First principles study of lithium nitrides as anode materials for lithium rechargeable batteries

Wu, Shunnian

2013

Wu, S. (2013). First principles study of lithium nitrides as anode materials for lithium rechargeable batteries. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/51113>

<https://doi.org/10.32657/10356/51113>

**FIRST PRINCIPLES STUDY OF LITHIUM NITRIDES
AS ANODE MATERIALS
FOR LITHIUM RECHARGEABLE BATTERIES**

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

2013

Acknowledgements

There are many people to thank for their support and encouragement, without whom this research would not have been completed.

First of all, I would like to express my most sincere appreciation to my supervisors Prof. Freddy Boey and Dr. Dong Zhili from School of Materials Science and Engineering of Nanyang Technological University (NTU) and Dr. Wu Ping from Institute of High Performance Computing (IHPC) for their supporting, guidance, understanding and encouragement. Their wide knowledge and precise attitude to research always inspired me and their stimulating advice benefited me in overcoming various obstacles throughout my Ph.D. study. It was my great pleasure to conduct the thesis work under their supervision.

It is a pleasure to thank Sheng Yiqiang, Ding Hui and You Lu from School of Materials Science and Engineering of NTU for the interesting working time, helpful ideas and useful discussions throughout the duration of my studies.

I am also grateful to my colleagues from IHPC, Dr. Bai Kewu, Dr. Yu Zhigen, Dr. Jin Hongmei, and Dr. Zhang Jia for their useful discussion and various assistances to my research.

In addition, I would like to thank Dr. Michael B. Sullivan from IHPC for professional grammatical and typographic corrections to my writings.

I greatly appreciated School of Materials Science and Engineering of NTU and Institute of High Performance Computing for providing resources and funding to this research.

At last, I would like to express my deepest gratitude to my beloved wife, parents and brothers. I am deeply indebted to them for their endless love and support.

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Summary

Lithium nitrides have emerged as promising anode materials in lithium rechargeable batteries. First principles density functional theory (DFT) methods based on plane wave basic sets and projector augmented wave have been proven to be useful tools for lithium nitride study. In this work, we employed DFT methods to study various lithium nitrides obtained from Li_3N by metal and non-metal doping for potential applications as anode materials.

We first investigated the electronic structure and the vacancy formation in parent Li_3N using first principles methods. Li vacancy formation energy decreases with an increase of nitrogen partial pressure, while N vacancy formation energy increases with an increase of nitrogen partial pressure. The Li(2) vacancy is found to be the dominant defect with the lowest formation energy under nitrogen-rich conditions, suggesting that a nitrogen-rich condition is preferred for Li_3N fabrication process for high Li ionic conductivity.

We subsequently studied the effect to 3d transition metal doping on the electronic and ionic conduction of Li_3N . The ionic radius of transition metal may determine its substitution site in Li_3N . Ti substitution energetically favors at Li(2) site while other 3d transition metals prefer Li(1) substitutions. V, Cr, Mn, Fe, Co and Ni substitutions significantly bring down energy band gap with localized electrons at the

Fermi level, suggesting introduced electronic conduction. Transition metal substitution generally reduces Li vacancy formation energy, and hence enhances the Li vacancy concentration, in particular by Sc, V and Cr. It is further revealed that transition metals except Co and Cu strongly trap the increased Li vacancies according to their dopant-vacancy binding energies, which could retard the Li ionic conduction. The reported excellent performance of Co doped Li_3N as anode material is confirmed due to its improved ionic and electronic conduction.

We further studied the electronic structure and bonding of transition metal M ($\text{M} = \text{Co}, \text{Ni}$ and Cu) substituted Li_3N . Co or Ni substitution can bring about mixed electronic and ionic conduction. Covalent bonding occurs between transition metal atom and coordinated N, which is confirmed both visually by valence charge density distribution and numerically by bond length variation. The covalent bonding reduces the nominal oxidation state of transition metal, leading to the formation of $\text{Li}_{2-x-y}\text{M}_x\Box_y\text{N}$ ($\Box = \text{Li vacancy}$) with y dependent on the transition metal nature and the substitution concentration.

We also investigated the effect of phosphorus and arsenic substitution of nitrogen on the electronic structure and conductive properties of Li_3N . Both P and As partial substitution reduce Li vacancy formation energy without appreciable alteration of energy band gap, indicating an improvement in ionic conduction. But a full substitution of P and As results in variation of crystal structure from the space group

$P6/mmm$ to $P6_3/mmc$, and reduction of energy band gaps of Li_3P and Li_3As , indicating an enhancement of electronic conduction. However, the full substitution brings about an increase of Li vacancy formation energies, suggesting degradation in ionic conduction.

Our calculations suggest that it will be viable to achieve designed electronic and ionic conduction of Li_3N by controlled metal or non-metal doping. This study provides instructive information for experimental researches on synthesizing new lithium nitride compounds with designed electrochemical properties.

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7. Shunnian Wu, Zhili Dong, Freddy Boey and Ping Wu. Screening 3d Transition Metal to Substitute Li_3N for Improved Ionic and Electronic Conduction, *43rd IUPAC World Chemistry Congress*, July 30 - August 7, 2011, Puerto Rico, USA.
8. Shunnian Wu, Su San Neo, Zhili Dong, Freddy Boey and Ping Wu. Adjusting Electronic Structure and Conductive Properties of Li_3N via Phosphorus and Arsenic Substitution, *4th EuCheMS Chemistry Conference*, August 26-30, 2012, Prague, Czech Republic.

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Chapter 1

Introduction

1.1 Motivation

The rapid growth of portable electronic devices in both military and civilian applications has stimulated considerable efforts to develop high energy density storage devices. Among the technologies existing for rechargeable solid-state batteries, lithium based batteries give the highest volumetric energy density and the highest gravimetric energy density as shown in Figure 1.1. Compared to the same capacity of nickel-cadmium (Ni-Cd) and nickel-metal hydride (Ni-MH) batteries, the weight of batteries can be reduced by half and the volume by 20% to 50%.[2] Lithium based batteries outperform many other systems, which thus account to 63% of worldwide sales values in portable batteries.[1]

Extensive attentions have been given to lithium rechargeable batteries due to its extremely high specific capacity. Their specific capacity is determined by the cathode and anode materials used in the lithium rechargeable batteries. Therefore, the selection of suitable electrode materials is of critical importance for their practical applications in versatile electronic mobile devices.

FIGURE 1.1: Comparison of different technologies in terms of volumetric and gravimetric energy density.[1]

The first ambient temperature lithium rechargeable batteries used elemental lithium as the anode electrode and the layered transition metal oxide as cathode electrode as shown in Figure 1.2a. The initial driving force for adopting lithium metal as anode in the lithium rechargeable batteries is due to its high electropositivity of -3.04 V and its light weight (equivalent weight $M = 6.94 \text{ g/mol}$ and specific gravity $\rho = 0.53 \text{ g/cm}^3$). [1] Owing to severe safety problems and

significant loss of capacity during cycling when such electrodes are used with organic solvent liquid electrolytes, this approach has almost been fully discarded.

FIGURE 1.2: Illustration of operation principle of lithium rechargeable batteries.[2]

In order to resolve the safety issues, the anode electrode is modified by substituting metallic Li for a second insertion material. The presence of Li in the ionic state instead of the metallic state avoids the dendrite growth in lithium metal anode electrode as seen in Figure 1.2b. The process in the battery involves

simultaneous intercalation-deintercalation of Li ions in two electrode materials, which is shown in Figure 1.2b. In 1991, Sony Energytech Inc. commercialized the first generation lithium-ion rechargeable batteries. However, they exhibit slightly lower energy densities though they are much safer. Lithium-ion batteries can produce three times more voltage as compared to Ni-Cd and Ni-MH batteries,[2] implicating that the electronic portable devices can be more scaled-down. Additional advantage of lithium-ion rechargeable batteries is that they do not exhibit memory loss with partial charging and discharging, which causes charging capacity of Ni-Cd batteries to be reduced by repeatedly charging and discharging to insufficient levels.

The commercial lithium-ion batteries are composed of carbon material as the anode, a layered transition metal oxide as the cathode, and a nonaqueous electrolyte. Materials such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 and various carbons are candidates for use in the first generation of lithium-ion cells. To date, all commercial Li-ion batteries use carbonaceous materials as the anode material. Among various carbonaceous materials, graphite and disordered carbons have been dominantly employed in Li-ion batteries. The limited gravimetric capacity of carbon ($< 370 \text{ mA}\cdot\text{h/g}$), however, has stimulated an intensive search for alternative materials that can intercalate lithium ions at low potential. Among the few candidates under consideration, lithium transition metal nitrides have recently emerged as one of the

most promising candidates. However, there is lack of the correlation between the geometrical structure, electronic structure and electronic and ionic conduction of lithium nitrides to guide the finding and developing of new lithium nitrides with higher specific capacity, conductivity and stability.

1.2 Objectives

The objective of this research is to establish the correlation between geometrical structure, electronic structure and electronic and ionic conduction of lithium nitride materials derived from Li_3N and to exploit new lithium nitrides with improved electronic and ionic conduction and stability through suitable atomic substitutions based on first-principles calculations.

The electronic structure and native defect formation in the parent Li_3N is studied to obtain fundamental understanding of the mechanisms of ionic conduction in the structure. The effect of transition metal doping and non-metal doping on the electronic structure and vacancy formation of the parent Li_3N will be investigated to obtain possible doped compounds with improved electronic and ionic conductivity and stability. The electronic structure and vacancy formation of selected ternary lithium nitride compounds will be further evaluated to

understand the nature of vacancy and valence electron delocalization in the structure.

1.3 Organization of the thesis

The thesis is divided into eight chapters. Chapter 1 presents the motivation and objectives of this research. Chapter 2 reviews the literature on previously studied anode materials with a focus on lithium nitrides. Chapter 3 describes the density functional theory (DFT) methods we employ in this research. Chapter 4 reports the electronic structure and vacancies in the parent Li_3N . Chapter 5 presents the Li site selection of 3d transition metal substitution and the electronic structure of 3d transition metal substituted Li_3N so as to screen suitable dopant candidate to improve the electronic and ionic conduction of Li_3N . Chapter 6 gives further description of the electronic structure and bonding in Li_3N doped with transition metal (Co, Ni, and Cu) to understand the mechanisms of their improved electronic and ionic conduction. Chapter 7 evaluates the effects of partial and full substitution of nitrogen in Li_3N by phosphorus and arsenic on the electronic structure and conductive properties. In the final chapter, we summarize our works and suggest some future research topics.

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Chapter 2

Literature Review

2.1 Criteria of anode materials

During the optimization and development of the anode materials, there are many criteria to be taken into consideration. These include: (1) energy density; (2) rate capability; (3) cycling performance; (4) safety and (5) cost. The energy density is determined by both reversible capacity and operating voltage of the material, which is mostly determined by the material intrinsic chemistry such as the effective redox couples and maximum lithiation/delithiation lithium concentration. For rate capability and cycling performances, electronic and ionic mobilities are key determining factors, though particle morphologies are also important factors due to the anisotropic nature of the structures and are even playing a crucial role in some cases. From the safety point of view, the volume change accompanying the lithiation/delithiation process has always been a challenge for designing high-capacity anode materials. The large volume change can mechanically disintegrate the material and result in particles that are not electrically connected, and even cause battery failure. Considering that the current carbonaceous anode materials in lithium-ion batteries are abundant in the earth and of relatively low cost,

this requires that newcomers of anode materials must be cost-effective and environmentally benign.

2.2 Potential anode materials

The current commercial Li-ion batteries use carbonaceous materials as the anode material. The relatively low gravimetric capacity of carbon ($< 370 \text{ mA}\cdot\text{h/g}$) has stimulated an intensive search for alternative anode materials. Figure 2.1 summarizes the anode materials presently used or under serious considerations for rechargeable Li-ion batteries. Efforts to exploit alternative anode materials are mainly devoted to two directions, one is to improve the properties of the available carbonaceous materials and to find new carbonaceous materials, and another is to search for carbon alternatives in the hope of finding materials with both larger capacities and slightly more positive intercalation voltages compared to Li/Li^+ . [1,2]

Several carbonaceous materials, such as mesocarbon microbeads (MCMB), carbon fibers, etc, are undergoing continuous improvement in the specific capacity; some new comers, such as pre-treated natural and synthetic graphite of low cost, have entered commercial application. Some special carbon materials such as carbon nanotubes are under study and development. As potential alternatives to

carbonaceous compounds, a series of anode materials including alloys, oxides and nitrides have been investigated.

FIGURE 2.1: Voltage versus capacity for cathode and anode materials presently used or under serious considerations for rechargeable Li-ion batteries.[1]

2.2.1 Metal alloys

Lithium alloys have been considered as alternatives to elemental lithium for a long time. Lithium metal alloys such as Li_xM ($\text{M}=\text{Sn}$, Pb , In , Al , *etc.*) in principle offer a much higher specific capacity than that of intercalated carbon,[3-5] for example, $\text{Li}_{4.4}\text{Sn}$ shows specific capacity of $710 \text{ mA}\cdot\text{h/g}$. [3] However, these alloy systems

generally undergo severe volume expansion and contraction during lithium intercalation and de-intercalation. The drastic volume changes limit the mechanical and cycling stability of the electrodes. Improvement in the cycle life can be achieved by the following approaches:

- (1) Decreasing the size of the host particle (or grain) to submicron or even nanoscale;[6-7]
- (2) Highly dispersing active phase into less active (*e.g.* SnSb_x) or even inert phase (*e.g.* SiSnO_3 , Sn_6Cu_5 , $\text{Sn}_2\text{Fe/SnFe}_3\text{C}$) to form multi-phase composite structures.[8-9]

However, the use of ultrafine alloy powders and inert compounds often leads to large irreversible capacities at the first cycle, which can create difficulties in the practical applications.

Another approach to make lithium alloys appealing electrode materials has been using intermetallic compounds, such as SnSb [6] and SnAg [10], SnM ($\text{M} = \text{Co}$, Ni , In , Pb) [11] and InSb [12]. The advantages include enhanced control of the volume changes and formation of a conductive “buffer”, which can improve the cycle life and power capability of lithium-ion batteries. However, structural changes evidently occur after lithium insertion.

2.2.2 Oxides

The convertible oxides are considered to be an alternation to lithium metal alloys. The oxides are converted to a fine composite microstructure containing fine particles of lithium–metal (*e.g.* tin) alloys in a matrix of Li_2O and glass by reaction with lithium in the first charging cycle. After this initial irreversible reaction, the electrochemical properties of these electrodes are essentially those of the resulting lithium alloys. A particularly favorable example is the use of SiO_2 . [13] The high initial irreversibility limits their practical use as anode electrodes in lithium-ion rechargeable batteries. However, CuCrO_2 shows different Li intercalation/de-intercalation behavior rather than being transformed to lithium-metal alloys. It probably corresponds to a reversible phase transformation between $\text{Li}_2\text{O}/\text{Cr}$ composite and Cr_xO_y phase. [14]

Another interesting oxide is tin-based amorphous composite oxide (TCO). [15] It demonstrates a specific capacity more than 50 percent higher than those of the carbon families. Per unit mole of TCO can accept as many as 8 moles of lithium ions during intercalation process. It contains Sn(II)-O as the active center for lithium insertion and other glass-forming elements, which make up an oxide network. Furthermore, the absence of structure deformation makes

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ an almost “zero” strain anode material characterized by a very good cyclability and by a very little capacity fade upon cycling.[16]

2.2.3 Metal–metalloid alloys

A different approach to metal alloys is the consideration of metal–metalloid alloys, including borides, silicides and nitrides.[17] Lithium can react with boron at intermediate and elevated temperatures to form a number of intermediate phases.[18-20] SiB_3 was reported to demonstrate a specific capacity of 440 $\text{mA}\cdot\text{h/g}$. [18] Mg_2Si , which has the anti-fluorite structure, is an anode material at both elevated and ambient temperatures.[21] It has a capacity of over 400 $\text{mA}\cdot\text{h/g}$ with an average potential of about 0.35 V vs. Li. Their relatively light weight indicates that it is not necessary that they react with large amounts of lithium to achieve attractive specific capacities. This leads to less mechanical distortion, and potentially to better behavior upon cycling.

2.2.3.1 Lithium nitrides

Lithium nitride Li_3N was mainly studied as a solid electrolyte. Li_3N has exceptionally fast ionic conduction, but its decomposition voltage is very low (0.44 V). Therefore, it cannot be used as anode material directly. It is found that

lithium transition metal nitrides have improved chemical stability and ionic conductivity.[22] Two methods have been used to prepare a majority of these phases: a standard high temperature “ceramic method”, and growth of submillimeter crystals from reactions containing molten electropositive metal.

Lithium transition-metal nitrides have emerged as a new potential class of anode materials owing to the large, stable and reversible capacity (600 mA·h/g) displayed by one family member, $\text{Li}_{3-x}\text{Co}_x\text{N}$. [2] Subsequent studies in the search for new lithium nitride anode materials have concentrated on two groups of ternary lithium nitride compounds – those forming anti-fluorite structures, and those derived from the parent lithium nitride. The structures exhibited by ternary lithium nitride Li-M-N (M = first-row transition metal) system follow a predictable trend. For Ti through Fe , an anti-fluorite structure is favored with Li and M in the tetrahedral sites, and M is present in a high oxidation state. For Co , Ni , and Cu , a structure based on $\alpha\text{-Li}_3\text{N}$ is formed, with M^+ substituting for lithium between the hexagonal Li_2N layers. Iron is unique in forming a metastable layered phase Li_4FeN_2 which displays ordering of Fe^{2+} with vacancies between the layers.[23] The group of ternary lithium nitride materials with the anti-fluorite structure is known to have high ionic mobility.[24-25] On the other hand, the group of ternary lithium nitrides of the $\alpha\text{-Li}_3\text{N}$ structure was shown to have very high lithium ionic conductivity.[26-28] $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ shows an attractive character with a high capacity

over 900 mA·h/g.[29-34] Such a large capacity is accompanied with an irreversible transformation of $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ from a crystal to an amorphous phase in the first lithium de-intercalation process. It is proven that lithium in the compound can be electrochemically intercalated and de-intercalated with high reversibility.[35]

Recently, ternary lithium nitride composites have attracted attention in an effort to improve the stability of any prospective anode material. Composite electrodes based on $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ and oxide insertion materials (as the second reactant species) can not only eliminate the initial irreversibility, but also provide a large reversible capacity.[36] To suppress the rapid capacity decay of the hexagonal $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ upon long cycles, Liu et al. proposed to substitute a certain amount of Co with Cu to enhance its electrochemical stability and interfacial compatibility.[36] $\text{Li}_{2.6}\text{Co}_{0.2}\text{Cu}_{0.2}\text{N}$ shows a greatly improved cycling performance, but suffers from a little capacity loss.

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Chapter 3

Theoretical Background

3.1 Density functional theory

First-principles methods have recently been widely applied in all areas of physics and chemistry, where the properties are related to electron densities.[1] They are quantum mechanical methods to numerically solve the Schrödinger equations for systems of electrons:

$$H\Psi(r) = E\Psi(r) \quad (3.1)$$

where H is the Hamiltonian operator, $\Psi(r)$ is the wave function of the system at a point r , and E is the energy of the system.

Hohenberg and Kohn established the basis of the density functional theory (DFT) in 1964.[2] Electron density is the fundamental variable in DFT. In this theory, the energy is not written in terms of the many-electron wavefunction as it is conventional in quantum chemistry, but as a function of the electron density. The

first Hohenberg-Kohn theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by the electron density:[2]

$$E = E[\rho(r)] \quad (3.2)$$

It declares that all of the ground-state properties of the system can be obtained once the electron density is determined. The second Hohenberg-Kohn theorem proved that a universal functional of the density exists.[2] However, Hohenberg and Kohn did not give any clue to the universal function. Kohn and Sham provided the method for turning DFT into a practical method.[3] The electron density was assumed to be written in terms of single-particle wave functions $\phi_k(r)$ of an auxiliary non-interacting system.

$$\rho(r) = \sum |\phi_k(r)|^2 \quad (3.3)$$

Therefore, the intractable many-body problem of interacting electrons is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, *e.g.*, the exchange and correlation interactions, which gives the Hamiltonian operator as

$$H = T + V + U + V_{xc} \quad (3.4)$$

where T , V , U and V_{xc} are the kinetic energy, electron-ion interaction, electron-electron interaction and exchange-correlation potential operator respectively. V_{xc} is the functional derivative of the exchange-correlation density functional energy with respect to the density at a point r .

3.2 Local density approximation and generalized gradient approximation

The Kohn-Sham equations are an exact solution to the interacting electron problems. However, except for the free electron gas, the exact functionals for the exchange and correlation energy are not known for a spatially varying charge density. It is very difficult to calculate the accurate exchange and correlation energy due to complex interactions between electrons. Therefore, it is necessary to make an approximation to carry out practical calculations. The method to overcome this problem is to perform exact many electron calculations on a constant system of interacting electrons which have a constant charge density.

Kohn and Sham first formulated one of the most widely adopted approximations called as the local density approximation (LDA).[3] The LDA

assumes that the functional depends only on the density at the coordinate where the functional is evaluated. The exchange and correlation energy at a given point depends only on the electron density at that same point. For slowly varying densities, it is reasonable to assume that the exchange-correlation energy contribution at each point is the same as a locally uniform electron gas of the same electron density. This idea is illustrated schematically in Figure 3.1. The exchange-correlation energy at point r_1 is the same for both the “A” and “B” electron densities in LDA since they are both equal to ρ_1 at this point.

Although the local density approximation is surprisingly simple, it is stunningly accurate, and forms the core of most modern DFT codes. This approximation works best in cases where the density is slowly varying, or equivalently, when the density gradients are small. It sometimes works reasonably well in systems where the charge density is rapidly varying.

Certainly, there are some shortcomings in LDA. It tends to underestimate atomic ground state energies and ionization energies, while overestimates the binding energies. It fails miserably when the electron density varies quickly, such as in the cases of molecules, surfaces and for strong correlated electron systems, for example, ionic semiconductors.

FIGURE 3.1: Schematic illustration of the difference between LDA and GGA.[1]

The exchange-correlation energy at point r_1 is the same for both the “A” and “B” electron densities in LDA because they are both equal to ρ_1 at this point. However, the exchange-correlation energy for A and B at r_1 is different in GGA because the electron densities are not the same at other points.

Over the past decades, a class of corrections to LDA has been developed that corrects this deficiency to a large extent by explicitly using the power law in regions of low density. This is usually carried out by introducing a dependence on the gradient of the density, which leads to the generalized gradient approximation

(GGA) proposed by Hohenberg, Kohn and Sham.[2-3]. It is evolved into the modern GGA by the following works of Langreth and Mehl [4], Perdew [5] and Becke [6]. The kernel of the GGA exchange-correction functional is a function of both the electron density and the gradient of the electron density. Therefore, the exchange-correlation energy at point r_i in Figure 3.1 is different for A and B since the electron densities are different at other points. Generalized gradient approximations are most appropriate in cases in which there are large density gradients, for example, isolated atoms.

Two main GGA methods, *i.e.* GGA-PW91 and GGA-PBE, have been developed in recent years. GGA-PW91, developed by Perdew and Wang [7], is an important GGA functional and commonly used by the solid state DFT community. It is an example of a non-empirical construction since it does not contain any parameters that are fitted to experimental data; it is determined from exact quantum-mechanical relations. GGA-PBE, developed by Perdew, Burke and Ernzerhof [8-9], is designed to give a simpler function form by retaining only the most energetically important conditions satisfied by GGA-PW91.

Kohn-Sham DFT treats the many-body problems as many non-interacting particles problems. In an infinite but periodic bulk crystal, it is necessary to reduce this problem to the study of a finite system. The approach has even been

employed to study aperiodic systems such as those that contain intrinsic defects or doping of a foreign element. Such system is contained in a supercell large enough so that the interaction between the defect (and dopant) and its neighboring images should be negligible on the total energy.

Since DFT incorporates both exchange and correlation effects, it is more computationally efficient and accurate than other methods such as Hartree-Fock theory (HF).[10] The major distinction in DFT is that the electron density is calculated instead of the electron wavefunction. However, DFT has well-known limitations including the treatment of excited electron states (*e.g.*, semiconductor band gaps and excitons-bound electron-hole pairs) and strong electron-electron correlation (*e.g.*, localized f-electrons in actinide materials). Nevertheless, DFT has since advanced to become a very important method for determining the energy of many-electron systems.

3.3 Plane wave expansion

Plane waves enjoy great popularity in solid state physics because they are the natural language of period functions and provide efficient solutions to the Schrödinger equations. The general form of the plane waves is

$$\psi = C \exp(ikx) \quad (3.5)$$

where k is a real vector, C is a constant.

In a periodic solid, the electronic wave function satisfies Bloch's theorem, *i.e.* it is the product of a wavelike part and a cell periodic part.[11]

$$\psi_i(r) = e^{ikr} u_i(r) \quad (3.6)$$

where $u_i(r)$ is the cell periodic part of the wavefunction. It can be expressed by expanding it into a finite number of plane waves whose wave vectors are reciprocal lattice vectors of the crystal.

$$u_i(r) = \sum_G c_{i,G} \exp[iG \cdot r] \quad (3.7)$$

where G is the reciprocal lattice vectors. These reciprocal lattice vectors are defined by $G \cdot l = 2\pi m$ for all l where l is a lattice vector of the crystal and m is an integer. Thus each electron wave function can be written as a sum of plane waves as

$$\psi_i(r) = \sum_G c_{i,k+G} \exp[i(k+G) \cdot r] \quad (3.8)$$

By using Bloch's theorem, the problem now becomes one of solving for wavefunctions only within a single cell instead of over all of space, albeit with an infinite number of possible values of k . In order to simplify the problem to controllable proportions, we need to impose some boundary conditions on the wave functions to restrict the allowed values of k . This can be dealt with by sampling the Brillouin zone at special sets of k points.

The electronic wave functions at each k -point are expressed in terms of plane wave basis set. In principle, this Fourier series is infinite; however, typically the coefficients $c_{i,k+G}$ with a small kinetic energy $\left(\frac{\hbar^2}{2m}\right)|k+G|^2$ are more important than those with large kinetic energy. This leads to a further truncation of plane wave expansion in plane-wave calculations. Namely, only the reciprocal lattice vectors whose kinetic energy lower than a predefined maximum cutoff energy E_{cut} are kept in the expansion, while the rest of the coefficients are set to zero. Therefore, the introduction of E_{cut} reduces the basis set to a finite size, which brings about an error to the total energy calculations. To see how this influences the problem, calculations are done at some cut off energy, and then repeated for a higher cut off energy until the calculated total energy has converged. However, the selection of a higher cutoff energy leads to an increase in computing cost.

This gives rise to another advantage of the plane-wave basis set in that the accuracy can be systematically improved by increasing E_{cut} . The main disadvantage of plane-waves is that they are not efficient at describing wave functions with large curvature such as in the core regions of atoms, consequently such regions of space require an unreasonably large number of plane waves to be sufficiently accurate, and so would dominate the convergence of E_{cut} . This problem can be overcome with the pseudopotential approximation which is described in section 3.5.

3.4 k -point Sampling

Blöch's theorem transforms the problem of calculating an infinite number of electronic states extended infinitely in space to one of calculating a finite number of eigenstates at an infinite number of k -points which are extended over a single unit cell. It seems to be only a minor improvement since still an infinite number of calculations are needed for the different k -points. Since the electronic wave functions at k -points which are close together will be very similar, it is possible to represent the wavefunctions of a region of k -space by the wave function at a single k -point.[12] Within this approximation, the electronic states at only a finite number of k -points are required to calculate the charge density and hence the total

energy of the solid. The error induced by this approximation can be systematically reduced by increasing the density of the k -point grids.

Though a denser set of k points will ensure the computing more accurate, more k points means increased computing cost. For insulators it turns out that usually only a small number of k -points is required to get good converged results. Since the volume of the Brillouin zone becomes smaller with increasing size of the supercell, a less number of k -points is needed for enlarged supercell. From a certain supercell size on, it is often justified to use just a single k -point, which is usually Γ -point. On the other hand, much denser k -point grids are required for metallic systems in order to get a precise sampling of the Fermi surface.

Usually k points are generated by the Monkhorst-Pack scheme in total energy calculations.[13] The main advantages of this scheme include its simplicity and the fact that convergence is easily verifiable. The Monkhorst-Pack special k -points are a uniform grid of $i \times j \times k$ point in reciprocal space given by

$$k(p, r, s) = u_p b_1 + u_r b_2 + u_s b_3 \quad (3.9)$$

where b_1 , b_2 and b_3 are the reciprocal lattice vectors, and u_p, u_r and u_s are defined as

$$u_p = (2p - i - 1) / 2i \quad p = 1, \dots, i \quad (3.10)$$

$$u_r = (2r - j - 1) / 2j \quad r = 1, \dots, j \quad (3.11)$$

$$u_s = (2s - k - 1) / 2k \quad s = 1, \dots, k \quad (3.12)$$

where i, j and $k \geq 1$. When $i = j = k$, the sampling scheme is referred to as MP-I³. Convergence can easily be ensured by increasing the values of i, j and k until the calculated value or property of interest does not change significantly.

In a supercell with high symmetry, some of the k -points may be equivalent due to the symmetry operations associated with that supercell. In this case the redundant k -points can be removed and the equivalent one that is left is weighted accordingly.

3.5 Pseudopotential approximation

The electrons in a solid can be divided into core electrons and valence electrons. The core electrons are localized around the nucleus in closed shells while the valence electrons take part in the bonding between atoms. As the chemical bonding and most physical properties of solids are mostly dependent on the valence electrons relative to the core electrons, a popular way to tackle this problem is replacing an all-electron wave function with the pseudopotential approximation,

which was developed by Phillip [14], Cohen and Heine [15], and Yin and Cohen [16]. This leads to solve the Kohn-Sham equation for an effective ionic potential acting on the valence electrons, which includes the effect of the tightly bound core electrons in addition to the coulomb potential of the nucleus. Such effective potentials are called “pseudopotentials”. Since the core atomic states almost remain unchanged from one system to another, the pseudopotentials are quite transferable between different systems. With introducing real pseudopotentials, we replace the true valence wavefunctions by so-called pseudo wavefunctions, which match exactly the true valence wavefunctions outside the ionic core region but are nodeless and smoother than the all-electron wavefunction inside the core. These pseudo wavefunctions can be expanded using a much smaller number of plane wave basis states. The all-electron potential and wavefunction and corresponding pseudopotential and pseudo wavefunction are illustrated schematically in Figure 3.2.

FIGURE 3.2: Schematic illustration of all-electron wavefunction ψ_v (solid line) and the corresponding pseudo wavefunction ψ_{pseudo} (dashed line) together with the respective all-electron potential and pseudopotential.[17] The radius at which all-electron and pseudoelectron values match is designated r_c .

The pseudopotential approximation has a number of other advantages in addition to reducing the number of plane wave basis states required to expand the electronic wavefunctions. Because the core electron states are removed from the

calculations, fewer electronic wavefunctions are required to be calculated. The removal of the core electrons from the calculation means that total energy differences between ionic configurations can be taken between much smaller numbers so that the required accuracy for the total energy calculations will be much less demanding than in an all-electron calculation. However, the value of total energy obtained in the pseudopotential calculation itself is no longer meaningful while the difference in total energy plays the role. A further advantage of pseudopotentials is that relativistic effects can be incorporated easily into the potential while further treating the valence electrons non-relativistically.

The smoothness of the pseudopotential is essential in plane wave calculations to decrease the number of expansion coefficients. There are several methods to build pseudopotentials. One of the earliest methods is the orthogonalized plane wave (OPW) method [18], which breaks the valence wavefunction into a smooth part and a rapidly oscillating part. The problem with this method is that the generated wavefunctions are not orthonormal, resulting in a pseudopotential that is not as smooth as one would like it to be. The norm conserving pseudopotential (NCPP) method [19] is based on calculations of atoms (or atom-like states), and the generated pseudopotentials satisfy the orthonormality condition. However, NCPPs are at best only moderately smoother than the all-electron functions though they give very accurate results for valence states at

the beginning of an atomic shell (1s2p3d *etc.*). The widely used ultrasoft pseudopotentials (USPP) [20] start on the same principle as that of orthogonalized plane wave method, but have increased accuracy due to additional auxiliary functions and overlap operators. Since the condition of norm-conservation is relaxed in USPP, the smooth pseudofunctions can be formed independently. Instead of representing the full valence wavefunction by plane waves, only a small portion of the wavefunction is calculated within the USPP scheme. This allows to substantially reducing the plane wave cutoff energy in the calculations compared to the NCPP methods. This in turn leads to softer potentials and smoother pseudo wavefunctions. However, since additional terms are introduced into the Kohn-Sham formalism, more operations are needed per computational cycle. Another disadvantage of USPP is that the construction of pseudopotentials for each atom requires a number of empirical parameters to be specified. Current DFT codes typically only include USPPs that have been carefully developed and tested, but they do in some cases include multiple USPPs with varying degrees of softness for some elements.

3.6 Projector augmented wave method

Another frozen core approach that avoids some of the disadvantages of USPPs is the projector augmented wave (PAW) method originally introduced by Blöchl [21] and later adapted for plane wave calculations by Kresse and Joubert [22]. It

contains the numerical advantages of pseudopotential calculations while retaining the physics of all-electron calculations, including the correct nodal behavior of the valence electron wavefunctions and the ability to include upper core states in addition to valence states in the self-consistent iterations. The crucial difference between the PAW and USPP methods is that the USPP method is a pseudopotential method while the PAW method is an all-electron method.

The PAW method is based on a transformation, that maps the physically all electron valence wavefunctions onto non-interacting pseudo wavefunctions. The transformation is designated by τ . This transformation completely transforms the shape of the Schrödinger equation wavefunction into the image of Heisenberg. The transformation is assumed to be unity ($\tau = 1$) unless the atom is centered on the nucleus.

$$\tau = 1 + \sum \tau_0 \quad (3.13)$$

The wavefunction of the system is characterized by two different features: the pseudo wavefunction at the valence (bonding) region and the oscillating wavefunction around the nucleus. The oscillation of the wavefunction is caused by the attractive potential of the nucleus. In the PAW method, the wavefunction $\psi_i(r)$ is denoted in term of ket $|\psi_i(r)\rangle$ and its complex conjugate $\psi_i^*(r)$ is

denoted by the bra notation $\langle \psi_i^*(r) |$. The pseudo wavefunctions are differentiated by tilde ($\sim$) from the all-electron wavefunctions and are written as

$$|\widetilde{\psi}_i(r)\rangle = \sum_i c_i |\widetilde{\psi}_i(r)\rangle \quad (3.14)$$

The corresponding all-electron wavefunctions are

$$|\psi_i(r)\rangle = \sum_i c_i |\psi_i(r)\rangle \quad (3.15)$$

The coefficients c_i are identical in both expansions and are the scalar products of the pseudo wavefunctions.

$$c_i = \langle \widetilde{P}_i | \widetilde{\psi}_i \rangle \quad (3.16)$$

for the linear transformation τ . The transformation from the pseudo wavefunction to the all-electron wavefunction is as follows:

$$|\psi_i(r)\rangle = \tau |\widetilde{\psi}_i(r)\rangle \quad (3.17)$$

After the transformation, the full wavefunction in the entire space is expressed as:

$$|\psi(r)\rangle = |\tilde{\psi}\rangle - \sum_i c_i [|\psi_i\rangle - |\tilde{\psi}_i\rangle] \quad (3.18)$$

With substituting the coefficients c_i in Equation 3.18, the full wavefunctions become as follows:

$$|\psi(r)\rangle = |\tilde{\psi}\rangle - \sum_i \left(\langle \tilde{P}_i | \tilde{\psi}_i \rangle \right) [|\psi_i\rangle - |\tilde{\psi}_i\rangle] \quad (3.19)$$

The above mentioned transformation can be determined by the following: the all-electron partial wavefunctions $|\psi_i(r)\rangle$ are obtained radially by integrating the Schrödinger equation of the atomic energy and the orthogonalization of the core states if necessary. The pseudo partial wavefunction must be identical to the corresponding all-electron partial wavefunctions outside the augmentation region and should themselves form a complete set of functions within the augmentation region.

The projector functions $|\tilde{p}_i\rangle$ for the pseudo partial wavefunction obeys the relation

$$\langle \tilde{p}_i | \tilde{\psi}_j \rangle = \delta_{ij} \quad (3.20)$$

and are localized in the augmentation region, even though more extended projector functions could in principle also be chosen. Since in the PAW method, the pseudo wavefunctions instead of the all-electron wavefunctions play the role of the variational parameters, we need to be able to obtain observable quantities as the expectation values of the pseudo wavefunctions. The pseudo operator is written as:

$$\tilde{A} = \tau^\dagger A \tau = A + \sum_{i,j} |\tilde{p}_i\rangle \left[\langle \psi_i | A | \psi_j \rangle - \langle \tilde{\psi}_i | A | \tilde{\psi}_j \rangle \right] \langle \tilde{p}_j | \quad (3.21)$$

The operator is needed for evaluating the charge density and total energy of materials. The said density can be divided into smooth charge density $\tilde{n}(r)$, which is evaluated on regular grids in Fourier or real space while the outer center charge densities $n^l(r)$ and $\tilde{n}^l(r)$ are evaluated on radial grids in angular momentum. The charge density at a point r in real space is the expectation value of the real space projection operator $|r\rangle\langle r|$. Hence the charge density is given by

$$n(r) = \tilde{n}(r) + n^l(r) - \tilde{n}^l(r) \quad (3.22)$$

$$\tilde{n}(r) = \sum_m f_m \langle \tilde{\psi}_m | r \rangle \langle r | \tilde{\psi}_m \rangle \quad (3.23)$$

$$n^l(r) = \sum_{m,(i,j)} f_m \langle \tilde{\psi}_m | \tilde{p}_i \rangle \langle \psi_i | r \rangle \langle r | \psi_j \rangle \langle \tilde{p}_j | \tilde{\psi}_m \rangle \quad (3.24)$$

$$\tilde{n}^l(r) = \sum_{m,(i,j)} f_m \langle \widetilde{\psi}_m | \widetilde{p}_i \rangle \langle \widetilde{\psi}_i | r \rangle \langle r | \widetilde{\psi}_j \rangle \langle \widetilde{p}_j | \widetilde{\psi}_m \rangle \quad (3.25)$$

The charge density $n^l(r)$ and $\tilde{n}^l(r)$ are localized around each atom.

Kresse and Joubert performed an extensive comparison of USPP, PAW, and all-electron calculations for small molecules and extended solids.[22] Their work shows that well-constructed USPPs and the PAW method give results that are essentially identical in many cases and, just as importantly, these results are in good agreement with all-electron calculations. In materials with strong magnetic moments or with atoms that have large differences in electronegativity, the PAW approach gives more reliable results than USPPs.

Overall speaking, the PAW method shows the advantages of both all-electron and pseudopotential methods. The PAW method gives access to the “true” wavefunction and electronic density of the system. Its efficiency is of the same order of ultrasoft pseudopotential approach. It is as accurate as an all-electron method and its convergence can be controlled. Consequently, we selected PAW implemented in VASP code in our calculations.

3.7 References

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Chapter 4

Electronic Structure and Vacancies of Parent Li_3N

4.1 Introduction

Li_3N exhibits exceptionally fast Li ionic conduction due to intrinsic defects and the resultant hopping of Li ions from occupied Li sites into unoccupied ones.[1] The nature of the defect plays a critical role in exploiting its applications for lithium rechargeable batteries.

Li_3N can be described as a sequence of $\text{Li}(1)$ and $\text{Li}(2)_2\text{N}$ layers perpendicular to c axis with space group of $P6/mmm$ as shown in Figure 4.1. Previous X-Ray diffraction and powder neutron diffraction studies observed 1-2% vacancies in $\text{Li}(2)$ position at room temperature.[1-2] The vacancy concentration can go up to 4% at high temperature. Conversely, recent powder neutron diffraction analysis found no Li vacancies in the temperature range of 20-673 K.[3] This contradiction is attributed to different crystal growing procedures. Therefore, a fundamental understanding of the nature of the vacancy and the impact of Li_3N growth environment is necessary to optimize crystal growth conditions.

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FIGURE 4.1: Structure of Li_3N as (a) a $3 \times 3 \times 3$ extension of unit cell, and (b) a $\text{NLi(2)}_6\text{Li(1)}_2$ unit plot. N is shown in blue and Li in red.

Available lattice energy program simulation showed that an interstitial defect cannot be generated in the structure.[4] The energetically favorable vacancy comes from Li(2) removal. Sarnthein et al. asserted that Li(2) vacancy must be formed in a negatively charged state based on the band structure.[5] An uncharged Li(2) vacancy would bring about a hole in the valence band and result in an energetically very

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unfavorable N^{2-} ion. However, quantitative comparison of the formation energy of various vacancies is not available. Therefore, we investigated the formation energies of all major intrinsic vacancies in Li_3N under different atmospheric conditions using first-principles calculations.

4.2 Methods of calculations

First-principles calculations were performed based on density functional theory (DFT) using the projector augmented waves (PAW) method as implemented in VASP.[6-8] We employed the generalized gradient approximation parameterized by Perdew, Burke and Ernzerhof (GGA-PBE) for the exchange correlation.[9-10] $2s2p$ for Li and $2s2p$ for N were treated as valence. All atoms in the supercells were allowed to move freely in the geometry optimization. The kinetic energy cutoff was set to be 400 eV. The electronic structure of the perfect Li_3N crystal was investigated with 4-atom primitive cell and $12 \times 12 \times 12$ k -point meshes according to the Monkhorst-Pack scheme.[11] The optimized lattice constant $a = 3.65 \text{ \AA}$ and $c = 3.88 \text{ \AA}$, is in good agreement with the experimental values of $3.64 \text{ \AA}$ and $3.87 \text{ \AA}$. [2-3]

Li_3N supercells containing 108 atoms were constructed for vacancy formation energy calculations by $3 \times 3 \times 3$ expansion of the unit cell. $4 \times 4 \times 4$ k -point meshes according to the Monkhorst-Pack method were employed in supercell calculations. Convergence with respect to k -points and kinetic energy cutoff was checked during all energy calculations. With this setup, total energies in our calculations are converged to

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within 0.01 meV. All coordinates of atomic positions were fully relaxed until the atomic forces were less than 0.01 eV/Å.

4.3 Results and discussion

4.3.1 Cutoff energy and k -point convergence test

The valence wavefunctions are in practice expanded in a plane-wave basis with certain cutoff energy. Convergence checks for the unit cell of Li_3N with 4 atoms were performed at cutoff energy of 300eV, 400eV and 500eV respectively as shown in Figure 4.2.

FIGURE 4.2: Calculated total energies for different cutoff energies. The blue line is for guide to the eye.

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It is seen from Figure 4.2 that total energy has insignificant variation as the cutoff energy increases from 400eV and 500eV. Though higher cutoff energy can increase the accuracy, more time will be taken for the computation. Our calculations indicate that a cutoff energy of 400eV is adequate to ensure sufficient accuracy and it was used for further calculations.

FIGURE 4.3: Calculated total energies for different k -point grids. The blue line is for guide to the eye.

It is known that a denser set of k -points can ensure a higher accuracy of the total energy computing. However, an increase of the density of k -point grids means a longer computation time. The computed total energy will converge as the density of the k -points increases and the error due to k -point sampling would gradually be insignificant to the calculations. Thus a k -point convergence test for the unit cell of Li_3N has been conducted

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as shown in Figure 4.3. It is observed that the total energy difference for k -point grids from $5 \times 5 \times 5$ to $6 \times 6 \times 6$ is less than 0.1 meV per unit cell. Therefore, the $5 \times 5 \times 5$ k -point grids were used for the structural optimization of the unit cell. We further increased the k -point grids to $12 \times 12 \times 12$ to obtain high quality density of states and electronic band structure of Li₃N unit cell. Since the involved supercells were constructed by $3 \times 3 \times 3$ expansion of the unit cell, $4 \times 4 \times 4$ k -point grids are thus sufficient for their total energy calculations.

4.3.2 Electronic structure of Li₃N

The obtained electronic band structure and density of states (DOS) of Li₃N are shown in Figure 4.4. The valence band maximum (VBM) and conduction band minimum (CBM) are located at A and Γ respectively, giving an indirect gap in consistence with previous experimental and theoretical reports.[4-5,12-13] The calculated energy band gap is 1.1 eV, which is underestimate by 1.1 eV as compared with the experimental value.[14] The band around -11.5 eV is dominated by N 2s state mixed with Li 2s and 2p. The conduction bands are mainly composed of Li 2s and 2p states, while the occupied valence bands originate from N 2s and 2p states. The partial overlapping of Li 2s state with N 2p state in the valence band region implicates Li(1)-N and Li(2)-N s-p covalent bonds. The different characteristics of p_x , p_y and p_z states of N atom show the anisotropy of Li₃N. Employing Bader's "atoms in molecules" scheme,[15] we obtained the nominal valences of N^{-2.44}, Li(1)^{+0.82} and Li(2)^{+0.81}. This quantitatively supports covalent bonding between Li and N, which is consistent with the real-space full multiple-scattering theory (RSFMS) calculations by Fister et al.[16] RSFMS is based on semi-infinite periodicity, rather than

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FIGURE 4.4: Electronic band structure (a) and DOS (b) of Li_3N . The local partial DOS components in (b) are: s black, p_x red, p_y blue, p_z green. The Fermi level is set to zero energy.

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translational invariance, and on the property of removal invariance of the scattering matrix of systems with semi-infinite periodicity.[17] It replaces the Brillouin-zone integrals in reciprocal space by a self-consistency equation determining the scattering matrix in real space. Therefore, RSFMS provides a unified treatment of the electronic structure of bulk materials, surfaces, interfaces and grain boundaries (coherent or incoherent), impurities of interstitial or substitutional kinds, and can be easily extended to treat concentrated, substitutionally disordered alloys, while those based on Blöch's theorem and the associated lattice Fourier transforms and Brillouin zone integrals, such as VASP, can only study a relatively restricted class of materials which possess full translational symmetry. The results by RSFMS agree well with those obtained through conventional techniques with close accuracy.

4.3.3 Vacancies of Li₃N

The formation energy of a charged vacancy $E_F(V^q)$ is defined as

$$E_F(V^q) = E_T(V^q) - E_T(bulk) + \mu_i + q(VBM + \Delta V + \varepsilon_F) \quad (4.1)$$

where $E_T(bulk)$ and $E_T(V^q)$ are the total energy of the defect-free supercell and the supercell with vacancy at charged state q , respectively; μ_i is the chemical potential of the atom removed from the supercell to generate the vacancy; ε_F is the Fermi energy with reference to VBM , which is the chemical potential of the electrons. The correction term

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ΔV aligns the reference potential in the defect supercell with that in the defect-free supercell.[18-19]

The atomic chemical potential μ_i is dependent on crystal growth conditions such as nitrogen partial pressure. The valid range of nitrogen partial pressure P_{N_2} can be determined by the Li₃N formation enthalpy $\Delta H_f^{Li_3N}$:

$$\frac{\Delta H_f^{Li_3N}}{kT} \leq \ln P_{N_2} \leq 0 \text{ with } \Delta H_f^{Li_3N} = 3(\mu_{Li} - \mu_{Li}^o) + (\mu_N - \mu_N^o) \quad (4.2)$$

where μ_{Li} and μ_N are the chemical potential of Li and N in Li₃N, respectively; μ_{Li}^o and μ_N^o are the calculated total energy of metallic Li in the most stable state and gaseous N₂ (per nitrogen atom); k is the Boltzmann constant and T the temperature in Kelvin. $\Delta H_f^{Li_3N}$ is calculated to be -1.59 eV per Li₃N, which is within the typical GGA errors from the experimental value of -1.73 eV per Li₃N.[20]

The formation energies of all major intrinsic vacancies in Li(1), Li(2) and N sites are calculated with Equation 4.1 and shown in Figure 4.5 as a function of Fermi energy at N-rich condition (*i.e.* $\mu_N = \mu_N^o$). The Li(2) site vacancies are located in N-containing layers, while the Li(1) site vacancies lie in the layers between these N-containing layers as seen from Figure 4.1. Li(2) site vacancy exhibits the lowest formation energy, which is in agreement with the experimental observations.[2-3] The negative $V_{Li(2)}^-$ vacancy is

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the most abundant one with the formation energy as low as -1.5 eV in extreme condition, indicating that thermal generation of vacancies is important even at low temperature consistent with experimental observations.[1] Therefore, the $V_{\text{Li}(2)}^-$ vacancies can contribute significantly to the unusually large ionic conductivity of Li_3N since they provide pathways for Li ion hopping. An increase in Li vacancy concentration corresponds to high Li ion mobility and thus high ionic conductivity.[21]

FIGURE 4.5: Vacancy formation energies as a function of Fermi level ε_F at nitrogen-rich condition. The inset is a megascopic graph of the rectangle area. The zero energy of ε_F corresponds to the valence-band maximum.

The Li vacancy formation energy in the Li(1) site is about 1.7 eV higher than that in the Li(2) site. Since the two nearly triply-negative nitrogen ions would now be

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repelled by their own ionic charges and by the effective negative charge of $V_{Li(1)}^-$ vacancy, removal of the lithium between the Li₂N layers is energetically unfavorable. The formation energy of uncharged nitrogen vacancies is found to be highest, and even the most stable V_N^{3+} vacancy among possible N vacancies show a formation energy being about 1.0 eV higher than that of $V_{Li(2)}$. This indicates that nitrogen vacancies rarely exist under nitrogen-rich conditions.

4.3.4 Effect of nitrogen partial pressure on vacancies of Li₃N

The vacancy formation energy as a function of nitrogen partial pressure is shown in Figure 4.6 for the Fermi energy close to VBM and CBM respectively. It can be seen that the atmospheric nitrogen conditions determine the type and concentration of vacancies in Li₃N. When the Fermi energy is close to VBM, V_N^{3+} and V_N^{2+} may form at similar concentration, since the difference in formation energy of V_N^{2+} and V_N^{3+} is only 0.01 eV. With an increase of nitrogen partial pressure, the formation energy of N vacancies rises while the formation energy of Li vacancies reduces. Therefore, V_N^{3+} has smallest formation energy at low nitrogen partial pressure, while $V_{Li(2)}$ has smallest formation energy at high nitrogen partial pressure. A turning point for alternation of predominating vacancy species from V_N^{3+} to $V_{Li(2)}$ occurs at the nitrogen partial pressure slightly above 4.66×10^{-15} pa. However, such low N partial pressure is unattainable in practical

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FIGURE. 4.6: Vacancy formation energies as a function of nitrogen partial pressure at Fermi energy close to VBM (a) and CBM (b).

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experimental conditions; this in fact excludes the possibility to form predominating V_N^{3+} in the prepared Li₃N. Since the formation energy of negative $V_{Li(2)}^-$ vacancy is 0.22 eV higher than that of the neutral $V_{Li(2)}$ vacancy, it is evident that neutral $V_{Li(2)}$ vacancy can become predominant at high nitrogen partial pressure. Therefore, the assertion of exclusive $V_{Li(2)}^-$ vacancy by Sarnthein et al.[5] is not supported when the Fermi energy is close to VBM.

When the Fermi energy is close to CBM, the negative $V_{Li(2)}^-$ vacancy forms exclusively in the structure, which supports the assertion by Sarnthein et al.[5] The formation energy of $V_{Li(2)}^-$ vacancy decreases greatly from -0.95 eV at low nitrogen partial pressure to -1.50 eV at high nitrogen partial pressure. This would bring about a remarkable increase in $V_{Li(2)}^-$ vacancies and thus Li ionic conductivity.

4.3.5 Electronic structure of Li₃N with charged vacancies

Formation of charged vacancies in Li₃N brings about significant variation of electronic band structure as shown in Figure 4.7. The formation of $V_{Li(2)}^-$ vacancy splits the peak at about -11 eV into two peaks separated by 0.3 eV. The accompanying highly splitted p_x , p_y and p_z states indicate occurrence of valence electron delocalization, and thus leads to enhanced electronic conductivity.[22] It is observed that the vacancy charge is unevenly

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FIGURE 4.7: Calculated DOS for supercells containing $V_{\text{Li}(2)}^-$ (a) and V_{N}^{3+} (b). The local partial DOS components are: s black, p_x red, p_y blue, p_z green. The Fermi level is set to zero energy.

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distributed among all atoms with the neighboring N atoms being allocated with the largest portion. This results in a decrease in the energy gap between VBM and CBM by -0.2 eV. Conversely, the formation of V_N^{3+} vacancy in Li_3N expands the energy gap by 0.2 eV. The p_x state of N shows moderate splitting in comparison with p_y and p_z state, indicating valence electron delocalization in Li_2N layers. This gives rise to increased anisotropy of Li ionic conduction. The alternation of band structure with vacancies implicates additional controlling of Li_3N conduction via vacancy adjustment.

4.4 Summary

The vacancies in Li(2) sites contribute to the experimentally observed nonstoichiometry of Li_3N . Their formation energy decreases with increasing nitrogen partial pressure. Since the fast Li ionic conduction of Li_3N is dependent on the vacancies in Li(2) sites, nitrogen-rich condition is preferred for Li_3N fabrication process to attain high vacancy concentrations and thus Li ionic conductivity. The formation of $V_{\text{Li}(2)}^-$ vacancies can also bring about valence electron delocalization to improve electronic conduction. Under extreme conditions, the dominant $V_{\text{Li}(2)}^-$ vacancy can arrive at formation energy as low as -1.50 eV, implicating that thermal generation of vacancies can play an important role in controlling vacancy level and therefore conductive mechanism.

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4.5 References

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Chapter 5

Screening 3d Transition Metal for Li₃N Doping to Improve Conduction

5.1 Introduction

The exceptionally fast Li-ion conduction of Li₃N suggests potential application as a solid electrolyte, which is inhibited only by its low thermodynamic decomposition potential (0.44 V at room temperature).[1] Moreover, Li₃N exhibits negligible electronic conductivity. It is proposed that the performance of Li₃N can be tailored via first row transition metal (M) doping for improved conductivity, stability and capacity as anode materials.[2] Li₃N can react with first row transition metals at approximately 600-900 °C to form two groups of ternary lithium nitride compounds, one with the anti-fluorite structure (such as Li₅TiN₃, Li₇VN₄, Li₉CrN₅, Li₇MnN₄),[3-5] and the other with the layered Li₃N structure (such as Li_{2.33}Mn_{0.67}N, Li_{2.7}Fe_{0.5}N, Li_{3-x}M_xN with M =Co, Ni, Cu).[1,4,6-7] The layered morphology is claimed to be beneficial to fast Li-ion conduction and low transition metal oxidation states.[6] Among the reported layer-structured ternary lithium nitrides, Li_{2.6}Co_{0.4}N exhibits excellent behaviors at low potential;[6,8-9] however, few other lithium nitrides display good capacity and stability. Unfortunately, the underlying mechanism that

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distinguishes lithium cobalt nitride from other ternary lithium nitridometallates is still ambiguous.

The fast Li-ion conduction of Li_3N is attributed to the hopping of Li ions between occupied Li sites and vacancies.[10-11] Dopants may significantly change the electronic properties of Li_3N and thus the concentration and distribution of Li vacancies, which subsequently influence its electronic and ionic conduction. Li_3N doped with nickel becomes electronically conductive.[12] A remarkable increase of vacancy concentration was observed in nickel or copper doped Li_3N . [13-14] Therefore, a better understanding of electronic property and vacancy formation of transition metal doped Li_3N is crucial to guide dopant selection for improved performance, which may turn ternary lithium nitridometalates into useful commercial materials. Consequently, we investigated the structure and electronic properties of 3d transition metal substituted Li_3N to screen dopant with excellent conduction performance.

5.2 Methods of calculations

First-principles calculations were carried out with the spin-polarized generalized gradient approximation (GGA) [15] (using the Perdew-Burke-Ernzerhof exchange-correlation parameterization [16]) to density functional theory (DFT), as implemented in VASP.[17] The projector-augmented wave method with a plane-wave basis set was employed.[18] We recognize that some recent studies on transition metal oxides and

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nitrides have used the DFT+U approaches, [19-22] however, most recent studies on lithium transition metal materials have employed DFT-GGA methodology without the on-site U parameter.[23-27] Our preliminary calculations showed that an excessive on-site Coulomb interaction parameter of 5 eV does not change the ground state geometrical structures. Since our aim in this study is to investigate the transition metal doping site in Li_3N and the resultant variation of electronic structure and vacancy formation, which are highly dependent on the ground state structures, therefore, electron-electron interaction is not considered in our calculations. Moreover, U is usually fitted to reproduce some experimental property, which virtually adds a semi-empirical component to the first-principle computations.

A 108-atom Li_3N supercell was adopted by $3 \times 3 \times 3$ expansion of unit cell with the lattice parameters obtained in previous work.[28] The kinetic energy cutoff was set to be 400 eV. The Brillouin zones have been sampled through Monkhorst-Pack $4 \times 4 \times 4$ k -point meshes. To model a doped system, one Li atom in a Li_3N supercell is replaced with a 3d transition metal atom (*i.e.* Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Cu, respectively), yielding a dopant concentration of 1.23 *at.*%. Li vacancy was generated by removing one Li atom from some designed sites in the supercell. All structures were fully relaxed according to the Hellmann-Feynman forces until the total ground state energy is converged to within 0.01 meV per formula unit in the electronic relaxation and the atomic forces were less than 0.01 eV/Å in the ionic relaxation.

5.3 Results and discussion

5.3.1 Substitution site selection

Hexagonal layer-structured Li_3N consists of alternating $[\text{Li}(2)_2\text{N}]$ and $\text{Li}(1)$ layers as shown in Figure 4.1. Two types of Li exist in Li_3N , i.e. one $\text{Li}(1)$ coordinated with 2 N atoms and two $\text{Li}(2)$ coordinated with 3 N atoms. Transition metal substitution for different Li will bring about different d orbital splitting and electronic configuration with discrepant thermodynamic stability. The substitution site can be determined by the total energy differences ΔE_{site} defined as

$$\Delta E_{\text{site}} = E_T(M_{\text{Li}(1)}) - E_T(M_{\text{Li}(2)}) \quad (5.1)$$

where $E_T(M_{\text{Li}(1)})$ and $E_T(M_{\text{Li}(2)})$ are the total energies of Li_3N supercell with one Li substituted by one transition metal atom in $\text{Li}(1)$ site and $\text{Li}(2)$ site respectively. A negative ΔE_{site} value indicates energetically preferred $\text{Li}(1)$ site substitution while a positive ΔE_{site} value indicates energetically favored $\text{Li}(2)$ site substitution.

The obtained ΔE_{site} values for Li_3N doped with various 3d transition metals are presented as a function of dopant size in Figure 5.1. The dopant ionic radii for six-coordination from Shannon [29] are used here since our main concern is to examine

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the trend in energetics between different Li site substitutions. Figure 5.1 reveals clear correlations between dopant size and ΔE_{site} .

FIGURE 5.1: Calculated ΔE_{site} as a function of ionic radius for various dopants. The blue lines are guides to the eye.

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It can be seen that transition metal with ionic radius much larger than that of Li prefers to substitute Li(2), while transition metal with ionic radius close to or smaller than that of Li prefers to substitute Li(1). However, the electron configuration may also contribute to substitution site selection. The positive ΔE_{site} value of Ti indicates that Ti energetically favors to replace Li(2). Owing to the larger size of Ti with respect to Li, Ti may deviate from the plane defined by three coordinated N due to restrictions in the Li-N substructure, and may bring about the distortion of the parent Li_3N structure.[4] This may explain the experimentally observed anti-fluorite structure for Ti substituted Li_3N . [30]

Conversely, the negative ΔE values of the rest 3d transition metals indicate that these transition metals substitute Li(1) to maintain the parent Li_3N structure. Layered structures of Li_3N doped with Mn, Fe, Co, Ni and Cu, have been confirmed by experimental observations.[30] These ternary lithium nitrides have M at a low oxidation state, which renders the opportunity to being oxidized to high oxidation state and to form considerable lithium vacancies.

5.3.2 Electronic configuration of transition metal in substituted Li_3N

The magnetic moments of transition metals in ternary lithium nitrides were further calculated to investigate their electronic configurations with exploration of their unpaired electrons. The total spin-only magnetic moment μ_m in (μ_B) of each

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substituted M in ternary lithium nitrides is given in Table 5.1. It is seen that μ_m increases continuously and monotonically from Sc to Mn and then decreases continuously and monotonically from Mn to Cu. The value of μ_m decreased by one unit from Mn to Cu.

TABLE 5.1: Calculated magnetic moments and proposed electronic configuration of M in ternary lithium nitrides.

Dopant	μ_m	electronic configuration
Sc	0	$(s)^2$
V	2	$(d_{xy}, d_{x^2-y^2})^2(s)^2$
Cr	3	$(d_{xy}, d_{x^2-y^2})^2(d_{yz}, d_{xz})^1(s)^2$
Mn	4	$(d_{xy}, d_{x^2-y^2})^2(d_{yz}, d_{xz})^2(s)^2$
Fe	3	$(d_{xy}, d_{x^2-y^2})^3(d_{yz}, d_{xz})^2(s)^2$
Co	2	$(d_{xy}, d_{x^2-y^2})^4(d_{yz}, d_{xz})^2(s)^2$
Ni	1	$(d_{xy}, d_{x^2-y^2})^4(d_{yz}, d_{xz})^3(s)^2$
Cu	0	$(d_{xy}, d_{x^2-y^2})^4(d_{yz}, d_{xz})^4(d_{z^2})^2$

* The total magnetic moment is corresponding to 2S in μ_B .

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According to the Crystal Field Theory, a high spin splitting of the five-degenerate d orbital is assumed to occur based on the obtained magnetic moment. Therefore, the electronic configurations are assigned as shown in Table 5.1. Since half-filled and completely filled subshells are particularly stable, this indicates that different amounts of Li vacancy may need to be generated for charge balance for 3d transition metals except Cu. Therefore, Cu doping may have inappreciable impact on Li vacancies, which is different from other 3d transition metals.

5.3.3 Electronic structure of transition metal substituted Li_3N

The density of states (DOS) for layer-structured Li_3N with Sc, V, Cr, Mn, Fe, Co, Ni and Cu substitution is shown in Figure 5.2. Li_3N with Ti substitution is excluded due to its lack of layered Li_3N structure. Some of these compounds have been synthesized, while others are purely theoretical. Obvious spin-polarization is observed in V, Cr, Mn, Fe, Co and Ni substituted Li_3N . Li_3N doped with these transition metals displays localized electrons at the Fermi level, which implies electronic conduction via electron hopping along the c direction at high doping level. Their energy band gaps are significantly narrowed down due to the occurrence of localized electrons. It is expected that the substituted Li_3N can even become a metallic conductor with formation of infinite, perpendicular N-M-N chains, ${}^\infty_1[\text{MN}_{2/2}]$, at elevated dopant concentration.[31]

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FIGURE 5.2: Total density of states for Li_3N doped with Sc (a), V (b), Cr (c), Mn (d), Fe (e), Co (f), Ni(g) and Cu (h) respectively. The Fermi level is set to zero. The blue and red curves correspond to up and down spin states, respectively.

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On the other hand, substitution by Cu brings about slight modification of energy band gap, implying insignificant impact on electronic conduction. Therefore, it is viable to adjust the electronic conduction of Li_3N by selecting suitable dopants and controlling the doping level for varied electrochemical applications.

5.3.4 Li vacancy formation in transition metal substituted Li_3N

Since Li ionic conduction in Li_3N relies on Li hopping between occupied sites and vacancies, the ionic conduction of Li_3N with various dopants is dependent on the Li vacancy concentration, which can be evaluated by Li vacancy formation energy E_F defined as

$$E_F = E_T(V) - E_T(bulk) + \mu_{Li} \quad (5.2)$$

where $E_T(V)$ and $E_T(bulk)$ are the total energies of supercell with Li vacancy and without vacancy, respectively; μ_{Li} is the chemical potential of Li atom removed from the supercell, and is constrained by the following condition:

$$l\mu_{Li} + m\mu_M + n\mu_N = \mu_{bulk} \quad (5.3)$$

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where μ_M and μ_N denote the chemical potential of transition metal and nitrogen atom, respectively, and μ_{bulk} is the chemical potential of studied system. l , m and n are the number of constituent atoms Li, M and N, respectively. The total energies per atom for nitrogen gas and bulk metals in their most stable forms were chosen as the upper limits of chemical potential of nitrogen and various transition metals, respectively. The calculated total energies per unit formula were applied as the chemical potentials of the studied systems. We consider the Li-poor limitation employed in practical synthetic conditions.

Our preliminary calculations excluded possible Li vacancies $V_{Li(1)}$ generated in Li(1) sites since the formation energies of $V_{Li(1)}$ for Li_3N with various transition metal substitution are much larger than those of the corresponding Li vacancies $V_{Li(2)}$ generated in Li(2) sites, which follows the trend of Li_3N .^[28] This is in agreement with the reported intraplanar Li vacancies.^[13,32-34] The calculated formation energies E_F of Li vacancy $V_{Li(2)}$ close to transition metal atom for studied ternary lithium nitrides are listed in Table 5.2. It reveals that $V_{Li(2)}$ formation energy E_F is generally reduced by transition metal substitution, in particular by Sc. The considerably decreased E_F can be expected to bring about significant increase of Li vacancy concentration, which should be beneficial to faster Li ion transport.

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However, the interactions between the dopant ions and the vacancies may bind the increased vacancies to the dopants, blocking the hopping of Li ions between occupied sites and vacancies. This adds on a binding energy term to the conduction activation energy, and thus retards ionic conduction. The dopant-vacancy binding energies (E_{bind}) were qualitatively defined as:

$$E_{bind} = E_f - E_{f-f} \quad (5.4)$$

where E_{f-f} is the formation energies of $V_{Li(2)}$ far from the transition metal atom under the same supercell framework.

TABLE 5.2: Calculated E_F (eV) and E_{bind} (eV) for Li_3N with various transition metal dopants.

Dopant	-	Sc	V	Cr	Mn	Fe	Co	Ni	Cu
E_F	0.50	-0.52	-0.32	-0.66	0.01	0.11	0.28	-0.18	0.43
E_{bind}	0	-1.74	-0.27	-0.28	-0.25	-0.35	-0.03	-0.29	-0.02

The interaction of vacancy with doped transition metal atom is supposed to be minimized when the vacancy is far away from the transition metal atom in the supercell. Therefore, the obtained E_{bind} can be regarded to describe the binding interaction of vacancy with the doped transition metal. A negative value indicates that

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there exists binding interaction between the vacancy and the doped transition metal with more negative value showing stronger binding interaction. Table 5.2 lists the calculated dopant-vacancy binding energies for various 3d transition metals. It can be seen that the dopant-vacancy binding energy varies greatly for different dopants. Sc shows remarkably strong binding interaction with vacancy, suggesting fixing of increased Li vacancies closed to doped Sc sites in Sc substituted Li_3N . This may lead to ordering of Li vacancies in Sc substituted Li_3N and bring about structural transformation from the layer-structured Li_3N . This may explain the fact that no Sc substituted Li_3N has been reported in layered Li_3N structure. V, Cr, Mn, Fe and Ni show relatively strong binding interaction with the increased Li vacancies in their substituted Li_3N , which suggests that the hopping of Li between occupied Li sites and these vacancies be greatly hindered by such dopant-vacancy interactions. This may bring about appreciable reduction in Li ionic conduction.

On the contract, Co or Cu substitution shows a negligible dopant-vacancy binding energy, indicating unsubstantial impact on Li ion hopping between occupied sites and vacancies. Since Co substitution markedly reduces Li vacancy formation energy and thus greatly increases Li vacancy concentration, Co substitution thus significantly improves Li ion conduction. However, Cu substitution only brings about trivial reduction of Li vacancy formation energy, thus it may slightly affect Li ion conduction. Moreover, Cu substitution does not supplement electronic conduction to Li_3N in comparison with Co substitution. Therefore, Co distinguishes it from other

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transition metals as the excellent candidate owing to negligible dopant-vacancy binding interaction, greatly increased Li vacancies and additional electronic conduction. This is consistent with the reported excellent performance of Co substituted Li_3N . [6,8-9] The underlying mechanisms to render Co substitution unique properties compared with other transition metals may be attributed to its smaller ionic size and its specified electronic configuration in coordinated states. For example, though transition metals except Cu rarely exist in the +1 oxidation state as M^+ , there are few reported Co^+ oxo-ligands [35-40]. The bonding between Co and N in lithium cobalt nitride is further studied in Chapter 6. It is disclosed that Co and N form strong covalent bonding and electrons of N is back-donated to Co to somewhat stabilize the Co^+ oxidation state. This may increase the delocalization of Co electron for excellent electronic conduction and facilitate oxidation of Co^+ to higher oxidation state during delithiation process for good capacity.

Furthermore, our results suggest that the Li ion diffusion and ionic conduction of Li_3N be tailored by designed transition metal substitution with desirable $V_{\text{Li}(2)}$ formation energy and dopant-vacancy binding energy.

5.4 Summary

Our theoretical study reveals that dopant size plays important role on substitution site selection in Li_3N . Larger Ti favors to substitute intraplanar Li(2) to form anti-fluorite

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structure, and other 3d transition metals prefer to substitute interplanar Li(1) to form layered Li_3N structure. This suggests that 4d transition metal substitution of Li_3N is difficult to maintain the parent layered structure. V, Cr, Mn, Fe, Co or Ni substitution remarkably reduces energy band gap of Li_3N , and exhibits localized electrons in Fermi level. Therefore, transition metal substitution can be employed to control electronic conduction of Li_3N , and even to change Li_3N into a metallic conductor.

Sc, V or Cr substitution distinctly reduces Li vacancy formation energy; however, the formed Li vacancies are strongly trapped by strong dopant-vacancy interactions. Therefore, Co substitution stands out as an ideal candidate due to the overall advantages of increased Li vacancies due to reduced Li vacancy formation energy and negligible blockage of ionic mobility resulting from inappreciable dopant-vacancy binding energy. This confirms the reported excellent electrochemical performance of $\text{Li}_{3-x}\text{Co}_x\text{N}$ as anode material in Li-ion rechargeable batteries. Therefore, our results shed an insight for designing doped Li_3N with tailored electronic and ionic conduction for versatile electrochemical applications.

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Chapter 6

Electronic Structure and Bonding of Li_3N Doped with Transition Metal (Co, Ni, Cu)

6.1 Introduction

Experimental observations and theoretical calculations have disclosed that transition metals (Co, Ni, Cu) replace Li in Li(1) sites of Li_3N as shown in Figure 6.1, irrespective of the doping level and the synthesis conditions applied.[1-5]

FIGURE 6.1: Schematic illustration of Li_3N doped with transition metals (Co, Ni, Cu).

However, two models have been put forward to dispute the substitution of Li by transition metals. Some claims that ostensibly isovalent substitution of Li^+ by M^+ takes place in Li_3N , giving rise to the formation of $\text{Li}_{3-x}\text{M}_x\text{N}$. Consequently, the Li vacancy concentration is close to 1~2% generally observed in the parent Li_3N . $\text{Li}_{2.57}\text{Cu}_{0.43}\text{N}$ showed 1~2% random Li vacancies as Li_3N , which was insensitive to the synthesis temperature.[1] Negligible lithium vacancies were observed in $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ by chemical composition analysis.[6] It is claimed that the charge balance of $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ was well described with monovalent cobalt.[6-7] Niewa et al. also claimed that transition metal ($\text{M} = \text{Ni}, \text{Cu}$) substituted Li_3N contains predominating M^+ species based on their X-ray diffraction data, thermal measurements, and chemical composition analysis.[4]

It is known that transition metals rarely exist in the +1 oxidation state as M^+ (Cu^+ and few Ni^+ , Co^+ oxo-ligands are exceptions [8-12]). Therefore, others claims that aliovalent substitution of Li^+ by M^{+2} occurs in Li_3N , which leads to the formation of $\text{Li}_{3-2x}\text{M}_x\Box_x\text{N}$ ($\Box = \text{Li}$ vacancy). Consequently, high concentration of Li vacancies is required to compensate the charge balance for divalent (or even trivalent) transition metals. Accordingly, Li vacancy concentration increases with the transition metal substitution level. LiNiN was asserted to serve as an excellent model compound of the stoichiometric $\text{LiNi}\Box\text{N}$ with 50% Li vacancies in the $[\text{Li}_2\text{N}]$ plane.[13] Duros et al. reported a series of stoichiometric $\text{Li}_{3-2x}\text{Ni}_x\text{N}$ ($0.20 \leq x \leq 0.60$) compounds with the existence of Ni^{+2} and correspondingly high Li vacancies.[14] $\text{Li}_{1.99}\text{Co}_{0.53}\text{N}$ synthesized by Gordon et al.,[2] $\text{Li}_{1.36}\text{Ni}_{0.79}\text{N}$ and

$\text{Li}_{2.25}\text{Cu}_{0.43}\text{N}$ by Gregory et al.,[3] and $\text{Li}_{2.2}\text{Cu}_{0.5}\text{N}$ by Weller et al.[15] were also proposed to support the predominant aliovalent substitution.

These two substitution models can lead to distinct transition metal oxidation states and thus Li vacancy concentrations. Since the ionic conduction of these substituted lithium nitrides originates from hopping of Li among the Li vacancies, an understanding of the nature of Li vacancies in transition metal substituted Li_3N is essential for their potential applications. In this study, we carried out first principles calculations to study the effect of transition metal substitution on the electronic structure and bonding in Li_3N .

6.2 Methods of calculations

First-principles total energy calculations were carried out using the plane-wave based Vienna *ab initio* simulation package VASP.[16-18] Exchange and correlation were treated within the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA).[19-20] For the electronic configuration, the states treated as bands were: Li (2s, 2p), Co (3d, 4s), Ni (4s, 3d), Cu (4s, 3d), and N (2s, 2p). The cutoff energy for the plane-wave expansion was set to be 400 eV, which is checked to give well-converged total energies and structures. $4 \times 4 \times 4$ k -point meshes according to the Monkhorst-Pack method [21] were employed in all total energy calculations. With this setup, total energies in our calculations are converged to within 0.01 meV.

Li_3N supercells with 108 atoms were constructed by $3 \times 3 \times 3$ expansion of Li_3N unit cell and one Li atom in Li(1) site was substituted to model the partially substituted structure. The lattice parameters of Li_3N supercells with doped transition metal were fixed as those in the relaxed Li_3N supercells, so as to obtain the clear effect of transition metal substitution without much interference from structural changes. Li vacancy was generated by removing one Li atom near to the transition metal atom to observe its effect more closely. Spin polarization was considered where possible excess spins are expected.

6.3 Results and Discussion

6.3.1 Electronic structure of transition metal (Co, Ni, Cu) substituted Li_3N

The calculated densities of states (DOS) and the partial densities of states (PDOS) of transition metal substituted Li_3N are shown in Figure 6.2. It is seen that transition metal substitution significantly changes the electronic structure of Li_3N . Spin-polarization is obvious in $\text{Li}_3\text{N}:\text{Co}$ and $\text{Li}_3\text{N}:\text{Ni}$. The valence bands in transition metal substituted Li_3N are composed of M $3d$ states and N $2p$ states, and the conduction bands mainly originate from Li $2s$ and $2p$ states. Co or Ni substitution of Li greatly reduces the energy band gap to 0.55 eV in comparison with 1.13 eV of Li_3N . This may be due to the formation of dangling bonds at the Fermi surface. This implies occurrence of electronic conduction via electron hopping in Co or Ni substituted Li_3N . It is reported that the substituted Li_3N can even become a metallic conductor with formation of infinite N-M-N chains,

FIGURE 6.2: DOS and PDOS for $\text{Li}_3\text{N}:\text{Co}$ (a), $\text{Li}_3\text{N}:\text{Ni}$ (b) and $\text{Li}_3\text{N}:\text{Cu}$ (c) respectively. The PDOS components are: s black, p_x red, p_y blue, p_z green, d_{xy} yellow, d_{yz} gray, d_{xz} cyan, d_{z^2} pink, $d_{x^2-y^2}$ dark red. The Fermi level is set to zero.

$^1_{\infty}[MN_{2/2}]$, with increasing dopant concentration.[22] However, Cu substitution insignificantly reduces the energy band gap by 0.07 eV and no dangling bonds are formed at the Fermi surface. Therefore, different transition metal substitution may be a viable approach to tailor the electronic conduction of Li_3N .

It is also seen from Figure 6.2 that the five-fold degenerate $3d$ states of transition metal splits to delocalized d_{xz} state and localized $d_{xy}/d_{x^2-y^2}$ and d_{yz}/d_{z^2} states. The overlapping of p_x/p_y states of N with $d_{xy}/d_{x^2-y^2}$ states of M in the valence band region suggests π bonding, while the d_{yz}/d_{z^2} states of M may interact with p_z state of N to form σ bonding. Partial $3d$ states of Co and Ni are found to be located at approximately 0.6 eV above the original valence band maximum of Li_3N , which interact with Li and N states being partly pushed to higher energies. The upward shift of valence bands decreases the cohesion and thus brings about the destabilization of the substituted Li_3N . On the other hand, the interaction of $3d$ states of Cu with N and Li states does not push N and Li states to higher energies, since the $3d$ states of Cu to form the valence bands are close to the original valence band maximum of Li_3N . Therefore, Cu substitution marginally affects the thermodynamic stability of Li_3N . This explains the experimental observation that ternary copper lithium nitrides are more stable than ternary nickel lithium nitrides and ternary cobalt lithium nitrides.[5] Similar destabilization by transition metal substitution was also observed in lithium borohydride and lithium amide-imide structures.[23-24] The destabilization may be beneficial to the intercalation and deintercalation processes in lithium

rechargeable batteries, which can contribute to improved charge-discharge cycling performance.

6.3.2 Bonding visualized by valence charge density difference

The different bonding in Li_3N and transition metal substituted Li_3N is visualized using the contour plots of valence charge density difference in [001] direction as shown in Figure 6.3. The valence charge density difference is defined as $\Delta\rho = \rho_{\text{solid}} - \sum \rho_{\text{atom}}$, i.e. the difference between the total charge density in the solid and the superposition of independent atomic charge densities placed at the atomic sites of the same solid. It is instructive to evaluate the valence charge density distribution. The weak interactions between s state of $\text{Li}(1)$ and the delocalized d_{xz} state of M in the $(\text{Li}(1), \text{M})$ layer are not shown here. Ionic bonding between Li and N is found to predominate in Li_3N . Electrons accumulate around the N atoms while deplete around the Li atoms, therefore, the charges transfer from Li to N . On the other hand, electrons accumulate between N and M in transition metal substituted Li_3N to form a marked directional bonding. This remarkable charge polarization shows formation of both ionic and covalent bonding between N and M , distinctly different from the predominant ionic bonding in Li_3N . The covalent binding can reduce the oxidation state of transition metal and thus gives rise to an effective oxidation state below the nominal +2 for transition metal. Therefore, Li vacancies required to compensate the charge balance derived from the nominal oxidation state of transition metal are reduced.

FIGURE 6.3: Valence charge density difference in [001] direction through transition metal atom for Li_3N (a), and $\text{Li}_3\text{N:Co}$ (b), $\text{Li}_3\text{N:Ni}$ (c) and $\text{Li}_3\text{N:Cu}$ (d) respectively. The contour interval is $0.0125 \text{ e}/\text{\AA}^3$. The electron accumulation is depicted by red lines, while the electron depletion is represented by blue lines.

This indicates that Li vacancies would form in the substituted Li_3N with increasing covalency between transition metal and N.

Therefore, both ostensibly isovalent substitution model and aliovalent substitution model could not describe the apparent oxidation state of transition metal and Li vacancy concentration due to occurrence of the marked covalent bonding between transition metal and N. Thus, transition metal substituted Li_3N rarely approaches the supposed composition $\text{Li}_{3-x}\text{M}_x\text{N}$ or $\text{Li}_{3-2x}\text{M}_x\text{N}$. LiNiN can be regarded as an exception owing to alteration of crystal structure and formation of ordered structure. It is evident that transition metal substitution may bring about the formation of $\text{Li}_{3-x-y}\text{M}_x\text{N}_y$ with y dependent on the covalency and concentration of transition metal in the structure. It is noted that the synthesis conditions may affect the covalent bonding between transition metal and N, consequently the Li vacancy concentration. For example, a series of $\text{Li}_{3-x-y}\text{Ni}_x\text{N}_y$ with x = 0.339, y = 0.126; x = 0.360, y = 0.162; x = 0.362, y = 0.320; x = 0.565, y = 0.412; x = 0.577, y = 0.188; x = 0.743, y = 0.626 reported by Stoeva et al.[5] show that Li vacancy concentrations are higher than 1-2% of Li_3N but lower than the corresponding substitution concentrations with ambiguous correlation.

6.3.3 Bond length variation

The covalency of transition metal is further manifested by variation of the bond lengths of both $d_{\text{Li}(1),\text{M}-\text{N}}$ and $d_{\text{Li}(2)-\text{N}}$ as listed in Table 6.1. The calculated $d_{\text{Li}(1)-\text{N}}$

TABLE 6.1: Comparison of bond lengths in Li_3N and transition metal substituted Li_3N .

	$d_{(\text{Li}(1), \text{M})-\text{N}} (\text{\AA})$	$d_{\text{Li}(2)-\text{N}} (\text{\AA})$
Li_3N	1.936 (1.939 [25])	2.101 (2.106 [25])
$\text{Li}_3\text{N}:\text{Co}$	1.801 (1.804 [2])	2.137 (2.156 [2])
$\text{Li}_3\text{N}:\text{Ni}$	1.844 (1.806 [5])	2.125 (2.155 [5])
$\text{Li}_3\text{N}:\text{Cu}$	1.896 (1.886 [2])	2.116 (2.124 [2])

*Values in the brackets are from experimental observations with nearest substitution concentration.

and $d_{\text{Li}(2)-\text{N}}$ in Li_3N are 1.944 Å and 2.106 Å respectively, which is in good consistence with the experimental values.[25] Transition metal substitution reduces the interplanar $d_{(\text{Li}(1), \text{M})-\text{N}}$ in the order $\text{Li}_3\text{N}:\text{Co} < \text{Li}_3\text{N}:\text{Ni} < \text{Li}_3\text{N}:\text{Cu}$, while increases the $d_{\text{Li}(2)-\text{N}}$ in $[\text{Li}_2\text{N}]$ layer in the order $\text{Li}_3\text{N}:\text{Co} > \text{Li}_3\text{N}:\text{Ni} > \text{Li}_3\text{N}:\text{Cu}$. This trend is consistent with experimental observations.[2-3,13,15,26] However, it is difficult to make strict comparison of the calculated bond lengths with the available experimental data, since these values are highly dependent on transition metal substitution concentration and Li vacancy concentration.[15] The covalent bonding between N and transition metal atom results in the decrease of $d_{(\text{Li}(1), \text{M})-\text{N}}$ with the reduction dependent on the covalent binding degree. Meanwhile, the

covalent bonding decreases the effective negative charge of N, thus weakens the N-Li binding in the $[\text{Li}_2\text{N}]$ layer, which leads to the extension of $d_{\text{Li}(2)-\text{N}}$. The reduction of $d_{\text{Li}(1),\text{M})-\text{N}}$ and increment of $d_{\text{Li}(2)-\text{N}}$ can be taken as a measure of the covalency, which is commensurate with the calculated valence charge density difference shown in Figure 6.3.

6.4 Summary

Transition metal (Co, Ni, Cu) substitution significantly influences the electronic structures and bonding of Li_3N . Co or Ni substitution can render appreciable electronic conduction to the parent Li_3N and even change it to metallic-like conductor, which has the advantage of mixed electronic and ionic conduction. Moreover, transition metal substitution reduces the thermodynamic stability of Li_3N . The destabilization may be beneficial to the intercalation and deintercalation of lithium during charge-discharge cycling in lithium rechargeable batteries.

Covalent bonding between transition metal atom and the coordinated N is disclosed by valence charge density difference and bond length variation. It gives rise to the weakening of the intraplanar binding and the strengthening of the interplanar binding. Such covalent bonding reduces the nominal oxidation state of transition metal, leading to the formation of $\text{Li}_{2-x-y}\text{M}_x\text{N}_y$ with y dependent on the transition metal nature and the substitution concentration. This suggests a

vacancy-controlled charge compensation system for active oxidation-reduction reaction during charge-discharge cycling.

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Chapter 7

Tailoring Conduction of Li_3N via P and As Substitution

7.1 Introduction

The application of Li_3N as fast lithium ion conductor is inhibited by its low decomposition potential (0.44 V at room temperature), however, lithium phosphide is reported to be stable up to 2.2 V.[1] Furthermore, a transition is observed from fast ionic conductor for lithium nitride to semi-metallic conductor for lithium arsenide from conductivity measurements.[2] Unfortunately, the mechanism for the transition is unknown.

Meanwhile, disputable structures have been reported for lithium phosphide Li_3P and lithium arsenide Li_3As . Li_3P and Li_3As is asserted to have the same layered structure as Li_3N with the alternating layer of pure hexagonal $\text{Li}(1)$ and $\text{Li}(2)_2\text{P}$ or $\text{Li}(2)_2\text{As}$ by Nazri.[1-2] However, theoretical *ab initio* Hartree-Fock calculations failed to describe the structure with experimentally reported lattice parameters.[3-4] Other researches suggested that Li_3P and Li_3As crystallize in a hexagonal structure with $P6_3/mmc$ space group, which is different from Li_3N . [5-6] They are stacked in two alternating layers perpendicular to the c -direction. The first layer is made up of a

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graphite-like Li(2) and P or As layer and the second layer is composed of a chair form cyclohexane-like Li(1) layer.

However, little theoretical research has been performed to understand the underlying conduction mechanism, and few attempts have been made to rationalize the fundamental electronic properties of these materials. Therefore, we investigated the structure and electronic properties of Li_3N with N partially or fully substituted by P and As in this study.

7.2 Methods of calculations

All energy calculations were carried out using the generalized gradient approximation (GGA) to the density functional theory (DFT), as implemented in the Vienna *ab initio* simulation package VASP.[7] The projector-augmented wave (PAW) method with the Perdew-Burke-Ernzerhof functional was chosen to represent the ionic potential.[8-10] A plane-wave basis with a kinetic energy cutoff of 400 eV and reciprocal-space k -point grids of $4 \times 4 \times 4$ were employed after convergence tests with respect to k -points and energy cutoff were carried out. All atoms in the constructed supercells were allowed to move freely according to the Hellmann-Feynman forces during structure optimization until the total ground energy is converged to be within 0.01 meV per formula unit.

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To model a partially P or As doped system, one N atom is replaced in a 108-atom $3 \times 3 \times 3$ supercell, yielding a dopant concentration of 3.70 at.%. The lattice parameters of doped Li_3N supercells were fixed as those of Li_3N supercells so as to establish clearly the effect of dopant without much interference from structural changes. Lithium vacancy was generated by removing one lithium atom close to the dopant to observe its effect more clearly.

Total energy calculations were performed for Li_3P and Li_3As of both $P6/mmm$ and $P6_3/mmc$ structures respectively to settle the above-mentioned structure dispute. Li_3P and Li_3As supercells of 144 atoms were constructed for vacancy formation energy calculations by $3 \times 3 \times 2$ expansion of the unit cell of selected $P6_3/mmc$ structure.

The atomic orbital energies of N, P, and As were calculated with inclusion of spin-polarization. The atom was put in a cubic unit cell of $13 \times 14 \times 15 \text{ \AA}^3$ and only Γ point in reciprocal space was used in total energy calculations.

Lithium vacancy formation energy E_F was evaluated as

$$E_F = E_T(V) - E_T(\text{bulk}) + \mu_{\text{Li}} \quad (7.1)$$

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where $E_T(V)$ and $E_T(bulk)$ are total energies of the supercells with Li vacancy and without vacancy, respectively; μ_{Li} is the chemical potential of Li atom removed from the supercell to generate the vacancy. μ_{Li} can vary under a correlation of

$$3\mu_{Li} + n\mu_N + x\mu_X = \mu_{bulk} \quad (7.2)$$

where μ_N and μ_X ($X = P$ or As) denote the chemical potential of N and X respectively, and μ_{bulk} the chemical potential of the studied system. n and x are the number of constituent atom N and X, respectively. The calculated total energies of per atom for nitrogen gas, bulk phosphorus ($P\bar{1}$) and bulk arsenic ($R\bar{3}m$) were chosen as the upper limits of chemical potential of nitrogen, phosphorus and arsenic, respectively. The total energies per unit formula were applied as the chemical potentials of the studied systems. We consider the Li-poor limitation in practical synthetic conditions for this study.

7.3 Results and discussion

7.3.1 Cutoff energy and k -point convergence test

The valence wavefunctions were in practice expanded in a plane-wave basis with certain cutoff energy. An excessive cutoff energy would increase the computing cost

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without significant improvement in computing results. The geometry of the built supercell was optimized employing different cutoff energies. The obtained total energies as a function of the cutoff energy are shown in Figure 7.1. It is seen that the difference in the total energy of supercell with 108 atoms is less than 0.01 meV when the cutoff energy was set to be 400 eV and 500 eV respectively. This indicates that a cutoff energy of 400 eV is enough to ensure the sufficient accuracy and it was thus used in all our further calculations.

FIGURE 7.1: Calculated total energies for different cutoff energies. The line is for guide to the eye.

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A denser sampling of k points can ensure a higher accuracy of total energy computing. However, an increase of the density of the k points also indicates that a longer time will be needed for the computation process. The computed total energy will generally converge when the density of the k points increases, and the error due to k point sampling will be insignificant to the calculations. The calculated total energies of the studied supercell structure for different k -point grids are shown in Figure 7.2. It is observed that the energy different between k -point grids of $4 \times 4 \times 4$ and $5 \times 5 \times 5$ is less than 0.01 meV, indicating converged total energy. Therefore, the k -point grids $4 \times 4 \times 4$ were employed for all the further calculations.

FIGURE 7.2: Calculated total energies for different k - point grids. The line is for guide to the eye.

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FIGURE 7.3: DOS and PDOS for Li_3N doped with P (a) and As (b). The local partial DOS components are: s black, p_x red, p_y blue, p_z green. The Fermi level is set to zero energy.

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7.3.2 Electronic structure and vacancy formation of Li_3N doped with P and As

We calculated the density of states (DOS), and projected density of states (PDOS) of Li_3N doped with P and As as shown in Figure 7.3. It is found that P and As doping does not bring about substantial change of the electronic band structure in comparison with that of Li_3N . Inappreciable discrepancy of energy band gap is observed in Li_3N doped with P or As. This indicates that the electronic conduction of Li_3N may not be affected at low P or As doping level.

TABLE 7.1: Li vacancy formation energies of Li_3N doped with P/As.

	Li_3N	$\text{Li}_3\text{N:P}$	$\text{Li}_3\text{N:As}$
$V_{\text{Li}(1)}$	2.22	0.38	0.03
$V_{\text{Li}(2)}$	0.51	0.20	0.08

The calculated vacancy formation energies for Li_3N doped with P and As are listed in Table 7.1. Both P and As doping significantly decrease formation energy of Li vacancies, and As doping displays the lowest Li vacancy formation energy. This means that Li_3N doped with As would have the highest Li vacancy concentration. Since ionic conduction of Li_3N relies on the hopping of Li from occupied sites to unoccupied ones, As doped Li_3N would exhibit markedly improved ionic conduction.

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The similar formation energy values of $V_{Li(2)}$ and $V_{Li(1)}$ in P and As doped Li_3N indicate a decrease in the anisotropy of Li ionic conduction as shown in Li_3N .

7.3.3 Evaluation of Li_3P and Li_3As structure

Structural optimizations were conducted for Li_3P and Li_3As with the space group $P6/mmm$ and $P6_3/mmc$ respectively. The experimental lattice parameters of Li_3P are $a = 4.2286 \text{ \AA}$, $c = 7.5566 \text{ \AA}$ [5] and of Li_3As are $a = 4.377 \text{ \AA}$, $c = 7.801 \text{ \AA}$ [6] respectively. The calculated lattice parameters and formation enthalpy ΔH_f for Li_3P and Li_3As are listed in Table 7.2. It can be seen that the theoretical lattice parameters of both Li_3P and Li_3As with the space group $P6/mmm$ differ remarkably from the experimental data, especially the c-values. Hartree-Fock calculations also gave great discrepancy in the lattice parameters, which were unreasonably attributed to polycrystalline samples used in the diffraction experiments by Seel and Pandey.[4]

Conversely, the calculated lattice parameters of both Li_3P and Li_3As with the space group $P6_3/mmc$ are in good agreement with the experimental data with a maximum discrepancy less than 1.5 %. The ΔH_f values of both Li_3P and Li_3As with the space group $P6_3/mmc$ are observed to be lower than those with the space group $P6/mmm$. ΔH_f is obtained by subtracting the summation of chemical potentials of constituent elements from total structural energy, therefore, which can be regarded as

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a measure of structural thermodynamic stability.[11] This suggests that the more stable structure for Li_3P and Li_3As be with the space group of $P6_3/mmc$. Therefore, a structural variation from $P6/mmm$ to $P6_3/mmc$ occurs while N in Li_3N is fully substituted by P and As to form Li_3P and Li_3As respectively, which is shown in Figure 7.4.

FIGURE 7.4: Variation from $P6/mmm$ for Li_3N to $P6_3/mmc$ for Li_3P and Li_3As .

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TABLE 7.2: Calculated lattice parameters and formation enthalpy ΔH_f of Li_3P and Li_3As in space group $P6/mmm$ and $P6_3/mmc$.

	$P6/mmm$			$P6_3/mmc$		
	a (Å)	c (Å)	ΔH_f (eV)	a (Å)	c (Å)	ΔH_f (eV)
Li_3P	4.38	4.75	-10.8	4.25	7.55	-14.0
Li_3As	4.52	4.91	-11.5	4.39	7.77	-13.3

7.3.4 Electronic structures of Li_3P and Li_3As

The calculated electronic band structures of Li_3P and Li_3As with the space group $P6_3/mmc$ are shown in Figure 7.5. The VBM and CBM for Li_3P and Li_3As are located at Γ and K point respectively, giving an indirect gap of 0.72 eV and 0.65 eV separately. They are much lower than the energy band gap of 1.14 eV of Li_3N .

It is known that GGA exchange and correlation functionals generally underestimate the material band gap severely.[12] Though our calculations might not be able to produce the accurate band gap values, the observed trend of band gap decrease from Li_3N to Li_3P and Li_3As is unambiguous.

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FIGURE 7.5: Electronic band structures of Li_3P (a) and Li_3As (b). The Fermi level is set to zero energy.

FIGURE 7.6: Density of states and projected density of states of Li_3P (a) and Li_3As (b). The partial DOS components are: s black, p_x red, p_y blue, p_z green. The Fermi level is set to zero energy.

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The significantly reduced energy band gap decreases the energy required for electrons transferring from valence bands to conduction bands, which can be reflected from the different colours of the prepared samples, e.g. red Li_3N to brownish Li_3As . The valence bands of Li_3P and Li_3As show an extended dispersion of 3.36 eV and 3.41 eV in comparison with 2.74 eV of Li_3N , suggesting increased delocalization of p electrons of P and As. This may also contribute to an increased electronic conduction of Li_3P and Li_3As . This may explain the experimental observation that lithium arsenide exhibits a high electronic conductivity.[2]

The total density of states and projected density of states of Li_3P and Li_3As are shown in Figure 7.6. The valence bands are mainly contributed by 3p states of P for Li_3P or 4p states of As for Li_3As , and the conduction bands are mainly derived from the 2s states of Li. The increased contribution of Li s states to the dominantly P or As valence bands indicates enhanced covalent character in Li_3P or Li_3As in comparison with Li_3N .

Since the valence bands of Li_3X ($\text{X} = \text{N}, \text{P}, \text{and As}$) are mainly derived from the p states of X, it seems that the energy band gap is determined by the ionization energy of the element X. The calculated atomic orbital energies for N, P and As in Figure 7.7 illustrate that the p orbital of P and As is higher in energy than that of N. Therefore, substitution for N in Li_3N by P and As reduces the energy band gap and is

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beneficial to improve its electronic conduction. This provides a guideline to render Li_3N electronic conductive and can avoid enumeration over all anions.[13]

FIGURE 7.7: Atomic orbital energies of N, P and As. Red/blue arrow indicate one electron in spin-up/spin-down state.

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7.3.5 Vacancy formation of Li_3P and Li_3As

The calculated Li vacancy formation energies of Li_3P and Li_3As are listed in Table 7.3. $V_{\text{Li}(2)}$ formation energies of both Li_3P and Li_3As are increased in comparison with Li_3N , which may be attributed to the enhanced covalent bonding between Li and P and As. The higher $V_{\text{Li}(2)}$ formation energy indicates that Li vacancies in Li_3P and Li_3As would be considerably lower than those in Li_3N . Therefore, the ionic conductivity of both Li_3P and Li_3As would be much lower than that of Li_3N . This is in consistence with the experiment observation.[2]

TABLE 7.3: Li vacancy formation energies of Li_3P and Li_3As .

	Li_3P	Li_3As
$V_{\text{Li}(1)}$	0.86	0.74
$V_{\text{Li}(2)}$	0.71	0.62

It can also be seen from Table 7.3 that the formation energies of $V_{\text{Li}(1)}$ and $V_{\text{Li}(2)}$ for Li_3P and Li_3As are very close, indicating that there may be approximately similar vacancy concentrations in $\text{Li}(2)_2\text{P}$ or $\text{Li}(2)_2\text{As}$ layer and Li(1) layer. This is remarkably different from the predominating $V_{\text{Li}(2)}$ vacancies in Li_3N . It implicates highly reduced anisotropic ionic conduction in Li_3P and Li_3As in comparison with Li_3N .

7.4 Summary

P and As doping is found to effectively reduce Li vacancy formation energy, thus it would significantly improve Li ionic conduction. However, fully substitution for N by P and As brings about remarkable increase of Li vacancy formation energies and significant reduction of energy band gap by 0.42 eV and 0.51 eV, suggesting depression of ionic conduction and contribution to experimental observed electronic conduction. Therefore, the increased ionic conduction in low doping level and the appearance of electronic conduction in Li_3As suggest that it is viable to achieve balanced ionic and electronic conduction by selecting suitable dopant and controlling the dopant level.

7.5 References

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Conclusions and Suggestion for Future Work

8.1 Conclusions

The aim of this study was to derive lithium nitrides from the parent Li_3N by transition metal and non-metal doping to use as anode materials using density functional theory (DFT).

We first determined the electronic structure and vacancies of the parent Li_3N . It is found that the Li vacancies in Li(2) sites contribute to the experimentally observed nonstoichiometry of Li_3N . Their formation energy decreases with increasing nitrogen partial pressure, which indicates that nitrogen-rich condition is preferred for Li_3N fabrication process to achieve high Li ionic conduction. Our calculations disclosed that the negatively charged Li vacancies in Li(2) sites can bring about valence electron delocalization to render electronic conductive to Li_3N . It is suggested that thermal generation of vacancies can play an important role in controlling vacancy level and therefore conductive mechanism.

We then determined the substitution site, transition metal electronic configuration and vacancy-dopant interaction in transition metal doped Li_3N . Dopant size is found to play an important role on substitution site of transition metal in Li_3N . Larger Ti favors to substitute intraplanar Li(2) to form anti-fluorite structure, and other 3d transition metals prefer to substitute interplanar Li(1) to form layered Li_3N structure. V, Cr, Mn, Fe, Co or Ni substitution remarkably reduces energy band gap of Li_3N , and exhibits localized electrons in Fermi level. Strong dopant-vacancy interactions occur in transition metal doped Li_3N except Co and Cu doped Li_3N . Our calculations successfully explained the outstanding electrochemical performance of ternary lithium cobalt nitride as anode material in Li-ion rechargeable batteries, based on the overall advantages of increased Li vacancies due to reduced Li vacancy formation energy and negligible blockage of ionic mobility resulting from inappreciable dopant-vacancy binding energy.

We further ascertained the influences of transition metal (Co, Ni, Cu) on the electronic structures and bonding of Li_3N . Co or Ni substitution renders appreciable electronic conductive to the parent Li_3N and may even change it to metallic-like conductor, which has the advantage of mixed electronic and ionic conduction. Moreover, transition metal substitution reduces the thermodynamic stability of Li_3N , which may be beneficial to the intercalation and deintercalation

of lithium during charge-discharge cycling in lithium rechargeable batteries. Covalent bonding between transition metal atom and the coordinated N is disclosed visually by valence charge density difference and quantitatively by bond length variation. Such covalent bonding reduces the nominal oxidation state of transition metal, thus decreases Li vacancies required for the charge compensation.

We also clarified the effects of P and As substitution on the electronic structure and electronic and ionic conduction of Li_3N . Partial P and As doping can effectively reduce Li vacancy formation energy to significantly improve Li ionic conduction. Fully substitution for N by P and As changes the crystal structure of the parent Li_3N to depress ionic conduction and facilitate electronic conduction. This suggests that it is viable to achieve balanced ionic and electronic conduction by controlling the dopant level.

Therefore, our results enhance our understanding of the physics of intrinsic defects and potential measures to control the vacancies in Li_3N and its derivatives, and provide guide for experimental researches on synthesizing lithium nitrides with manageable electronic and ionic conduction for various electrochemical applications.

It is noted that our results presented in this thesis are limited to electronic structures of lithium nitrides based on first principles DFT calculations. There are enormous work to be carried out in order to establish the relationship between the electron structure and electrochemical performance of the anode materials. Fortunately, both ionic and electronic conductivity of the anode material can be obtained from the total energy calculation, and they are crucial in simulating their performance in lithium-ion rechargeable batteries.

The ionic conductivity σ_i of the anode materials can be expressed as an exponential function of the activation energy E_a for lithium-vacancy diffusion as:[1]

$$\sigma_i = \sigma_0 / T \cdot \exp\left(-\frac{E_a}{k_B T}\right) \quad (8.1)$$

where σ_0 is a temperature-independent prefactor, and E_a is equal to the sum of the vacancy formation energy and the migration barrier. It is closely related to power performance (fast charge/discharge), degradation and safety.

On the other hand, the electronic conductivity σ_e of the anode materials can be related to microscopic parameters that describe the motion of the electrons (or other charge carrying particles such as holes or irons) as:[1]

$$\sigma_e = ne \left(e\tau / m^* \right) \quad (8.2)$$

where n is the carrier concentration, e the charge of an electron, τ the relaxation time between scattering event and m^* the effective mass of the electron. The effective mass m^* can be derived from the curvature of electronic band near the valence band maximum using[2]

$$m^* = \left(2\pi / \hbar \right)^2 (1 / \{ d^2 E / dk^2 \}) \quad (8.3)$$

The electron concentration n can be evaluated by[2]

$$n = 2 \left(\frac{m^* k_B T}{2\pi \hbar^2} \right)^{3/2} \exp[(\varepsilon_F - E_g) / k_B T] \quad (8.4)$$

where E_g is the energy band gap.

Available models[3] may then be employed to correlate the ionic and electronic conductivity to current density and capacity for anode material design. Simulations on cathode materials disclose that there is a trade-off between ionic and electronic conductivity, and neither best electronic or ionic conductivity can achieve best specific energy.[4]

8.2 Suggestion for future work

Following the investigation described in this thesis, several interesting directions listed below can be carried out in the future:

- (1) Carry out a series of total energy calculations to determine the optimal P or As doping concentration in Li_3N at which the Li vacancy formation energy is the minimum.
- (2) Conduct transition state calculations using nudged elastic band method to determine lithium migration pathways and energy barrier.
- (3) Carry out molecular dynamic simulations to evaluate Li mobility in transition metal and non-metal doped lithium nitrides.

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