deposition temperature. Compared to the TiO\(_2\) thin films deposited on SiO\(_2\) substrate, the thin films deposited on SS show similar phase transformation trend.

When the temperature increases, the anatase phase will transform to rutile phase. However, the transformation occurs at relatively lower temperature as shown in Figure 8-7. The pure anatase phase with space group I41/amd and preferred orientation(101) will form at 350 °C and the mixed anatase –rutile will form at 450°C. The increased temperature can’t form pure rutile phase. In opposition, the unknown second phase was investigated at 34 degree. It may be the phase of inter-diffusion between SS and TiO\(_2\) thin film.

Figure 8-8 shows the FESEM images of the films deposited at different substrate temperatures. At room temperature, a continuous film can’t form. There isn’t enough kinetic energy to form a dense film. The surface morphologies of films deposited between 350 to 650 °C are similar. A typical island morphology consisting of fine particle was observed. However, the pores appear between fine grains and the pores will shrink and disappear at higher deposition temperature. At 800 °C, the porous structure will form and the pore size is about 50nm. From the cross-sectional view of the film grown
on the SiO₂ substrate as shown in Figure 8-8(e), the film thickness is estimated to be about 150 nm.

The X-ray photoemission spectrum of the TiO₂ film /SS deposited at different temperature were shown in Figure 8-9(a)(b). The Ti 2p₃/₂ and 2p₁/₂ are located at 459.78 and 464.38eV for thin film deposited at 450˚C that indicate the presence of Ti⁴⁺ oxidation states. The Ti 2p 3/2 and 2p1/2 are located at 458.48 and 464.18eV for thin film deposited at 800˚C, the lower binding energy imply the oxygen vacancy form during the low oxygen at high temperature process. Surface OH ratio can be also estimated by the O 1s signal, two components are shown in the typical O 1s XPS spectrum as shown in Figure 5(b). One represents the oxygen element in titania lattice (530.3 eV) and the other corresponding to the surface hydroxyl species (532.3 eV). It should be noted that the thin film samples has higher surface hydroxyl concentration (14.4%) than commercial P25(less than 10%) that imply the thin films has a larger surface area.

8.3.3 Charge-Discharge Studies of TiO₂ Thin Films

The electrochemical properties of the TiO₂ thin films were investigated using lithium half-cells with a constant current 0.02mA/cm². In order to measure the electrochemical properties, the stainless steel was used as a substrate and current collector. The first discharge/charge profiles between 3.5 and 1.0V are shown in Figure 8-10(a)(b). The specific capacity of all films were estimated by theoretical density of anatase TiO₂(3.8cm³/g) and the thickness was examined by SEM. The lithium intercalation/deintercalation reaction in this region can be written as:

\[ \text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2 \]  

(8-2)
The amount of lithium insertion depends on the crystallinity, morphology as well as the microstructure. In our work, the discharge capacity and grain size for thin films deposited at 350, 450 and 650°C are (184.6mAh/g, 10.3nm), (274.8mAh/g, 32.9nm), (230.35mAh/g, 57.3nm) respectively. The thin film deposited on 450°C exhibits the largest capacity. The XRD result shows the film deposited at 450°C exhibits mixed phases of anatase and rutile. It seems the nanosize rutile and anatase phase contribute extra capacity. Wagemaker et al[99] have shown that anatase TiO$_2$ nanoparticles can completely convert to the Li$_1$TiO$_2$ phase if the particle size is smaller than 7nm. Although the grain size of thin film is larger than 7nm, some LiTiO$_2$ phase should form during the Li insertion process. Nevertheless, the nanosziezd rutile TiO$_2$ can also supply the extra capacity [106, 189-192] although only small amount of lithium can insert in to bulk rutile. As Figure 8-10(a) shows, there is an obvious plateau around 1.75V for TiO$_2$ thin films deposited at 350 and 450 °C that corresponds to the occurrence of the two phase equilibrium of Lithium-poor (Li$_{0.01}$TiO$_2$) and Lithium-rich (Li$_{0.6}$TiO$_2$) domains[123]. However, there is only very small voltage plateau observed for the TiO$_2$ thin film deposited at 650°C. From the XRD pattern, dominant rutile phase may be the contributing factor to the sloping voltage curve[106]. The length of the plateau region also changed with different deposition temperature that corresponds to the ratio of anatase phase. At 350°C, the pure anatase phase exhibits the longest plateau region. With the temperature increasing, the ratio of anatase phase decrease and the plateau shrink. Moreover, the thin film samples shows longer sloping length that also shows that reducing the crystalline size reduces the miscibility gap of two phase reactions up lithiation[22]. With the decreasing of the particle size, the increasing of the elastic
energy penalty lead the decreasing of the mixing Gibbs free energy at the two phase boundary that extend the sloping region. Moreover, Li ions insertion into the surface layer of the nanosized thin film may be another reason contributing to the sloping region[101].

8.3.4 Rate Capability Studies of TiO₂ Thin Films

Without the addition of the carbon black and PVDF, the thin film electrode is an ideal sample to explore the intrinsic properties of TiO₂ material itself. To study the rate capability of TiO₂ electrodes, the cells were discharged to 1V at various current rates (C/4, C/2, C, 2C, C, 4C and 8C). The measured discharge capacities with different current density were shown in Figure 8-11. Clearly, the thin films deposited at 350˚C show better rate performances than 450˚C and 650˚C. The discharge capacity of the TiO₂ thin film tested at C still retains 75.89% of its capacity, compared to the capacity at C/4. On the other hand, the discharge capacity of TiO₂ thin film deposited at 450˚C tested at C decreased to 50.41%, compared to the capacity at C/4.

The true size effects, which involve changes of actual materials and the trivial size effects which depend on the surface-to-volume ratio and the shape and the pores of the nanomaterials both affect the performance of electrochemical properties[100].

For example, anatase and rutile TiO₂ materials show different Li-insertion properties and different diffusion coefficient. Wagemaker et al[99, 124] use static ⁷Li NMR T2 relaxation measurements to probe the Li-ion mobility of micro and nanosize anatase TiO₂. The result shows that the lithium diffusion coefficient for nanomaterials is lower than that for the microsized materials. For rutile TiO₂, it owns one-dimensional diffusion channels, the lower Li⁺ diffusion coefficient along ab plane limits the transportation of the lithium ions. Malik et al[22] prove that for the decreasing of particle
size with the 1D diffusion channel, the diffusion constant will increase. The lithium ion diffusion pathway will be blocked if static defects exist in bulk material. Because there are limit defects for smaller particles, lithium ions can move with high rate without obstruction. Since the thin film deposited at 450°C has relatively larger grain size of anatase and nanosized rutile phase, compared to thin film deposited on 350°C. The lithium diffusion coefficient for thin film deposited at 350°C should be lower than that for the thin film deposited at 450°C. Nevertheless, our electrochemical data clearly show that the TiO₂ thin film deposited at 350°C has superior rate performance.

Besides the structure effects, the trivial size effects should be the key factors that contribute to the excellent rate capability. From the SEM pictures and the grain sizes extracted from XRD pattern, the porous structure of TiO₂ thin film deposited at 350°C may lead to larger electrode/electrolyte contact area that can improve the ionic conductivity. At the same time, nanostructured materials can supply the short Lithium ions and electron transportation distance, the Li diffusion time may be much lower for porous anantase thin film. Moreover, the larger surface area of nanostructured thin film electrodes that suggested from XPS analysis also can significant diminish the specific current density of the cell. The high capacity can maintain even testing at higher rate with the low specific current density.

**8.3.5 Cycling Performance of TiO₂ Thin Films**

The cycling performance of TiO₂ thin films deposited on different temperature at a constant current density (C/4) was shown in Figure 8-12. As we can seen, the TiO₂ deposited on 650°C show a fast fading with the increasing of cycle number, while there is virtually no fading for the thin films deposited at 350°C. This film have poor cycling performance may due to the dense structure and possibly serious inter-diffusion
between stainless steel and TiO$_2$ thin film. TiO$_2$ thin film deposited on 350°C and 450°C with nano-grains, nano-porous structure show an excellent cycling performance with high capacity. This makes it a promising anode material for all solid state Li-ion batteries. The porous structure can supply the space to accommodate the volume change and avoiding the during the de-lithiation and lithiation process.

**8.3.6 Characterization of All Solid State Thin Film Battery**

The cross section of TiO$_2$/LiNi$_0.5$Mn$_{1.5}$O$_4$ / L$_{3.4}$V$_{0.6}$S$_{0.4}$O$_4$/SiO$_2$/Si stack was fabricated using focus ion beam by Dr. Santhanaqopalan in my group. The cross section of all-solid-state thin film battery was examined by SEM as shown in Figure-8-13. The thickness of TiO$_2$ anode, LVSO solid electrolyte and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode are 150nm, 900nm and 300nm respectively. The total thickness of the stack is about 1.5um that is suitable for *In-situ* TEM investigation. Moreover, there is no crack or holes even after the anode TiO$_2$ deposition. The TEM images and selected area diffraction pattern are shown in Figure 8-14 confirming the random orientation of cathode and anode thin films as observed in XRD results. In spite of the FIB processing and the e-beam observation the solid electrolyte is amorphous as shown by the diffraction pattern. The interfaces between the layers are found to be sharp and well defined.

**8.4 Summary**

In this work, Li$_4$Ti$_5$O$_{12}$ and TiO$_2$ thin films were fabricated by PLD method at different temperature. The relationships between crystal structure, surface morphology and electrochemical properties of thin films were examined. The Li$_4$Ti$_5$O$_{12}$ thin film with pure spinel phase only can be deposited at high deposition temperature that limits its application.
The TiO$_2$ thin film deposited at 450˚C with mixed rutile and anatase phase exhibits the largest capacity coupled with excellent cycling performance. The smaller grain size of the rutile and anatase phases in the thin films most likely enables the formation of the new LiTiO$_2$ phase during the lithiation process. However, enhanced rate performance can only be achieved if the thin film is deposited at 350˚C. The porous thin film deposited at 350˚C leads to a larger electrode/electrolyte contact area and shorter solid-state path lengths for both Li-ion and electron transport that results in the better rate capability. The cycling performance was also significantly improved by the porous structure of the thin films deposited at this lower temperature. Finally, the all solid state thin film battery with TiO$_2$/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ / $L_3V_{0.6}S_{0.4}$O$_{4}$/SiO$_2$/Si stack was fabricated successfully only by PLD process.
Figure 8-1. XRD pattern of Li$_4$Ti$_5$O$_{12}$ powder synthesized by sol-gel method and solid state method.

Figure 8-2. XRD pattern of Li$_4$Ti$_5$O$_{12}$ thin film deposited on SiO$_2$/Si.
Figure 8-3. FESEM images of \( \text{Li}_4\text{Ti}_5\text{O}_{12} \) thin film deposited at different temperatures (a) 500°C (b) 600°C (c) 700°C (d) 800°C (e) 700°C on Au (f) 700°C on Au
Figure 8-4. Charge/Discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (a) powder and (b) thin film.
Figure 8-5. X-ray diffraction patterns of the TiO$_2$ target.

Figure 8-6. X-ray diffraction patterns of TiO$_2$ thin films deposited onto a SiO$_2$/Si substrate.
Figure 8-7. X-ray diffraction patterns of TiO$_2$ thin films deposited onto a stainless steel substrate
Figure 8-8. FESEM images of TiO2 thin films deposited at different temperature (a) 25°C (b) 350°C (c) 450°C (d) 650°C (e) 850°C (f) cross section of thin films deposited at 450°C.
Figure 8-9. XPS plots of the Ti2p(a) and O1s(b) region scans for the TiO$_2$ thin films.
Figure 8-10. (a) First discharge curves of TiO$_2$ thin films (b) First charge curves of TiO$_2$ thin films
Figure 8-11. Rate capability comparison of TiO$_2$ thin films deposited at different temperatures.
Figure 8-12. Cycling Performance of TiO$_2$ thin films deposited at different temperatures.
Figure 8-13. Cross-sectional SEM image of the all-solid-state battery prepared by PLD and subsequent FIB processing.

Figure 8-14. TEM image of the all-solid-state battery prepared by PLD and diffraction pattern of all the three layers.
CHAPTER 9
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

9.1 Conclusion

The main goal of this study, as delineated in the introduction, is to develop strategies to improve the electrochemical performance of electrodes for Li-ion batteries.

First, in order to improve the rate capability of the high voltage spinel material, a series of bi-doped spinel oxides of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ (0<x<0.5, 0<y<0.5) have been studied. Their crystal structure, electronic structure and electrochemical properties are compared. Although the capacity of the doped spinel materials decreases with the increasing doped Cu amount, LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ spinel oxide exhibits higher capacity than undoped LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel at high rates. The good rate capability of LiCu$_{0.25}$Ni$_{0.25}$Mn$_{1.5}$O$_4$ spinel oxides attributed to the single phase reaction during charging, the lower Li diffusion barrier induced by Cu doping that calculated by first principles theory, and possibly higher electronic conductivity contributed by Cu doping. A new explanation of the voltage profile for LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ is proposed, supported by the results from first principles computation, and confirmed by electrochemical property measurement and in situ XAS experiment.

Second, titanium dioxide flakes were fabricated by a simple spreading method. After a 400 °C calcination process, the flakes transformed into a pure anatase phase that is free of any impurity. In this phase, the flakes are characterized to have 8 nm grains and the 7nm pores. The crystal structure, surface area, pore size, electronic properties and electrochemical properties are compared for flakes and nanoparticles. The nano-sized grains (8 nm) of the calcined flakes may lead to the absence of two-phase in single particles during lithiation, improving the cycling performance.
significantly. A larger contact area between electrode and electrolyte, short diffusion path for both Li-ion and electron movement and lower specific current density of in the CF-TiO₂ lead to a much better rate capability.

Third, the various thin film electrodes and electrolyte were prepared by PLD process, including LiNi₀.₅Mn₁.₅O₄ cathode, LVSO solid electrolyte, Li₄Ti₅O₁₂, and TiO₂ anodes.

The thin film electrodes offer the ability to probe the surface of the material without the need of a conductive agent and polymer binder typically used in composite electrodes. The surface stability of the high voltage Li ion cathode LiMn₂ₓNiₓO₄₋δ (x = 0.5, 0.45) were compared by comparing thin film and powder composite electrodes after cycling using X-ray photoelectron spectroscopy. The results from this analysis implies that the surface of the NiMn spinel material is not directly contributing to the SEI formation mechanism; rather the SEI formation seen in the composite electrodes is a result of the incorporation of carbon black and PVDF.

LVSO solid electrolyte was also prepared by PLD method successfully. The low oxygen deposition condition will form the dense amorphous. Although some oxygen vacancy exhibit in the thin film because of the low oxygen deposition pressure, LVSO thin film with exact stoichiometry and high uniformity can be fabricated.

Li₄Ti₅O₁₂ and TiO₂ thin films were also fabricated by PLD method at different temperature. The relationships between crystal structure, surface morphology and electrochemical properties of thin films were examined. The Li₄Ti₅O₁₂ thin film with pure spinel phase only can be deposited at high deposition temperature that limits its application.
The TiO$_2$ thin film deposited at 350-450˚C show high capacity coupled with excellent cycling performance. The smaller grain size in the thin films most likely enables the formation of the new LiTiO$_2$ phase during the lithiation process. The porous thin film deposited at 350˚C leads to a larger electrode/electrolyte contact area results in the better rate capability. Finally, the all solid state thin film battery with TiO$_2$/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ / L$_{3.4}$V$_{0.6}$S$_{0.4}$O$_4$/SiO$_2$/Si stack was fabricated successfully only by PLD process.

9.2 Suggestions for Future Work

First, the refinement works of LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ (0<x<0.5, 0<y<0.5) electrode show that Cu will move to tetrahedral site that may block the diffusion of Lithium and lead to the induction of the capacity. Moreover, the configuration of the super cell and structure of materials proposed by the computation do not identical to materials fabricated by high temperature sol-gel synthesis work. Low temperature synthesis method should be used to prepare the materials with similar configuration compared to the computation and inhibits the possibility of Cu in tetrahedral site. Moreover, the capacity of the doped spinel materials LiNi$_x$Cu$_y$Mn$_{2-x-y}$O$_4$ (0<x<0.5, 0<y<0.5) decreases with the increasing doped Cu amount, the new doped element should be selected by first principles theory and the experiment should be performed to find the materials has high capacity and high rate.

Second, the electrochemical properties of flakes cannot excel those of other nanostructures prepared by other groups although the electrochemical properties of flakes is better than TiO$_2$ nanoparticles while tested in the same condition, there are two factors that negatively affect the electrochemical properties of the flakes: (1)In order to fabricate suitable electrode for electrochemical testing by conventional method, large
amount of PVDF (20%) must be added to fabricate a well-adhered electrode on Al-foil. 

(2) In the electrode-making process, the flakes may be partially destroyed due to ball-milling. The authors suggest a graphene paper-flakes composite and further improve the electrochemical properties by which the addition of PVDF can be diminished and the flakey shape of TiO$_2$ can be kept. Moreover, it is also possible to improve the volumetric energy density by packing the sheets of flakes aligned in a horizontal orientation by this method.

Third, scanning probe microscopy (SPM) approach, referred to as electrochemical strain microscopy (ESM) is an excellent tool to explore Li-ion transport in thin films. The thin films electrodes deposited at different conditions and different lithiation level were used to explore the Li-diffusivity in nano-scale. Moreover, the in situ nano-scale observation of chemical and structural changes across the interfaces of the all-state thin film batteries will also performed by TEM.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Ming-Che Yang was born in Taipei of northern Taiwan. He did his undergraduate studies at the Applied Chemistry Department at National Chiao Tung University, and got his master’s degree in materials science and engineering at National Tsing Hua University, Hsinchu, Taiwan. After a three month military training, he worked for four and half years as an assistant researcher in National Nano Device Laboratory, Hsinchu, Taiwan. He focus on the research about High-K, Low-K ferroelectric materials and develop a novel method to fabricate Si-Nanogress by simple hydrogen etching method, this structure was used as a field emission source, a antireflection layer, a superhydrophobic surface and a Mold for polymer nanotip. He also got the patent in Taiwan and Korea for this technique. He published eight papers in peer-reviewed journals and presented his results in five conferences when he worked in Taiwan.

He continued his education in pursuit of a Doctor of Philosophy degree in the Department of Materials Science and Engineering at University of Florida, Gainesville. He worked with Dr. Shirley Meng in UF since 2008 on developing and optimizing novel electrodes of Li-Ion Batteries. Now his research interests are high-voltage spinel materials, nanosized anode materials and all-solid-solid-state thin film Lithium ion batteries. By using the all-solid-state thin film batteries, the intrinsic properties of materials can be explored, especially for the interface between the electrode and electrolyte. He published four papers in peer-reviewed journals and gave 6 presentations in conference when he stayed in Dr. Shirley Meng’s group.