

Surface study of doped and coated Li-rich Mn-based cathode materials and their interactions with the electrolyte content

by

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THESIS

Submitted in fulfilment of the requirements for the degree of

DOCTOR OF PHILOSOPHY (PhD)

In

PHYSICS

in the

FACULTY OF SCIENCE AND AGRICULTURE

(School of Physical and Mineral Science)

at the

University of Limpopo,

South Africa

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2024

Declaration

I declare that the thesis titled “Surface study of doped and coated Li-rich Mn-based cathode materials and their interactions with the electrolyte content” hereby submitted to the University of Limpopo, for the degree Doctor of Philosophy (Physics) has not previously been submitted by me for a degree at this or any other university; that is my work in design and execution, and that all material contained herein has been duly acknowledged.



Ramogayana, Brian

02 September 2024

Date

Dedication

I dedicate this work:

My mother

Mamareme Julia Ramogayana

My brothers

Isaac and Kgopotso Ramogayana

All my family

The *Ramogayana, Nkadimeng, Maduana* and *Khumalo*

Acknowledgements

This work is part of the research programme of the Material Modelling Centre (MMC), Energy cluster at the University of Limpopo. My greatest acknowledgements go to my supervisors, Prof Phuti E. Ngoepe and Prof Khomotso P. Maenetja for their guidance throughout this project. I also appreciate Prof Nora H. de Leeuw and Dr David Santos-Carballal for their great collaboration on this project and support during my visit to the University of Leeds, UK. The work was performed using the computational facilities of the University of Limpopo, Materials Modelling Centre (MMC), SEBATA and the Centre for High-Performance Computing (CHPC) now called the National Integrated Cyber-Infrastructure System (NISIC) facilitates based in Cape Town, South Africa. Also, the United Kingdom (UK) computing facilities, which are the UK national supercomputing service (ARCHER2) accessed through the University of Leeds, and the supercomputing Wales (SCW) machines through Cardiff University operated by the ARCCA division. For financial support, the work was funded by the National Research Foundation (NRF), South Africa. Engineering & Physical Sciences Research Council (EPSRC Grant No. Ep/K009567/2 and No. Ep/K016288/1), the Economic and Social Research Council (ESRC Grant Es/N013867/1) during my visit to the University of Leeds. Having the greatest support system is key, so I appreciate the greatest support from my fellow MMC colleagues, Leeds lab mates Xuan Chu and Xingyu Wang, my favourite Murendeni Mudau, my closest friends Cecil Botchway, Letsiri Matsebane, Mohlao Seabi, and many others who kept me sane through my PhD journey. Most of all, I raise my hands to the Almighty for his grace, endless opportunities, and protection throughout my studies.



Abstract

Since its introduction, lithium manganese-based lithium-ion batteries have advanced in terms of safety, capacity, power, cycle stability, and energy density. These have been attributed to the use of innovative and customised active (cathode) materials with increased capacity, potential, and thermal stability. Furthermore, given the high global manganese output and the present load-shedding situation, South Africa stands to gain considerably. However, modern Li-ion batteries must be replaced over time owing to deterioration caused by cathode interactions with the electrolyte, which causes capacity fading. As a result, modifications such as surface coating and element doping are used to enhance and minimize deterioration processes. The density functional theory technique was used in this work to investigate the effect of surface Nb-doping and α -Al₂O₃ surface coating on the LiMn₂O₄ major surfaces.

First, the bulk characteristics of both LiMn₂O₄ and α -Al₂O₃ were studied, as well as the stability and precision of our materials in comparison to reference data. The estimated lattice characteristics, average atomic charges, and bond distances matched the provided values. With Mn e_g and O $2p$ hybridization along the Fermi level, the electronic density of states of LiMn₂O₄ bulk displayed a half-metallic behaviour. Similarly, the α -Al₂O₃ exhibited insulating behaviour with a large band gap of 5.90 eV, which was consistent with the literature results.

Second, the ethylene carbonate electrolyte (EC) interactions with the α -Al₂O₃ (0001) surface were investigated, even with increasing EC coverage. When put parallel (flat) to the surface and interacting with the carbonyl oxygen, the EC molecule favoured attaching to the surface. A minor charge transfer was found during single EC adsorption, suggesting physical interactions with the surface. When compared to single EC adsorption, increasing the EC coverage destabilizes the surface and increases average adsorption. Bader charge accumulation was seen on the interacting EC oxygen atoms, with substantial steric hindrance at high coverages, resulting in the EC molecule detaching from the surface. Steric hindrance was also

shown by the symmetric and asymmetric blue shift of $\nu(\text{CH}_2)$ vibrational modes. Furthermore, we created $\alpha\text{-Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ heterostructures to simulate the $\alpha\text{-Al}_2\text{O}_3$ coated LiMn_2O_4 surfaces. We discovered that the $\alpha\text{-Al}_2\text{O}_3$ (11 $\bar{2}$ 0) and (0001) surfaces match the LiMn_2O_4 (001) and (111) facets with {1132} and {3121} configurations, respectively, with 2.40% and 2.75% misfits. The highest adhesion energies were determined for the $\alpha\text{-Al}_2\text{O}_3$ monolayer on the (001) and (111) surfaces, which dropped as the thickness increased. A minor average charge transfer on the LiMn_2O_4 substrate surfaces was computed, and charge depletion on the interacting Mn atoms creating MnO_6 units at the heterojunction was observed. Following partial delithiation, the vacancy formation energies rise, prompting minor charge depletion on neighbouring Mn atoms in the form of charge redistribution. When compared to pure surfaces, the computed work function rises, indicating that the coated interfaces become less reactive.

Finally, surface Nb doping was studied on the LiMn_2O_4 (001), (011), and (111) surfaces. It was discovered that substituting Nb at Mn ion locations in the second surface layers ($\text{Nb}_{\text{second}}$) increased (111) surface stability, forming a larger (111) facet on the morphology. However, Nb-doping on the top (Nb_{first}) and both top and bottom (Nb_{both}) surface layers results in the same stability as clean surfaces. Furthermore, we examined EC and HF adsorption on pristine/Nb-doped surfaces, and both adsorbates favoured interactions with the facets via Nb atoms over Mn atoms. A higher binding energy was calculated for EC on $\text{Nb}_{\text{second}}$ (011) surface and HF on Nb_{both} (111) surface. EC Adsorption results in physical interactions with surfaces, whereas HF decomposes into H and F atoms that adhere to surface O and Mn atoms, respectively and both improve the $\text{Nb}_{\text{second}}$ (111) surface stability. A minimal charge transfer was observed upon HF and EC interacted with pure or Nb-doped surfaces. These findings are noteworthy because improving the (111) surface on the morphologies could promotes the formation of a stable solid electrolyte interface (SEI), which reduces dissolution of Mn while enhancing EC and HF adsorption.

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CHAPTER 1

1. INTRODUCTION

This chapter presents the fundamental importance of energy in various aspects of life, provides a brief historical background of a battery and its origin, and discusses the advantages of current Li-ion batteries over other commercialized batteries. Secondly, give a brief discussion of cathode materials starting from the traditional LiCoO_2 cathode material. Lastly, outline the rationale, the aim of the study, research questions, and objectives of the study.

1.1. Background

Every element of human existence is governed by the fundamental notion of energy. It is often characterized as the capability of completing tasks or bringing about change. It is the driving force behind all motion, from the tiniest molecule to massive machinery. It may be used for anything from cooking to powering cities, and it comes in many different forms, including heat, light, music, and electricity. As the population grows, more people have access to modern technology, the most pressing issue we face today is increased energy usage. Because the use of primary energy sources has resulted in a variety of environmental issues, such as air and water pollution and climate change, this growing demand is not inexpensive. Besides, primary fossil fuels also are running out [1, 2]. To solve these challenges, engineers, and scientists from all over the world are working to develop novel and imaginative methods of creating and utilizing energy. One of the most practical answers is renewable energy, which is derived from pure, recyclable natural resources. These include solar electricity, wind power, hydropower, geothermal energy, rechargeable batteries, and so on [3, 4, 5, 6].

With our civilization reliant exclusively on technology, it is only feasible for the power sources to reside within our gadgets. One of the portable solutions that has modernized and helped to realize a sustainable civilization is the use of batteries [7]. Benjamin Franklin coined the term "battery" in 1749 to characterize his electrical experiments with a series of connected capacitors [8, 9]. Most of the publications state that an Italian physicist named Alessandro Volta created the first real battery around 1800. This battery consisted of alternating copper and zinc paired disks separated by cardboard or cloth soaked in salt water [10]. The Parthian battery, also known as the Cu/Fe vinegar/wine battery is believed to be around 2000 years old and was discovered in 1936 by railroad workers near Baghdad [11]. When the Jar is filled with vinegar or a liquid electrolyte, it generated 1.1 to 2.0 V. It is comprised of an iron rod encircled by a copper cylinder. However, numerous more types of batteries that could only be used once (primary cell) were developed utilizing various materials.

It was until 1859, that the French physician Gaston Planté [12] paved the way by inventing the first secondary rechargeable lead-acid battery which gave off 2.2 – 2.27 V. Secondary batteries became more desirable as a choice for usage in a variety of applications due to their better energy density, versatility, ability to be recharged and used once more, cheaper long-term cost, and minimal influence on the environment. Then, several batteries made of Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , etc [13, 14, 15, 16]. Lithium-based batteries receive the most attention when compared to other battery types since they are the most practical option for many applications due to their short charge/discharge periods and up to ten times longer lifespans with more than 80% rate capacity.

Currently, Li-ion battery research and development have advanced remarkably in recent years. Electric vehicles can now be powered by them as well as tiny, portable electronics like cell phones, laptops, and electric cigarettes. They are also frequently thought of as a viable

alternative to fossil fuels for usage in homes and grids in stationary storage systems (also known as smart grids). Ever since their first commercialization in 1991 by Sony [17], lithium-ion batteries have continued to advance based on safety, capacity, power, cycling stability, and energy density.

This significant advancement is attributable to the development of new and modified active (cathode) materials with improved thermal stability, high potential, and increased capacity [18, 19, 20, 21, 22]. The comparatively long lifespan of lithium-ion batteries is another benefit. Lithium-ion batteries may persist for thousands of charge and discharge cycles, unlike other types of batteries like lead-acid batteries, which quickly deteriorate over time. Because they do not need to be updated as frequently, they are long-term cost-effective alternatives. Based on energy density, [Figure 1.1](#) compares these battery types to the dominant Li-ion batteries.

With about 150 Wh/kg, LIBs display a higher energy density when compared to several branded batteries. Although lithium metal batteries have about 200 Wh/kg, their practical uses are limited due to their low ability to be recharged, and their prolonged use can result in fire or explosion [23, 24]. Though they may likely take a few decades to complete, recent promising advancements in Li-S and Li-air batteries have rekindled widespread interest [25]. Lithium-ion batteries are most likely to play an increasingly significant part in the energy storage landscape in the upcoming years, despite having a lower energy density than Li-metal batteries. However, there are certain disadvantages to employing lithium-ion batteries. One of the most important is safety, which results from the electrolyte's action toward the active components that cause cell breakdown. Lithium-ion batteries have been known to catch fire on occasion, especially when used in electric cars [26, 27]. Further adjustments and increasing examination of lithium-ion battery safety have resulted from this.

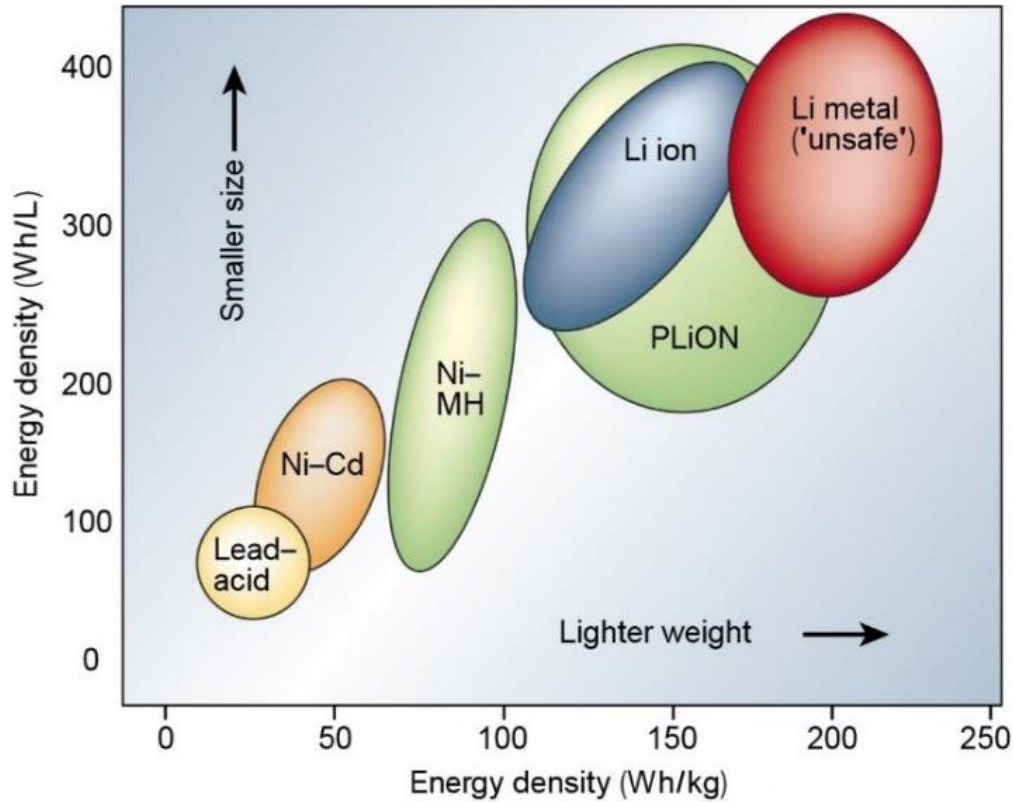


Figure 1.1: Comparing energy densities of different battery types and Li-ion batteries [28].

The cathode material (also known as the active material) is one of the three components of a Li-ion battery which is responsible for the battery's electrochemical performance. Lithium cobalt oxide (LiCoO_2) with a layered rhombohedral structure ($R\bar{3}m$), which was first proposed by Mizushima et al. [29] in 1980, is an early example of cathode material innovation. LiCoO_2 has an impressive theoretical capacity of 274 mAh/g, but practical applications are limited by a charging voltage limit of 4.45V, providing only about 170 mAh/g (less than 50% of its theoretical capacity) [30]. The capacity of the material decreases after ten cycles, mostly because of (i) structural phase transitions followed by lattice deformations, which cause particle strain and crack development, and (ii) interactions between the surface and electrolytes, which cause Co to dissolve and oxygen to be drawn away from the surface. Utilizing cobalt also comes with significant economic and environmental risks [31]. Various LiCoO_2 substitutes have been investigated and structurally divided into three groups: layered [32, 33, 34], spinel [35, 36, 37], and olivine [38, 39, 40].

Despite their differences, Mn-based cathode materials have made significant progress, with the maximum energy density surpassing 250 mAh/g and operating voltages of around 3.4 V [41, 42]. Because manganese is less hazardous than Co and is more prevalent on Earth, the spinel LiMn_2O_4 looked to be the ideal alternative for LiCoO_2 [43, 44, 45]. It possesses a three-dimensional structure that permits Li to diffuse smoothly during cycling [46], while the parent completely delithiated MnO_2 stays intact [47].

However, the application of LiMn_2O_4 with 148 mAh/g theoretical capacity provides only a 120 mAh/g practical capacity [48], which likewise succumbs to fading capacity due to its reactivity with the electrolyte. These led to cathode electrolyte interphase (CEI) formation [49, 50], Jahn-Teller distortion of Mn^{3+} ions [51, 52, 53] and the dissolution of manganese (Mn^{2+}) ions into the electrolyte [54, 55, 56, 57]. Hence, it is critical to understand surface stability, electrolyte interactions, and Li diffusion upon pristine and modified facets.

1.2. Motivation

As traditional fossil fuels contribute to global warming, there is a strong demand for energy supply for our daily household uses (primarily in our current South African Loadshedding crisis) and autos. In addition to the abundance of energy alternatives, lithium-ion batteries have undergone since their introduction. The low-cost Li-Mn-O based cathode materials have improved the performance of Li-ion batteries. Due to its plentiful, less poisonous, and affordable manganese content, spinel LiMn_2O_4 , which Thackeray *et al* [58] first announced in 1983, is frequently regarded as an efficient LiCoO_2 replacement. LiMn_2O_4 has a three-dimensional structure that allows for unimpeded Li^+ movement while maintaining the structural integrity of the parent Mn_2O_4 material throughout full delithiation [59, 60]. However, LiMn_2O_4 faces capacity fading as a cathode material due to electrolyte activity, which results in Mn^{3+} ion Jahn-Teller distortion [51, 52, 53], cathode-electrolyte interphase (CEI) formation

[49, 50] and Mn^{2+} ion dissolution into the electrolyte [61, 57]. To address these problems, many approaches have been taken, including cation/anion doping [62, 63, 64], protective coating materials [65, 66, 67], and increasing the proportion of the LiMn_2O_4 (111) surface on the morphology [68, 69, 70].

The quantity of manganese (Mn^{3+}) ions which undergo Hunter's [71] disproportionation process (*i.e.* $2\text{Mn}^{3+}_{(\text{solid})} \rightarrow \text{Mn}^{4+}_{(\text{solid})} + \text{Mn}^{2+}_{(\text{solution})}$) can be reduced most effectively by cation doping [72] in LiMn_2O_4 . Limiting the development of Mn^{2+} , which dissolves easily, by substituting dopants for Mn^{3+} . Numerous dopants have been studied in the past and have demonstrated better stability and capacity enhancement in a variety of cathode materials. These structural strengthening dopants are mostly classified into low valence (+2 [73, 74] and +3 [75, 76]), and high valence (≥ 4) [63, 77, 78]. High-valence dopants such as Ti^{4+} , V^{5+} , Nb^{5+} , Ru^{4+} , Sn^{4+} , etc, have shown a great structural enhancement. The Nb^{5+} was chosen as one of the structural strengthening dopants as it has a higher Nb-O binding energy compared to Mn-O [79]. Additionally, it has an ionic radius comparable with Mn^{4+} and Li^+ ions, which makes it possible for it to substitute either the Li or Mn sites [80].

Li et al [81], who investigated the effect of Nb doping on the structure and electrochemical characteristics of LiMn_2O_4 spinel, discovered that doping with modest levels of Nb lowers crystal volume and lattice parameters without impacting Li^+ transport. They also observed that at varying Nb concentrations, the diffraction peaks had totally spinel structure, despite the presence of minor residues of LiNbO_3 impurities. Later, Li et al [82] addressed how Nb doping in spinel LiMn_2O_4 may increase capacity and electrochemical performance while also strengthening crystal development in the (111) and (400) planes. Other later research found that Nb doping, like Cr doping, increases Li diffusion in lithium manganese-based cathode [83, 84, 85, 77, 86]. Doping the bulk spinel with atoms of varying sizes and charges, on the other

hand, can produce variable degrees of cation order, resulting in differences in capacity and cycle stability [87, 88]. As a result, there is a need to understand the effect of surface doping on the spinel LiMn_2O_4 and its reactivity with electrolyte components.

Subsequently, surface coating emerges as a strong strategy to hinder electrolyte-cathode interactions while preserving LiMn_2O_4 structural composition. Various coating materials, including metallic oxides (e.g., TiO_2 [89, 90], Al_2O_3 [91, 92], ZnO [93, 94, 95], MgO [96, 97]), fluorides (*i.e.* SrF_2 [100], LaF_3 [101] and AlF_3 [98, 99]), and phosphates (*i.e.* LaPO_4 [102, 103]), YPO_4 [104], FePO_4 [105], AlPO_4 [106]), have been explored. Among these, $\alpha\text{-Al}_2\text{O}_3$ stands out as a promising candidate due to its exceptional mechanical and thermal stability, corrosion resistance, and low electrical conductivity [107, 108]. A notable feature is its ability to react with the acidic electrolyte medium, hydrofluoric acid (HF), resulting in an additional coating layer, AlF_3 {via chemical equation: $\text{Al}_2\text{O}_{3(s)} + 6\text{HF}_{(aq)} \rightarrow 2\text{AlF}_{3(s)} + 3\text{H}_2\text{O}_{(l)}$ }, further attenuating electrolyte-cathode interactions [109]. However, the interfacial interaction between the cathode and the coating surfaces is not fully understood.

1.3. Intentions of the Study

This work used density functional theory calculations to analyse the surface properties of spinel LiMn_2O_4 , the impact of surface modification (Nb-doping and $\alpha\text{-Al}_2\text{O}_3$ surface coating), and the reactivity of the modified surfaces towards the electrolyte content. The goal of this work is to study surface modification of spinel LiMn_2O_4 and understand the electrolyte reactivity. First, the impact of the organic ethylene carbonate (EC) on the major $\alpha\text{-Al}_2\text{O}_3$ (0001) surface at various coverages will be assessed using their adsorption energies, Bader charges and surface-free energies values. This will provide an idea about the interaction behaviour between the coating material $\alpha\text{-Al}_2\text{O}_3$ surface and the organic electrolyte component. Vibrational properties and scanning tunnelling microscopy (STM) images will also be discussed. Additionally, the

major spinel LiMn_2O_4 surfaces and the $\alpha\text{-Al}_2\text{O}_3$ surfaces will be used to model the $\alpha\text{-Al}_2\text{O}_3//\text{LiMn}_2\text{O}_4$ heterostructure considering a range of configurations (based on surface-surface unit cell expansions) to attain near coincident interfaces. Geometry misfit (μ) calculations will be used to assess the alignment of the surfaces, with the $\mu \geq 5$ being the most preferred. The stabilities will be evaluated by calculating their adhesion energies for different coating thicknesss. The electronic properties of each heterostructure will be assessed, considering the effect of partial delithiation. This will give an understanding of the impact of the electrolyte on the coating layer, heterostructure stability, and the effect of Li vacancy formation during cycling.

The other part of this work will discuss niobium doping affects the LiMn_2O_4 (001), (011), and (111) surfaces. The stability upon doping will be analysed by calculating their surface-free energies in comparison with the pristine surfaces. Furthermore, the adsorptions of the two electrolyte components, i.e. ethylene carbonate and hydrogen fluoride, will be investigated as well as their effect on the particle morphology. Lastly, the electronic properties of the doped and EC/HF adsorbed surfaces will be studied together with their vibrational frequencies.

1.4. Research Questions

Considering the surfaces as the first contact during reactions; stability and reactivity of LiMn_2O_4 surfaces is crucial in enhancing the electrochemical performance of Li-Mn-O based batteries. Understanding the impact of surface modification towards the stability and reactivity of the electrolyte would shed light on the quest to attain an improved capacity and cycling stability. Hence, these questions will be addressed to verify and compare the effect of niobium-doping and $\alpha\text{-Al}_2\text{O}_3$ coating of the major LiMn_2O_4 surfaces.

- (i) What is the impact of the ethylene carbonate (EC) on the coating $\alpha\text{-Al}_2\text{O}_3$ (0001) surface layer?
- (ii) How will the increase in EC coverage impact the interactions of the molecule with the surface?
- (iii) The $\alpha\text{-Al}_2\text{O}_3$ surface coating has been shown to improve the electrochemical performance of the battery, but how does the coating layer interact with the cathode material?
- (iv) How can Li cycling affect the $\alpha\text{-Al}_2\text{O}_3//\text{LiMn}_2\text{O}_4$ heteroepitaxial interface stability? And the neighbouring Mn atomic charge upon the formation of Li vacancies?
- (v) How can surface Nb-doping on the top layers affect the surface stability as compared to the pristine surfaces?
- (vi) What is the impact of Nb-doping on the particle morphologies?
- (vii) How do the electrolyte adsorption energies compare with the pristine surfaces? And how much charge was transferred upon adsorptions?
- (viii) Upon surface coating, how does the organic electrolyte, ethylene carbonate (EC) interact with the major $\alpha\text{-Al}_2\text{O}_3$ surface? And the impact of increasing EC coverage?

1.5. Objectives

The objectives of the research were:

- (i) to discuss the organic electrolyte interactions towards the major aluminium oxide (α - Al_2O_3) coating layer and the effect of increased coverages on the stability, electronic and vibrational properties.
- (ii) to model the heteroepitaxial α - Al_2O_3 // LiMn_2O_4 interfaces and study the geometry, stability, and electronic structure.
- (iii) to explain the effect of partial delithiation based on lithium vacancy formations.
- (iv) to provide an understanding of the impact of surface element substitution towards the stability, morphology, and electronic structure of the major LiMn_2O_4 surfaces.
- (v) to understand the effect of ethylene carbonate and hydrogen fluoride adsorptions on pristine and Nb-doped facets.
- (vi) to examine the surface adsorbed EC/HF Bader charge transfer and the reactivity by calculating their respective work function.

1.6. Outline of the Study

This thesis has the following:

Chapter 1 consists of a brief background, motivation, intention of the study, research question, objectives, and research outline. **Chapter 2** provides the literature review, which outlines the brief historical development of Li-ion batteries, operation principle, cathode material (three families), degradation mechanism and proposed modification strategies, and then discusses surfaces and morphology, and finally, remarks. **Chapter 3** details the theoretical method utilised, details of the parameters used to run the calculations and the background of the properties explored in this study. **Chapter 4** discusses the geometry convergence, structural properties, and electronic properties of the bulk LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ structures. **Chapter 5** discusses the effect of organic electrolyte, ethylene carbonate (EC) interactions with the major coating $\alpha\text{-Al}_2\text{O}_3$ (0001) surface layer. Considering the great impact of surface coating with $\alpha\text{-Al}_2\text{O}_3$ and its scavenging effect towards the acidic hydrofluoric acid (HF), it is crucial to also understand the organic electrolyte component interactions with the major $\alpha\text{-Al}_2\text{O}_3$ (0001) surface layer even at an increased EC coverage. **Chapter 6** investigates the formation of $\alpha\text{-Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ heteroepitaxial interface to simulate a coated LiMn_2O_4 surface with $\alpha\text{-Al}_2\text{O}_3$. It also explains the electronic properties, and stability of the heterostructures upon partial delithiation. **Chapter 7** discusses niobium doping on the (001), (011) and (111) LiMn_2O_4 surfaces, its impact on the particle morphology, stability, electronic structure and vibrational frequencies and electrolyte (ethylene carbonate and hydrogen fluoride) interactions. Chapter 8 presents the summary and conclusion of the entire study and provides recommendations and future work.

CHAPTER 2

2. LITERATURE REVIEW

Since its initial commercialization by Sony in 1991, lithium-ion batteries (LIBs) have been successfully industrialized throughout the years [17]. The three 2019 Nobel laureates, John B. Goodenough, M. Stanley Whittingham, and Akira Yoshino, deserve most of the credit for discovering and development of rechargeable LIBs [110]. They are currently commonly used in both portable electronics and large-scale applications like stationary smart grids and electric vehicles. Although there are many different types of batteries, LIBs are popular due to their environmental friendliness, safety, rapid charging, and self-discharge resilience. However, some difficulties have been identified that have resulted in capacity diminishing. As a result, this chapter provides a brief history, development, and application of LIBs. A discussion of the three types of active (cathode) materials used (layered, olivine, and spinel). Limitations, degradation processes (Jahn-Teller distortion and manganese dissolution), electrolyte components, and reactivity. Finally, discuss the proposed solutions (surface coating, doping, etc.) and provide comments.

2.1. Overview - Origin and Development of LIBs.

Historically, Li-ion batteries can be traced back to experiments conducted by G.N Lewis in 1912 [111, 112]. But in the 1970s, they attracted a lot of attention and started to play an innovative part in battery technology. Development of lithium/metal sulfide batteries was started in 1975 [113] at Argonne National Laboratory (ANL), located in the United States. These high-temperature lithium-sulfur batteries had a solid anode/aqueous electrolyte/solid cathode configuration ($\text{LiAl/LiCl-KCl/FeS}_x$), a cell voltage that was just under 2V, and they

operated at a temperature of around 450 °C [114, 115]. In 1976, M.S. Whittingham at Exxon demonstrated the $\text{Li}^+/\text{Li}_x\text{TiS}_2$ insertion and extraction of ternary systems over the compositional range of $0 \leq x \leq 1$ and 2V cell voltage was maintained within this range at the current of 1-10 mA/cm² [116]. Also showed that when the ternary structures are generated by an intercalation reaction rather than a chemical bond reaction, cell reversibility is maximized. Johan Coetzer at Council for Scientific and Industrial Research – CSIR, South Africa recognized the corroding nature of molten sulfur, proposed an idea of preventing and containing sulfur within a solid electrode matrix using zeolitic structures, which had only one plateau between the voltage cut-offs 1.0 - 2.3 V and calculated theoretical energy density of 635 Wh/kg [117]. Using the same ANL configuration as Coetzer and the high-temperature LiAl/LiCl , $\text{KCl}/\text{zeolite-sulphur}$ cells, R.C. Galloway [118] investigated the use of Na instead of Li and developed Na/zeolite-sulphur with an operating voltage of 2.35 V at 270 degrees. Coetzer thereafter abandoned the use of sulphur-containing electrodes in favour of those containing chlorinated iron carbides (Fe_xCCl_y) and iron dichloride (FeCl_2) [119]. This zeolite-containing battery was dubbed ZEBRA (for Zeolite Battery Research in Africa, which has since been renamed *Zero Emission Battery Research Activity*) [120]. Because NiCl_2 cathode with traces of FeCl_2 has a greater operating potential, it is used in recent ZEBRA batteries [121, 122].

The following research investigated the usage of less corrosive metal oxides as alternatives to FeS_2 and FeCl_4 electrodes. Godshall et al [123] 1980 investigated the Li thermodynamic reaction with metal oxides MnO , LiCoO_2 and LiFeO_2 , and discovered that the ternary iron and cobalt oxides have a quicker current density ranging between 10-15 mA/cm², with LiCoO_2 having the greatest specific capacity of 539 Wh/kg. Similarly, John B. Goodenough and colleagues [124] investigated Li electrochemical extraction from LiCoO_2 ternary rock-salt and demonstrated that reversibility at $x = 0.5$ and 1 mA/cm² current densities appear promising for

practical application. LiCoO_2 possesses O layers that are highly polarized towards Co due to the presence of low-spin Co(IV)/Co(III) , resulting in more Li diffusion channels than other LiMO_2 oxides at the time.

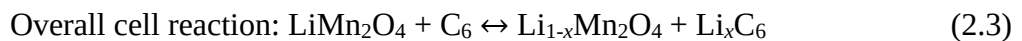
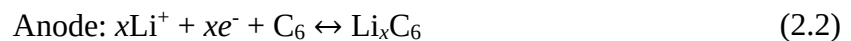
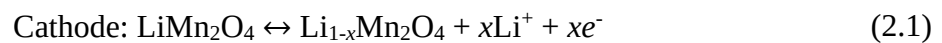
Later in 1981, the discovery of the cubic closed-packed oxygen structure of iron oxide (Fe_3O_4) [125] which remains inert upon lithiation/delithiation process at high temperatures led to studies on $\text{Li[TM}_2\text{]O}_4$ (where TM = Fe, Mn, etc.) spinel structures for Li-ion battery applications [126, 127]. Akira Yoshino of Japan's Asahi Kasei Corporation produced the first LIBs operational prototype in 1983, using a LiCoO_2 cathode and a graphite anode [128]. To achieve the ionic conductivity required by the battery, Yoshino's design used an electrolyte made of Li salts dissolved in organic solvents. The prototype, however, was not adopted by the industry upon its construction due to safety concerns about employing an organic electrolyte. Tokio Yamabe and Shizukuni Yata reported in 1997 that a nano-carbonaceous-PAS (polyacene) anode was successful in a conventional liquid electrolyte [129].

Sony Corporation launched the first lithium-ion battery in 1991 [17]. With the success of Sony's lithium-ion battery, the technology swiftly extended to other industries. Lithium-ion batteries were widely utilized in portable gadgets (i.e. phones, computers, digital cameras etc.) in the early 2000s. In recent years, the usage of lithium-ion batteries has spread to electric vehicles, grid energy storage systems, and even aerospace applications. Despite their widespread use, lithium-ion batteries continue to encounter hurdles in terms of cost, safety, and environmental effects. However, current research and development are making considerable progress in resolving these difficulties, intending to make lithium-ion batteries even more efficient, reliable, and sustainable. To achieve these, various studies indicated that the improvement of the electrochemical performance of LIBs greatly influenced by the type/nature of active

(cathode) material used [130]. Hence, the next section provides a discussion of various LIBs cathode materials, their attractive features, and individual practical limitations.

2.2. Lithium-ion Batteries Operation Principle

A conventional lithium-ion battery has three components: a cathode, an anode, and an aqueous electrolyte that links the two electrodes. The electrolyte functions as an ionic separator between the two electrodes, allowing only Li^+ to transfer. The transport of Li ions to and from the electrodes in the presence of a load or power source governs how the LIBs function. Charging (or delithiation) involves the transport of Li^+ from the cathode to the negative electrode, whereas discharge is the converse process. During the charging process, lithium ions are removed from the cathode material and transferred via the electrolyte medium to the anode material, where they are temporarily stored. At the same time, Li electrons go over an external circuit to the anode material, where they recombine into Li atoms. Charging requires an energy source, which is like ascending a mountain. After complete delithiation, Li^+ returns to the cathode material via the electrolyte, while electrons exit via the external circuit. This is referred to as a discharge process, which occurs naturally (similar to falling from a cliff). [Figure 2.1](#) outlines the processes and electrochemical reactions that occur at both the cathode and anode materials separated by an aqueous Li^+ -containing electrolyte, as follows:



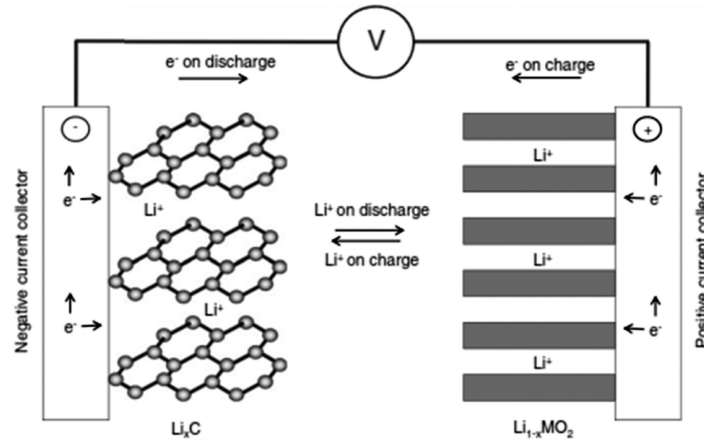


Figure 2.1: Schematic diagram showing the working principle of a lithium-ion battery [131].

2.3. Cathode Materials

Cathode materials are one of the key components of lithium-ion batteries, which are identified by the positive electrode. Their composition and qualities have a considerable impact on the electrochemical performance of the battery. There are many cathode materials with varying operating voltages, capacities, and potential differences (See [Table 2.1](#) and [Figure 2.2a](#)). According to Thackeray et al [132], an ideal cathode material for Li-ion cells should have the following properties: (i) To provide high electrode capacities, the host cathode material should be as light as feasible and able to tolerate a substantial number of lithium ions. Because systems with high voltage and electrode capacities will have high energy and power densities. (ii) To provide high electrode capacities, the host cathode material should be as light as feasible and able to tolerate a substantial number of lithium ions. Because high voltage and electrode capacities result in high energy and power densities. (iii) For the cell to be high-rate capable, the lithium diffusion coefficient of the host cathode should be as high as feasible. (iv) The material used for the host cathode should be a stable, excellent electronic conductor that does not react with the electrolyte components. (v) To achieve good Li^+ reversibility, the host cathode material should be modified minimally, and the lattice characteristics should be varied little. (vi) Its manufacture should be inexpensive, and the material used should be environmentally friendly.

Table 2.1: Electrochemical performance of cathode materials for Li-ion battery.

Structural type	Cathode material	Specific capacity (mAh/g)		Potential vs Li^+/Li (V)	Ref.
		<i>Theoretical</i>	<i>Practical</i>		
Layered	LiCoO_2 –LCO	274	140	3.9	[133]
	LiNiO_2 –LNO	275	200	3.7	[134]
	$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ – NMC 111	275	160	3.8	[135]
	$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ – NMC 811	275	200	3.8	[136]
	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ – NCA	280	160	3.8	[137]
Olivine	LiFePO_4 – LFP	170	150	3.5	[138]
	$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ – LMFP	171	160	4.1	[139]
Spinel	LiMn_2O_4 – LMO	148	120	4.0	[140]
	$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ – LNMO	147	125	4.7	[141]

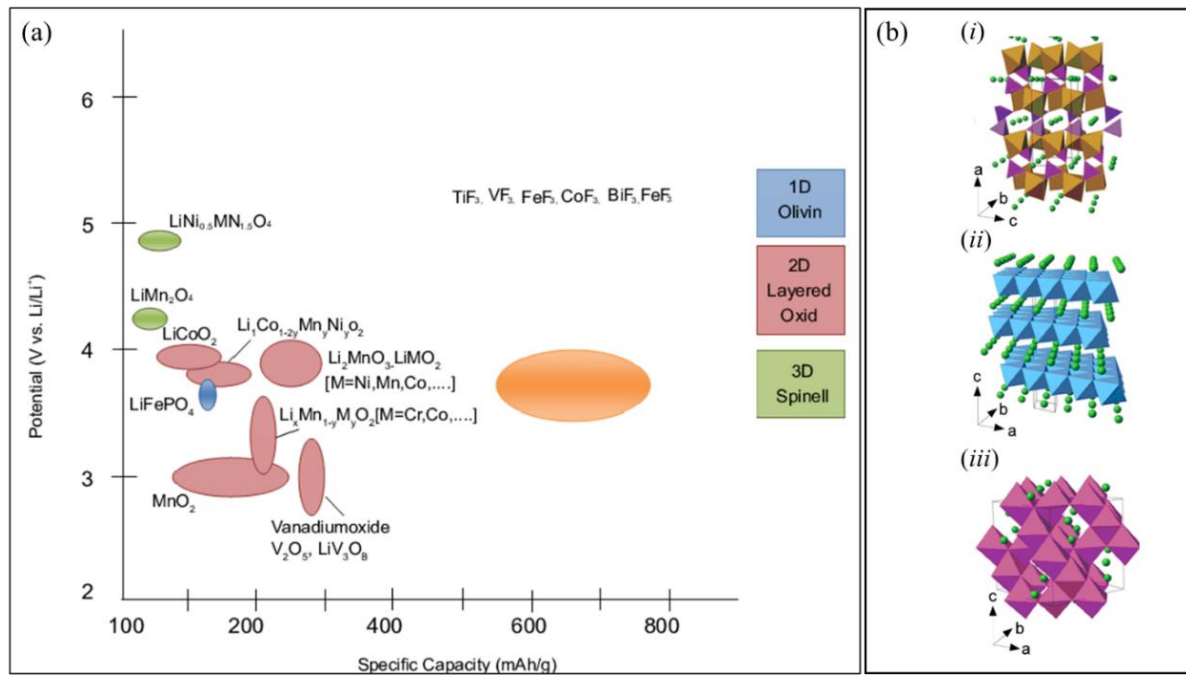


Figure 2.2: (a) Comparison between the cathode materials based on their voltage and specific discharge capacities [142]. (b) Crystal structure of the three lithium-insertion compounds (i) olivine, (ii) layered and (iii) spinel frameworks [143, 144].

2.3.1. Olivine

The 1D cathode material class, which is frequently the phosphate LiFePO_4 material first discovered by Padhi et al [145]. This cathode material displays appealing characteristics such as low cost, environmental friendliness, abundance, minimal volume expansion, relatively high specific capacity, and good safety. A typical LiFePO_4 give off a practical capacity of 150 mAh/g (approximately equal to the theoretical capacity of 170 mAh/g) and a flat plateau at 3.4 V [146]. The material has a $Pnma$ space group, with P atoms occupying $4c$ tetrahedral sites and Li and Fe filling $4a$ and $4c$ octahedral sites, respectively. The oxygen atoms, on the other hand, are organized in a slightly deformed hexagonal close-pack configuration. The LiO_6 coordination creates an octahedra linear-edged shared chain parallel to the PO_4 tetrahedron, while the corners in the bc plane are shared by FeO_6 octahedra.

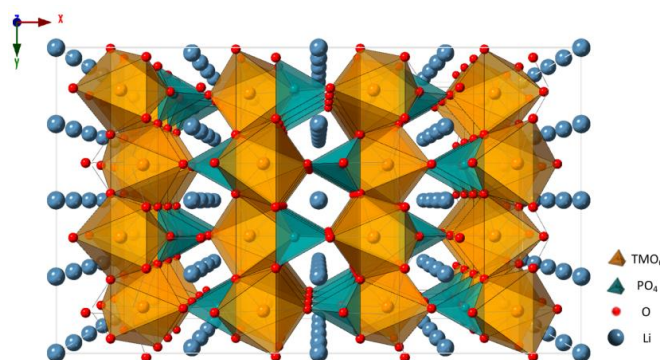


Figure 2.3: Olivine Li(TM)PO_4 crystal structure (TM = Fe, Co, Mn, Ni, etc.) [147].

When cycling, this material exhibits an outstanding low-capacity fading. However, the separation of the PO_4 and FeO_6 polyanions has a considerable effect on electrical conductivity, resulting in decreased Li mobility [148]. The LiFePO_4 cycle process has been studied since it is thought that Li ions diffuse along the b -axis rather than in other directions. The space group and volume of a completely delithiated LiFePO_4 structure FePO_4 differ by 6.8% [149]. Several mitigating strategies to increase Li transport were examined, including element replacement (mostly at the Fe element) with TM = Nb, Mo, Co, V, Mn, Ni, Zn, Cu, Mg, and Cr, as well as

particle/grain size reduction and the application of a conductive layer over the LiFePO_4 [150, 151]. Because of particle growth and agglomeration during high-temperature calculations, the normal synthesis technique of LiFePO_4 by conventional solid-state reaction often gives a large particle size with a low surface area. As a result, a few research investigated various synthesis strategies such as hydrothermal and sol-gel procedures, which resulted in nanoparticles larger than 100nm and delivering 157 - 123 mAh/g when discharged at 1-10 C. A higher surface area, on the other hand, may result in more cathode-electrolyte side reactions, which means more Li ions may be consumed to produce solid electrolyte interphase (SEI). Alternatively, Martha et al [139] demonstrated that classic LiFePO_4 doped with Mn has very rapid capability, high thermal stability, and a capacity of roughly 165 mAh/g with a $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ composition.

2.3.2. Layered

The second class is the layered cathode material (with a 2D configuration), which was first discovered in 1958 by Johnston et al [152]. It has the same layered structure as $\alpha\text{-NaFeO}_2$, with Li^+ and Co^{3+} organized in an alternating (111) plane and oxygen atoms arrayed in a cubic-closed pack array with an $R\bar{3}m$ space group. Delmas et al. [153] characterized the LiCoO_2 structure as O3-type, meaning Li^+ form an octahedron surrounded by six oxygen and the 3 specifies the oxygen packing type (*i.e.*, ABCABC...). JB Goodenough [153] was the first to investigate LiCoO_2 as a cathode material in 1981. According to [Table 2.1](#), the earliest layered LiCoO_2 has a theoretical capacity of around 274 mAh/g, which is higher than the pristine spinel LiMn_2O_4 and polyanion LiFePO_4 . However, its practical use generates about 170 mAh/g (less than half of its theoretical capacity) [30]. The capacity fully disappears after 10 cycles, owing to (i) structural phase change, followed by lattice deformation, which produces particle strain and crack development, and (ii) surface-electrolyte interactions, which cause surface Co dissolution and O_2 loss. From an industrial standpoint, normal LiCoO_2 isn't the most practical choice as a cathode material for LIBs due to factors like safety, energy density, longevity, and

price. Researchers explored two methods to increase the efficiency and practical capacity retention of LiCoO_2 , namely, totally replacing the poisonous cobalt or using transition metals (TM) to regulate phase shift and improve the Li diffusion rate.

The complete replacement of Co for Ni led in the discovery of LiNiO_2 (LNO), which has a theoretical capacity of 275 mAh/g and an operating voltage of 3.7 V versus Li^+/Li . Dyer et al [154] were the first to synthesise LiNiO_2 with the same crystal structure as LiCoO_2 . Dahn et al [155] explored this material as a cathode material substitute for Li-ion batteries using Li_xC anodes. The LNO has outstanding cycle stability and rate capability, making it a desirable cathode material for high-power systems. The $\text{Ni}^{3+}/\text{Ni}^{4+}$ 3d band barely brushed the top of O 2p before oxygen loss, indicating that the bulk of the Li^+ could be recovered from LiNiO_2 , resulting in a high capacity of 200 mAh/g [156]. Despite its appealing features and performance, the LiNiO_2 cathode material has significant issues that must be solved. One significant disadvantage of this material is that stoichiometric LiNiO_2 is difficult to manufacture and should exist as $\text{Li}_{1-y}\text{Ni}_{1+y}\text{O}_2$ [157]. Another problem encountered when cycling is the material's potential to undergo structural changes while cycling, which can result in capacity fading and poor cycling stability [158]. The structural alterations are caused by Ni ion migration from octahedral to tetrahedral positions in the crystal lattice, which can result in permanent structural changes.

The discovery of Li-rich Mn-based cathode with the formula $x\text{Li}_2\text{MnO}_3 \cdot (1-x) \text{LiMO}_2$ (TM = Ni, Mn, Co, etc.) is now regarded as the next-generation LIBs cathode materials. This is owing to their higher specific capacity of almost 250 mAh/g and operating voltages of 3.4 V [41, 42]. These cathode materials are made up of two-parent structures: Li_2MnO_3 and LiMnO_2 . The greatest theoretical capacity is 459 mAh/g for monoclinic layered Li_2MnO_3 (also written as $\text{Li}[\text{Li}_{0.33}\text{Mn}_{0.67}]\text{O}_2$). However, in earlier studies [132, 159], the parent Li-rich Li_2MnO_3 structure was considered electrochemically inert because it cannot be further lithiated because

all of the octahedral Mn sites are filled and delithiation is difficult because the tetravalent manganese (Mn^{4+}) cannot oxidize further. Furthermore, the inability to oxidize Mn beyond +4 restricts Li^+ extraction from Li_2MnO_3 since Li^+ ion removal is accompanied by Mn oxidation [160].

The following research supplied a clearer explanation in reference to the nonstoichiometric $\text{Li}_4\text{Mn}_5\text{O}_{12}$ [161, 162], that Li^+ extraction from Li_2MnO_3 material is attainable by simultaneous removal of Li and O (extraction of Li_2O) to balance the charge [163]. Wang et al [164], on the other hand, observed that Mn migrates into the lithium layer during delithiation and can swing reversibly in the (001) plane during charge/discharge operations.

According to Gummow et al [43]'s constructed Li-Mn-O phase diagram (see [Figure 2.3](#) below), delithiation of the Li_2MnO_3 leads to the creation of materials such as layered LiMnO_2 and spinel LiMn_2O_4 . During the first delithiation process, the Li_2MnO_3 structure converts into a layered LiMnO_2 , which eventually transforms into a spinel-like structure (through the process $\text{Li}_2\text{MnO}_3 \rightarrow \text{LiMnO}_2 \rightarrow \text{LiMn}_2\text{O}_4 \rightarrow \lambda\text{-MnO}_2$). Hunter [165] originally observed that further delithiation of the spinel-like structure results in the creation of manganese oxide ($\lambda\text{-MnO}_2$). However, Rana et al [166] demonstrated via X-ray absorption spectroscopy that the samples obtained after cycling are not compatible with the spinel structure, but rather with the hypothesized P3 structure. Paik and colleagues [167] also voiced some uncertainty in the creation of the spinel phase, because the XRD patterns of a re-lithiated sample mirrored that of a pristine Li_2MnO_3 and EXAFS fits for a cycled-delithiated sample revealed no existence of the spinel-like structure. However, transmission electron microscopy (TEM) experiments by Gu et al [168] revealed some tiny randomly oriented domains of LiMn_2O_4 spinel phases inside the amorphous surrounds, resulting in the collapse of the Li_2MnO_3 parent lattice during cycling.

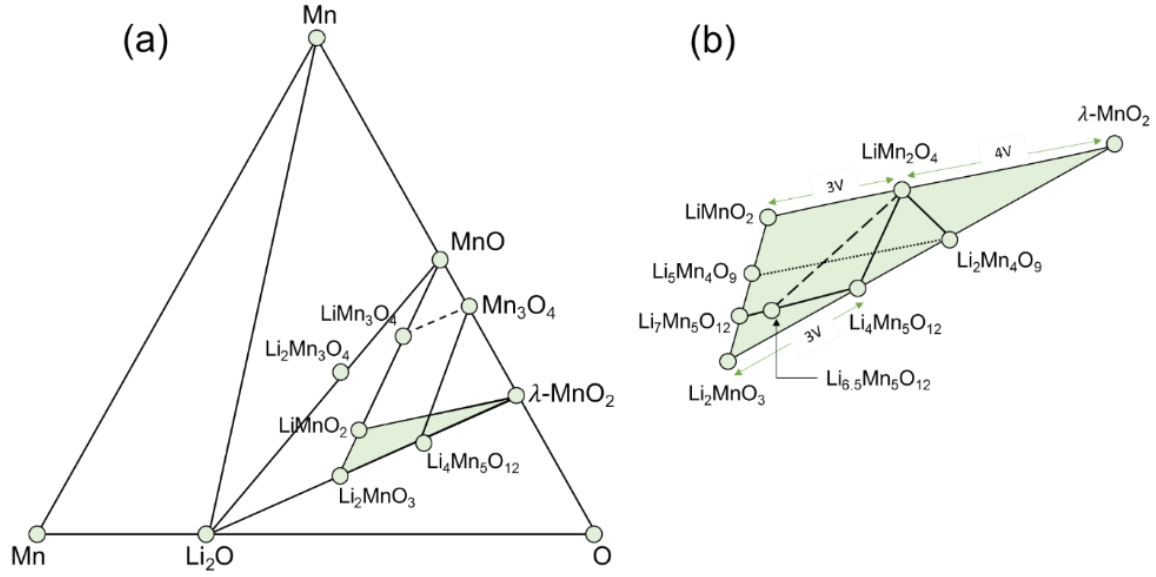


Figure 2.4: Reconstructed (a) Li-Mn-O phase diagram and (b) a close-up of the $\text{Li}_2\text{MnO}_3 \rightarrow \text{LiMnO}_2 \rightarrow \text{LiMn}_2\text{O}_4 \rightarrow \lambda\text{-MnO}_2$ insert of the Li-Mn-O phase diagram [43].

Tang et al [169] observed a prominent occurrence of $\text{Li}^+ \text{H}^+$ ion exchange during cycling based on the battery's electrochemical cycling circumstances and the frequently used LiPF_6 -based non-aqueous electrolyte, which undergoes oxidation to yield $\text{HF}_{(aq)}$ and tiny quantities of $\text{H}_2\text{O}_{(l)}$. A similar phenomenon was seen in various Mn^{4+} Li-Mn-O structures, including the $\text{Li}_4\text{Mn}_5\text{O}_{12}$ and spinel LiMn_2O_4 phases [170, 171]. Using XRD, Robertson et al [172] discovered an extra peak that might be connected to the hydroxide or oxyhydroxide structure. When hydrogen forms an O-H-O bond within the O layer, the stacking sequence changes from O3 (ABCABC) to P3 (ABBCCA). Rana et al. [173] described and summarized the $\text{Li}^+ \text{H}^+$ ion exchange route as follows: $\text{Li}_{x+\delta}^+ \text{Mn}^{4+} \text{O}_{3-y}^{2-} \leftrightarrow \text{H}_x^+ \text{Mn}^{4+} \text{O}_{3-y}^{-2+\delta} + (x + \delta) \text{Li}^+ + (x + \delta) \text{e}^-$. Furthermore, the H^+ is pushed out of the lattice upon re-lithiation by electrochemical reduction inside the electrolyte, resulting in the recreation of layered Li_2MnO_3 . However, a prolonged shearing of the oxygen layers during cycling may result in crystallinity loss and decreased intercalating capacity. $\text{Li}_{x+\delta}^+ \text{Mn}^{4+} \text{O}_{3-y}^{2-} \leftrightarrow \text{H}_x^+ \text{Mn}^{4+} \text{O}_{3-y}^{-2+\delta} + (x + \delta) \text{Li}^+ + (x + \delta) \text{e}^-$. Furthermore, it was indicated that during re-lithiation, the H^+ is driven out of the structure by

the electrochemical reduction within the electrolyte, resulting in the formation of layered Li_2MnO_3 . However, this prolonged shearing of the oxygen layers during cycling could lead to crystallinity loss and intercalating ability.

2.3.3. Spinel

The third low-cost, commercially used class of cathode materials is the spinel cathode material LiM_2O_4 (where $\text{M} = \text{Mn}, \text{Fe}$, etc.), first explored by Thackeray *et al* [174] in 1983. It emerged as the ideal alternative for LiCoO_2 not just because it contains Mn which is earth-abundant, less poisonous, and less expensive manganese than Co. The LiMn_2O_4 structure has a three-dimensional intact framework with Li^+ diffusion routes that remain intact during charge/discharge operations. Hunter [165] investigated the treatment of LiMn_2O_4 spinel-type with aqueous acid and discovered the production of almost pure $\lambda\text{-MnO}_2$ with a preserved LiMn_2O_4 structural framework. The resultant $\lambda\text{-MnO}_2$ lattice parameters and density were determined to be 8.03 Å and 4.46 g/cm³, respectively, compared to 8.24 Å and 4.49 g/cm³ for spinel LiMn_2O_4 . Thackeray *et al.* [175] reported in 1984 that electrochemical Li removal at 15A/cm² from virgin LiMn_2O_4 generates the $[\text{Mn}_2]\text{O}_4$ structure with a stable spinel framework. Thackeray *et al* [174] investigated the insertion of Li into Mn_3O_4 and LiMn_2O_4 at room temperature and discovered that the spinel framework is preserved, but Li^+ ions are inserted to occupy the spinel's interstitial octahedral sites, while manganese ions are displaced from positions *a* to octahedral interstitial sites. [Figure 2.5](#) shows that the theoretical capacity of LiMn_2O_4 is 148 mAh/g at 3.0 - 4.3 V, with a specific energy density of roughly 490 Wh/kg.

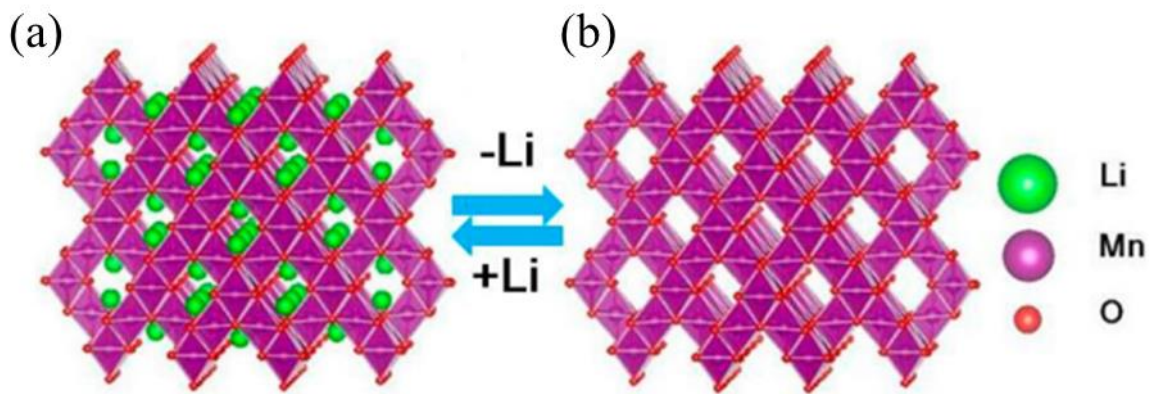


Figure 2.5: Crystal-structural representation of the (a) lithiated LiMn_2O_4 and (b) delithiated spinel $\lambda\text{-MnO}_2$.

The crystal structure of LiMn_2O_4 belongs to the spinel group of crystals, which was discovered in 1915 by Bragg [176] and Nishikawa [177]. LiMn_2O_4 , like the spinel MgAl_2O_4 , has the general chemical formula of $(\text{A})_{\text{tet}}[\text{B}_2]_{\text{oct}}\text{O}_4$ (space group: $Fd\bar{3}m$, No. 227). The primitive unit cell consisting of 56 atoms, comprised of 8 Li occupying $8a$ tetrahedral sites (0.125, 0.125, 0.125), 16 Mn on the $16d$ octahedral (0.5, 0.5, 0.5) with an equal amount of $\text{Mn}^{3+/4+}$ ions averaging +3.5, and 32 O atoms orientated in a close-packed cubic array at the $32e$ (0.259, 0.259, 0.259) sites, which forms a face-centred cubic crystal. Lithium ions diffuse between the $8a$ and $16d$ during charge/discharge cycles, generating three-dimensional channels. When lithium-ions diffuse across the structure, they first go from the $8a$ site to the next $16d$ site, then back to the $8a$ site, allowing for three-dimensional lithium diffusion. The Mn ions align with oxygen octahedra, whereas the MnO_6 octahedra form a three-dimensional host for the Li guest ions. However, it really emits 120 mAh/g (80% of the predicted capacity of 148 mAh/g). This is due to capacity fading caused by electrolyte activity, which results in Jahn-Teller distortion of Mn^{3+} ions [51, 52, 53], formation of cathode electrolyte interphase (CEI) [49, 50], and dissolution of manganese (Mn^{2+}) ions into the electrolyte [54, 61, 56, 57]. Small quantities of element dopants such as Al, Ni, Co, and others were suggested to stabilize and restrict Jahn-

Teller in the LiMn_2O_4 cathode material. Among the several dopants, the addition of Ni has been one of the most effective, resulting in $P4_332$ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Because the Ni^{2+} reduces the quantity of Mn^{3+} in the structure, it can undergo a disproportionation reaction and create two voltage plateaus at 4.7 V, making it a viable high energy cathode material. Amine et al [178] discovered this cathode material ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) in 1996. Despite the presence of Mn^{3+} traces in an oxygen-deficient $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ system, Jahn-Teller distortion is still repressed. Malatji et al [179] examined and discovered an average maximum Li^+ intercalation voltage of 4.8 eV for the stable composition $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, with little temperature influence on the voltage. Cen et al [180] discussed the cation Mn/Ni defects in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and guided defect-controlled synthesis.

2.4. Degradation Mechanisms - LiMn_2O_4

A thorough analysis was undertaken to determine how the deterioration of LiMn_2O_4 -based Li-ion batteries occur during cycling, and numerous processes were found. (i) Surface manganese dissolving into the electrolyte is thought to account for most of the capacity loss. (ii) Jahn-Teller distortion, resulting in tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ phase transition. (iii) Electrolyte breakdown results in the formation of an acidic hydrofluoric acid (HF), which corrodes the electrodes and causes a variety of side reactions inside the electrolyte. (iv) Oxygen flaws resulting from the synthesis process or electrolyte action toward the cathode. (v) The production of microcracks as a result of irreversible phase change, and (vi) manganese deposition on the anode material reduces the development of the solid electrolyte interface (SEI). [Figure 2.6](#) outlines the reasons for the deterioration in LiMn_2O_4 -based cathodes.

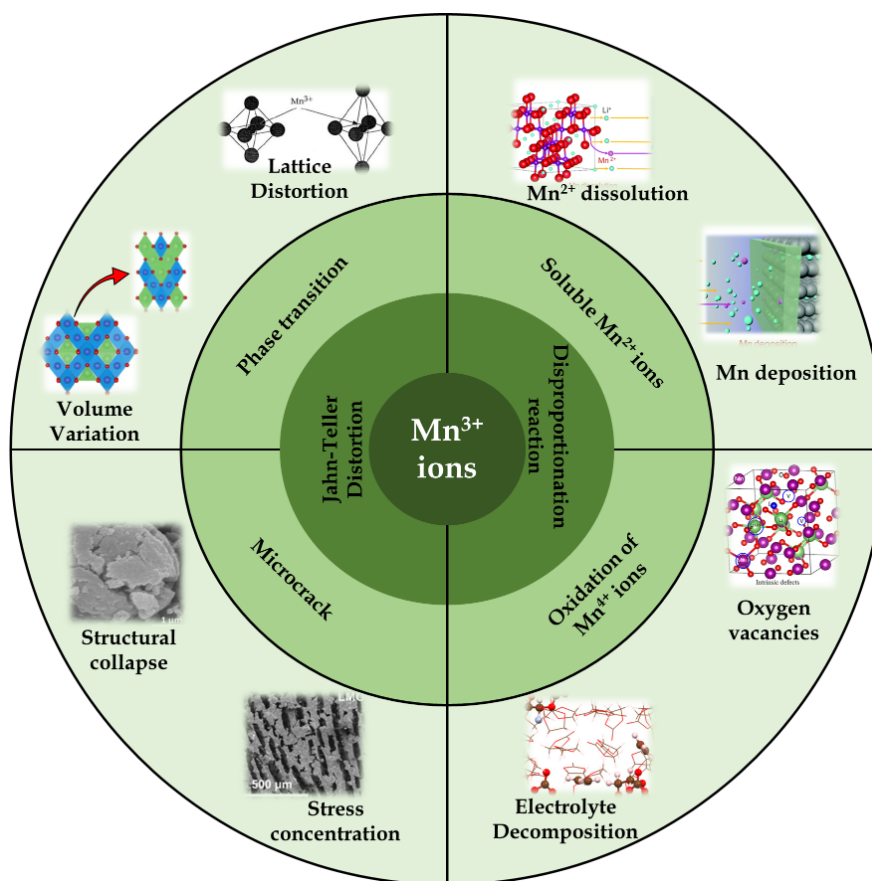


Figure 2.6: Summary of the degradation mechanisms causing LiMn_2O_4 capacity decay reconstructed from Zhang et al [85].

2.4.1. Jahn-Teller Distortion

Despite the host $[\text{Mn}_2]\text{O}_4$ spinel framework's stability, the LiMn_2O_4 structure has an equal quantity of trivalent (Mn^{3+}) and tetravalent (Mn^{4+}) ions, with an average charge of +3.5, rendering it prone to dynamical Jahn-Teller (J-T) distortions. Hermann Jahn and Edward Teller [181] proposed the J-T distortion in their 1973 research of polyatomic molecules in degenerate electronic states. According to the hypothesis, “stability and degeneracy cannot coexist unless the molecule is linear”. The updated and phased version of this postulate is that “any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy”.

The theorem states that unless the degeneracy is abolished and a system with reduced symmetry and energy is produced, the degenerated electron state of a nonlinear system will remain unstable. The J-T is most seen in octahedral and tetrahedral complexes where two axial bonds might be shorter or longer than those in equatorial links. Looking at the electronic structure of octahedral Mn 3d in LiMn₂O₄ and comparing the Mn³⁺ and Mn⁴⁺ ions (see [Figure 2.7](#)). Mn³⁺ ions typically display high-spin states, with three electrons occupying the t_{2g} orbital and one at the e_g orbital ($t_{2g}^3 e_g^1$), resulting in asymmetrical e_g occupancy. The electrons are spread among the d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$ orbitals, with an empty d_{z^2} . This asymmetrical charge distribution results in varying degrees of shielding effects in different orientations of the manganese nuclei. The total arrangement no longer corresponds to the octahedral symmetry, preventing Mn³⁺ instability. As a result, the longitudinal Mn-O bonds will lengthen while the four horizontal Mn-O bonds will contract to stabilize. As a result, the ensuing symmetry will be changed from octahedral to tetragonal to minimize system energy, which distorts the crystal structure. Unlike Mn³⁺ ions, Mn⁴⁺ has three electrons scattered in the t_{2g} orbital with no electrons in the e_g orbital ($t_{2g}^3 e_g^0$), hence only Mn³⁺ ions may cause J-T distortion [182].

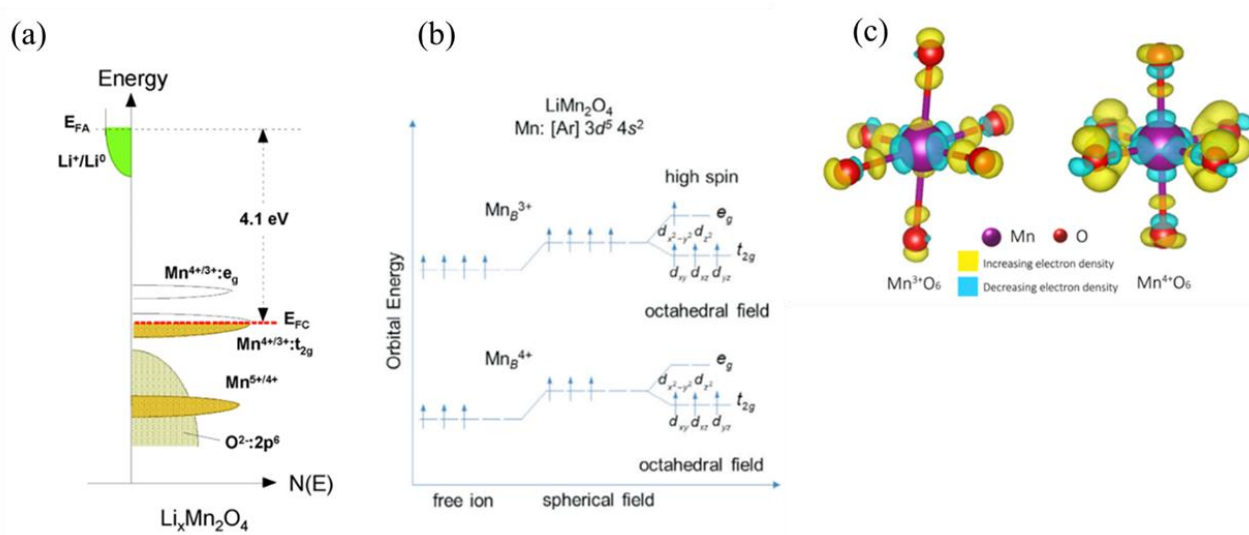


Figure 2.7: (a) LiMn_2O_4 density of states showing Fermi energy of $\text{Mn}^{4+/3+}$ redox pair [182]. (b) Illustration of 3d Mn electron crystal field splitting in high spin octahedral coordination environments Mn_B^{3+} and Mn_B^{4+} in LiMn_2O_4 [179]. (c) Charge densities distribution of Mn^{3+}O_6 and Mn^{4+}O_6 computed. The blue and yellow sections show diminishing and rising electron density, respectively. The charge density iso-surface of 0.015 e/Bohr [183].

2.4.2. Disproportionation Reactions

The interaction of the electrolyte and its oxidation has a major impact on the electrochemical performance of the lithium-ion battery and contributes LiMn_2O_4 cathode degradation. Basic lithium-ion batteries use an aqueous electrolyte made up of a lithium salt (such as LiPF_6) [184] dissolved in an organic solvent (commonly ethylene carbonate, diethylene carbonate, propylene carbonate, dimethylene carbonate, ethyl methyl carbonate, etc.) [185] and other electrochemical performance-enhancing additives. The solvents' operating voltages are generally between 1.0 and 4.7 V vs. Li/Li^+ , and any cathode material that utilizes or demands more than that causes electrolyte oxidation and breakdown. The electrolyte, including its additives, can degrade and form a passivation solid electrolyte interface (SEI) layer on its surface. This SEI layer is formed during the first cycle when the electrolyte interacts with the anode (graphite) and is composed of inorganic salts such as LiF and Li_2CO_3 , as well as some

organic species. The SEI shields the anode from further interactions while keeping the cell operational by allowing just Li ions to flow through. It forms a cathode electrolyte interface (CEI) layer on the cathode material, the composition of which is unknown. Furthermore, due to the nature of metal oxide cathode material oxidation, the electrolyte may degrade, resulting in CO₂ gas emissions. Because both electrolyte salts and organic solvents exist, we must properly comprehend their breakdown.

2.4.2.1. *Decomposition of LiPF₆ within the electrolyte*

Because of its superior conductivity, thermal stability, and affordability, LiPF₆ is commonly used as salt electrolyte in lithium-based batteries. It is often dissolved in carbonate-based solvents, which have benefits such as strong ionic conductivity and oxidation durability [96]. When LiPF₆ is dissolved, it completely dissociates into coordinated Li⁺ and uncoordinated PF₆⁻. Reassociation of F anions with Li⁺ through the reaction (LiPF₆ ↔ LiF + PF₅) might occur depending on the solvating strength of the solvent towards Li⁺. The presence of water in the electrolyte induces several side reactions, resulting in an acidic electrolyte. Hider et al [186] and Aurbach et al [187] investigated the reaction processes between water and the LiPF₆ salt in an organic-based electrolyte and addressed the following half-reactions. The produced PF₅ can then react with H₂O molecules within electrolyte to form the scavenging hydrogen fluoride (HF) and POF₃ (through: PF₅ + H₂O → POF₃ + 2HF). The scavenging HF generated might hasten the disproportion reaction of Mn³⁺ to Mn²⁺, which then dissolves into the electrolyte and deposits on the negative electrode. Yang et al [188] investigated the thermal stability of LiPF₆ salt in dry and wet circumstances, as well as when dissolved in organic EC, DMC, and EMC and heated to 107°C. The dry sample decomposed into LiF_(s) and PF_{5(g)}, but the wet sample gave off POF₃ and HF with a lower onset temperature of around 87°C. The FTIR measurement of LiPF₆ in organic solvents heated to 267 °C revealed no new products,

indicating that there was no interaction between the solvent and salt. Han et al [189] summarized the products generated during LiPF_6 breakdown in the presence of water and in a dry sample as a function of temperature (see [Figure 2.8](#)).

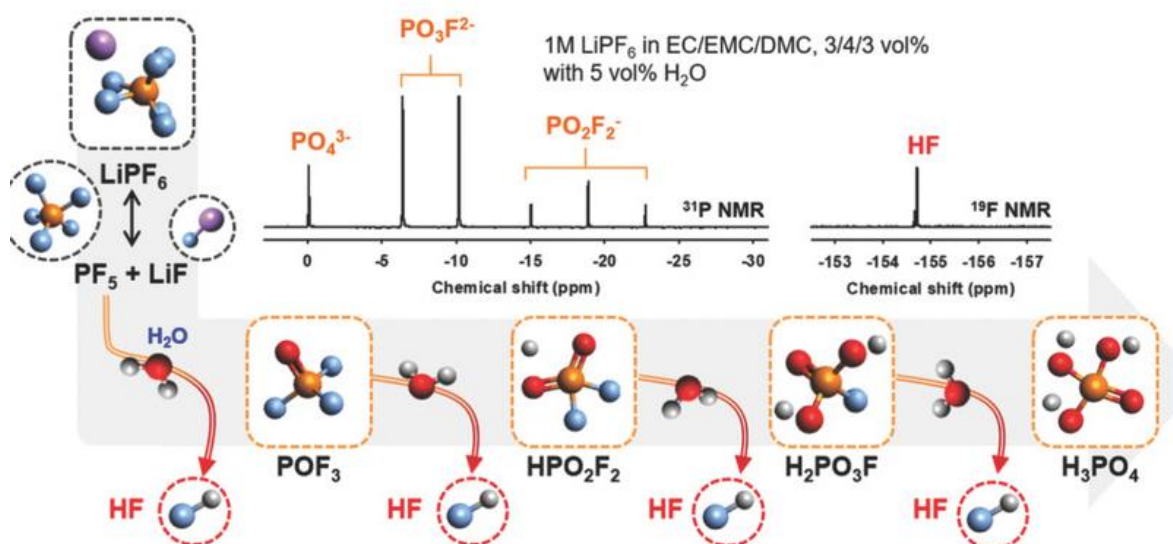


Figure 2.8: The ^{31}P and ^{19}F NMR spectra of LiPF_6 -containing electrolytes after storage for 22h at room temperature and sequential hydrolysis of LiPF_6 [189].

2.4.2.2. Organic solvent decomposition

Organic electrolyte components also degrade into various compounds. Based on its high melting point of 36.4°C , higher dielectric constant of 90.5, and perfect molecular symmetry, the EC is commonly utilized as an electrolyte. Using online electrochemical mass spectrometry (OEMS), Jung et al [190] postulated that liquid ethylene carbonate decomposes into carbon and/or oxygen-containing gases such as CO_2 , CO , C_2H_4 , and so on layered oxide cathode materials. Previous simulations using density functional theory offered insight into the EC breakdown on various cathode surfaces. Using the Gaussian program, Xing et al [191] and Li et al [192] defined several breakdown paths of isolated ethylene carbonate, indicating that the generation of CO is more difficult than CO_2 (see the schematic diagram in [Figure 2.9a](#)). The presence of PF_5 (which is formed by the dissociation of LiPF_6 into $\text{LiF}_{(s)}$ and $\text{PF}_{5(g)}$) can catalyse

ring opening and promote the formation of carbonate motif-containing polymer species, which can result in a variety of products such as carbon dioxide and poly(ethylene oxide), as shown in [Figure 2.9b](#). Fuhst et al [193] investigated several EC bond-breaking routes on the LiCoO_2 ($10\bar{1}4$) surface and discovered that the most favourable exothermic reaction with $\Delta E = -0.85$ eV produces carbon dioxide (CO_2) and acetaldehyde ($\text{C}_2\text{H}_4\text{O}$). Leggesse et al [194] investigated the disintegration of EC on the $\text{Li}_x\text{Mn}_2\text{O}_4$ (100) surface and found that the most favoured process includes ring opening, followed by decarboxylation, which produces CO_2 and acetaldehyde species. Young and Smeu [195] used DFT and AIMD simulations on the Ca metal anode and demonstrated that the creation of CO_3^{2-} and C_2H_4 is energetically preferred, while the generation of $\text{C}_2\text{H}_4\text{O}_2^{2-}$ and CO dominates due to solvent molecule interactions. Similarly, Østergaard et al [196] investigated EC oxidation on lithium metal oxide (LiTMO_2 , TM = Co, Mn, Ni) surfaces using nudged elastic band (Ci-NEB) method and discussed that the H atoms formed on the surfaces upon $\text{C}_e\text{-H}$ bond breaking strongly bind with the surface, leaving no possibility of H_2O release.

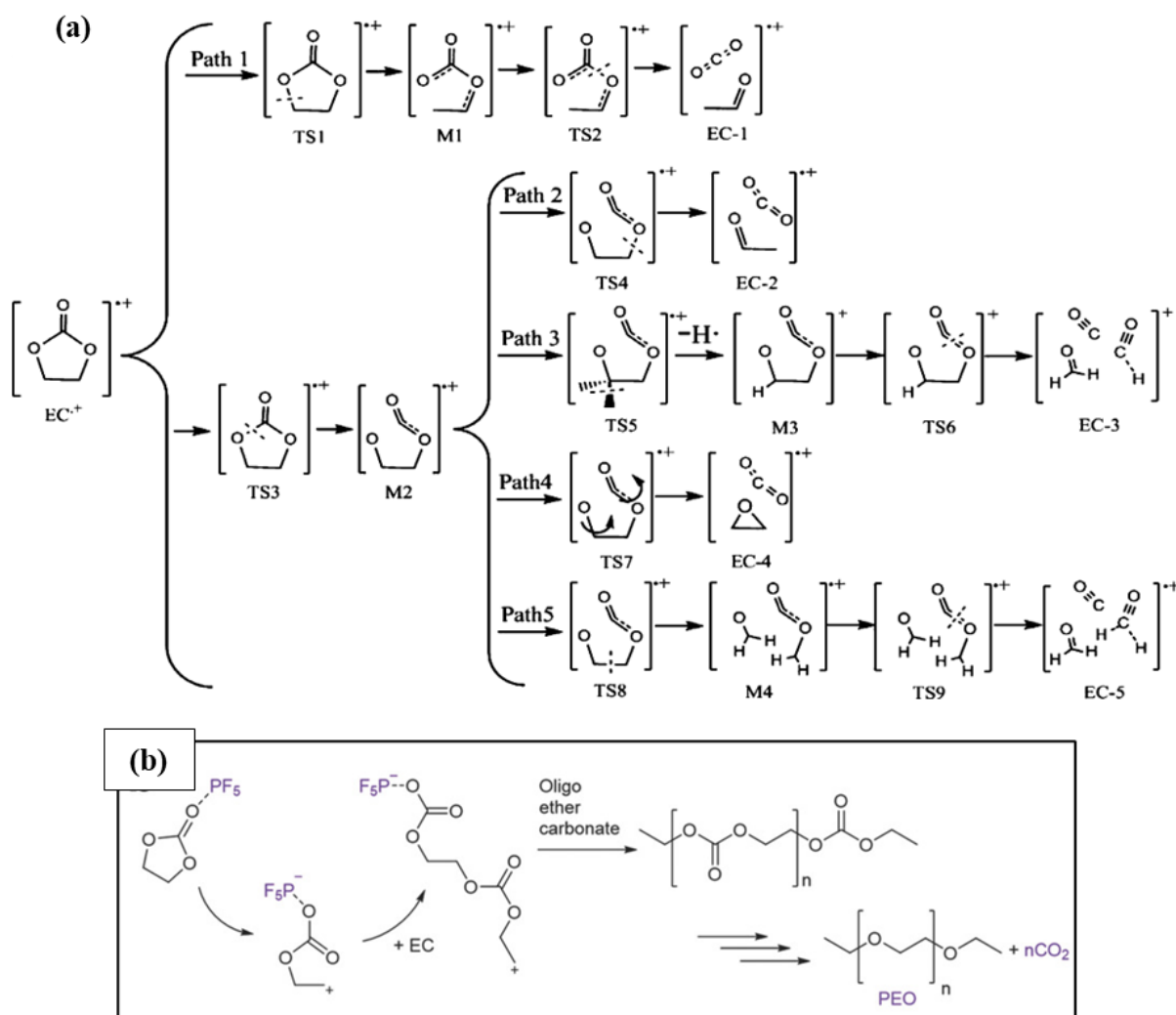


Figure 2.9: (a) The schematic diagram of ethylene carbonate (EC) decomposition into various products, through different pathways [191] and (b) ring opening in the presence of PF_5 [197].

2.4.3. Manganese Dissolution

Manganese dissolution was discovered long before the use of LiMn_2O_4 in LIBs. Hunter [165] investigated the LiMn_2O_4 conversion to $\lambda\text{-MnO}_2$ by chemical delithiation in 1981 in an acid medium. The resulting $\lambda\text{-MnO}_2$ retained the spinel's three-dimensional architecture while removing Li^+ from the tetrahedral positions. However, considerable lattice contraction (from 8.24 Å to 8.03 Å) was found, leading to the proposal of the disproportionation reaction, denoted as $2\text{LiMn}_2\text{O}_4 + 4\text{H}^+ \rightarrow 3\lambda\text{-MnO}_2 + 2\text{Li}^+ + 2\text{H}_2\text{O} + \text{Mn}^{2+}$. The foregoing reaction can be summarized as $\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$. More Li ions diffuse back to the cathode LiMn_2O_4 bulk

surface occupied by Mn^{3+} hopping to Mn^{4+} during charging because of both Li and Mn removal. Manganese dissolution is eventually enhanced by a highly acidic electrolyte medium, high temperatures, a wide surface area, and a greater potential [55]. Aoshima et al [198] investigated the process of capacity fading in cathode materials containing 50-50% Mn^{3+} and Mn^{4+} (see [Figure 2.9](#)). They said that dissolved Mn^{2+} generally forms a layer on the cathode surface constituted of MnF_2 and orthorhombic- $(\text{Mn}^{4+})\text{O}_2$ and another Mn metal layer on the anode material created by Mn deposition. Hirayama et al [199] used X-ray refraction (XRR), ex-situ transition electron microscopy (TEM) and X-ray diffraction (XRD) to determine that the (110) surface is less stable and more vulnerable to Mn-dissolution than the (111) surface.

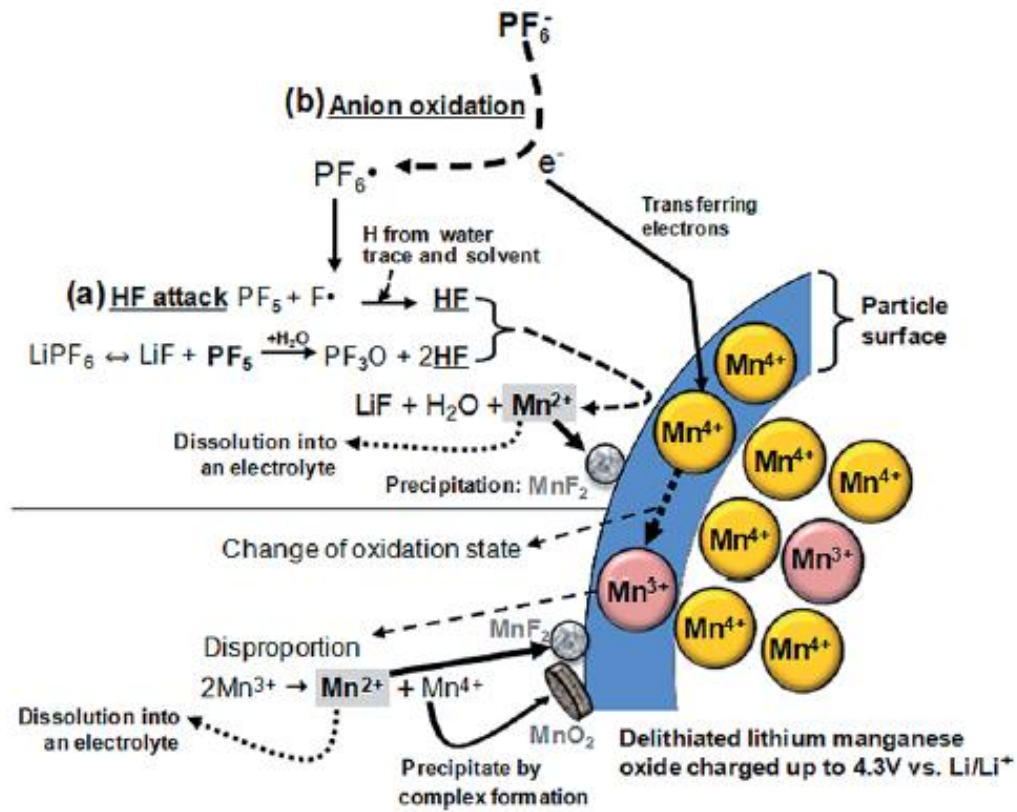


Figure 2.10: Schematic presentation for the manganese dissolution out of a delithiated LiMn_2O_4 cathode (a) by the HF attack, (b) by the PF_6^- anion oxidation [57].

2.5. Modification Strategies

To prevent these constraints, several techniques were examined, including the use of protective coating materials [65, 66, 200, 67], element cation/anion doping [62, 63, 64], and the enhancement of the LiMn_2O_4 (111) surface on morphology [68, 69, 70].

2.5.1. Element Doping

Element doping was first used on spinel LiMn_2O_4 cathode materials more than three decades ago to increase the battery's electrochemical performance [201]. Several features, including (i) phase change control, (ii) structural strengthening, and (iii) Li^+ diffusion booster, were previously proposed for various reasons [202]. Zhang et al [85] summarized the element dopants for LiMn_2O_4 cathode material in a periodic table based on the three substitution causes, see [Figure 2.11](#) below. Low valence (+2 and +3) and high valence (≥ 4) structural strengthening dopants are the most common. Elements with low valence dopants include Al^{3+} [76, 203, 204], Co^{2+} [205], Ni^{2+} [206, 74, 207], Na^+ [208, 209, 73], F^- [210, 75], etc, are the most often used low valence dopants due to their availability, eco-friendliness, and stability. Duan et colleagues [211] found a capacity retention of 93.2% after 150 cycles for $\text{LiMg}_{0.08}\text{Mn}_{1.92}\text{O}_4$, which is a significant increase over the pristine LMO, which had a retention of roughly 87.3% after 40 cycles. Tan et al [212] investigated the creation of porous $\text{LiMn}_{1.9}\text{Al}_{0.1}\text{O}_4$ microspheres with 82% retention after 700 cycles, and a capacity of ~ 121 mAh/g. Various other dopants substantially enhanced and stabilized the structure; nevertheless, Ni demonstrated strong crystallinity and exposed a large number of (111) planes on high-resolution transmission electron microscopy (HRTEM) [213], which greatly inhibited Mn dissolution. The $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ concentration was identified as the most promising and structurally stable Ni-doped LMO concentration [214]. In use, the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ is composed of 135 mAh/g and high voltage of 4.7V against Li/Li^+ [215]. Aside from the excellent structural and

electrochemical performance, the structure has a few limitations caused by the synthesis technique yielding variable Ni/Mn and the operating high voltage, which might impair electrolyte interaction/promote electrolyte breakdown. For its practical uses, much more research and development is required.

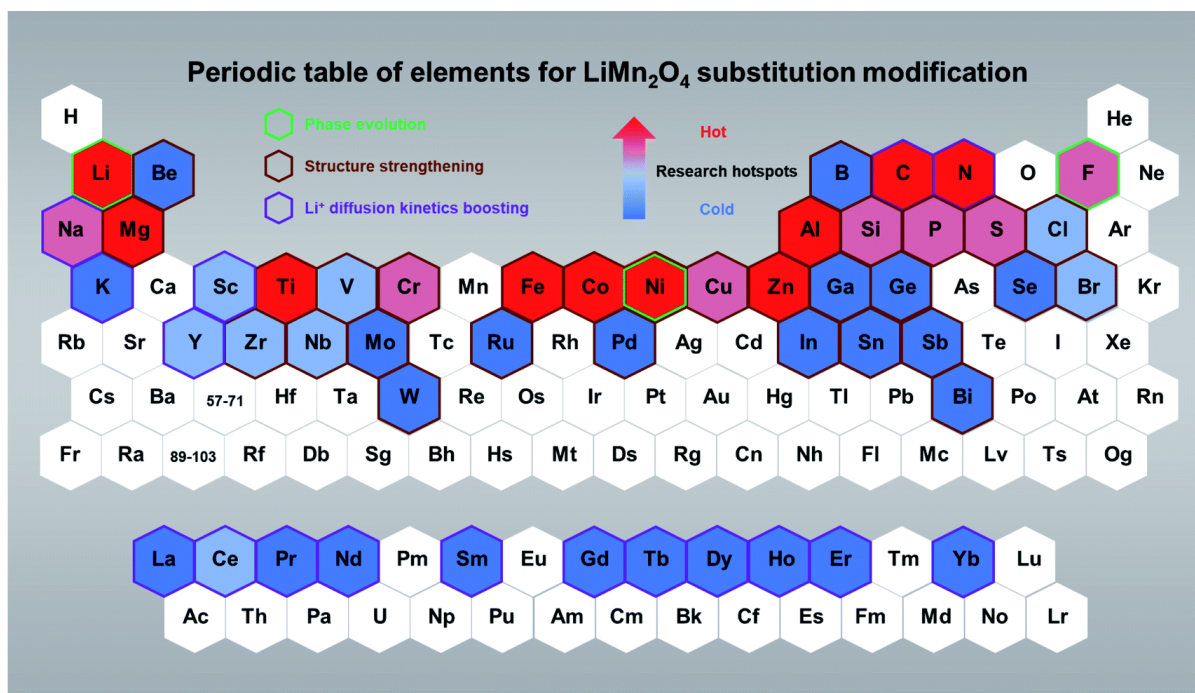


Figure 2.11: Periodic table of elements for LiMn_2O_4 substitution modification [85].

However, the addition of high valence dopants to the $\text{Mn}^{3+/4+}$ prevents capacity loss, and the addition of guest ions improves the stability of LiMn_2O_4 . Ti^{4+} [78], Nb^{5+} [77, 85], Ru^{4+} [216], $\text{Sn}^{4+}/\text{Ge}^{4+}$ [217], and other high-valence dopants for LiMn_2O_4 are examples. The LMO stability of Ti-doped $\text{LiMn}_{1.97}\text{Ti}_{0.03}\text{O}_4$ was much enhanced, with an outstanding rate property and increased cycle performance even at high temperatures. They reported discharge capacity of 125.3 mAh/g, capacity retention per cycle of 0.12 mAh/g with comparison to pristine LMO of 0.35 mAh/g. A modest quantity of $\text{Si}^{4+}/\text{P}^{5+}$ doped LMO resulted in a bigger and more regular octahedral $[\text{MnO}_6]$ compatible with $\text{Mn}^{3+/4+}$ [217, 218]. Another noteworthy structural stabilizer is Nb^{5+} , which has a higher Nb-O bonding energy than Mn-O [79]. Furthermore, the ionic radius of Nb^{5+} is equivalent to that of Mn^{4+} and Li^+ ions, allowing doping on either the

lithium or manganese sites [80]. Li et al [81] reported that doping with low amounts of Nb alters structural volume and lattice without affecting Li^+ transport while investigating the effect of Nb doping on the structure and electrochemical properties of LiMn_2O_4 . They also demonstrated that for different Nb concentrations, the diffraction peaks are entirely spinel, despite the presence of small LiNbO_3 impurities. Li et al [82] later highlighted how Nb doping in spinel LiMn_2O_4 might improve performance and boost capacity while also strengthening crystal development along the (400) and (111) facets. Nb doping, like Cr doping, enhances Li diffusion in Li-Mn-O cathode materials, according to later research [83, 84, 85, 77, 86]. Bulk doping with atoms of varying size/charge, on the other hand, might result in varying amounts of cation order, resulting in changes in capacity and cycle stability [87, 88].

2.5.2. Surface Coating

Surface coating is the introduction of an extra layer on the cathode surface which acts as a protective barrier between the cathode structure and electrolyte components. A coating material should restrict side reactions, operate as a cathode material stabilizer, improve conductivity, avoid phase shift during cycling, and aid in reducing acidity caused by the electrolyte near the cathode material (act as an HF scavenger). Metallic oxides [90, 91], fluorides [98, 99], phosphate [102, 103], and Li-composites [219] have all been investigated as coating materials.

Because of their outstanding mechanical and thermal stability, corrosion resistance, and low electrical conductivity, metal oxides stand out as viable options [107, 108]. The ability to react with the acidic electrolyte medium, hydrofluoric acid (HF), results in the development of an additional coating layer, such as AlF_3 , via the molecular equation $\text{Al}_2\text{O}_{3(s)} + 6\text{HF}_{(aq)} \rightarrow 2\text{AlF}_{3(s)} + 3\text{H}_2\text{O}_{(l)}$, thereby attenuating electrolyte-cathode interactions [109]. Surface modification of LiMn_2O_4 with $\alpha\text{-Al}_2\text{O}_3$, for example, as reported by Kanna and Manthirram [220] and Eftekari [221] provides increased long-term cyclability, structural integrity, crystallinity during cycle,

and capacity retention even at high temperatures. Tu et al [222] used a melting impregnation approach to create a nano-Al₂O₃-coated LiMn₂O₄, resulting in enhanced capacity retention at ambient temperature with a degrading rate of 0.037% per cycle. The Al atoms presence on the surface was verified using X-ray absorption fine structure (XAFS). Ouyang et al [223] used DFT calculations to show that the presence of the Al₂O₃ coating restores the bonding of the undercoordinated octahedral manganese with oxygen on the (001) surface LiMn₂O₄. Notably, as noted by Nisar et al [224], a desirable coating material should have features such as thinness, electrochemical stability, strong ionic and electronic conductivity, cost-effectiveness, and simplicity of synthesis. Sol-gel, chemical vapour deposition, hydrothermal, solvothermal, atomic layer deposition (ALD), and other processes are used to create Al₂O₃ coatings [225, 226, 227, 228]. ALD has developed as a viable technology for Al₂O₃ coating fabrication, allowing for precise thickness and control on the LiMn₂O₄ surface [229, 230, 91]. ALD is a binary process that involves trimethylaluminum (TMA = Al(CH₃)₃) and water vapour, yielding methane (CH₄) as a byproduct via the reaction: $2\text{Al}(\text{CH}_3)_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4$. A few investigations have used ALD to cover LiMn₂O₄ with Al₂O₃. For example, Gaun et al [229] found higher electrochemical performance, indicating that 10 ALD cycles resulted in better cycling than 20 ALD cycles, owing to increased polarization and resistance caused by increased coating thickness. When ALD was deposited over LiMn₂O₄, Waller et al [231] demonstrated an enhanced capacity retention and capability, as well as the production of Al-F bonds during cycling and the presence of Mn in the coating layers. Lai et al [232] obtained similar results for LiMn₂O₄ wrapped with Al₂O₃ nanosheets. Warburton et al [230, 233, 234] have extensively investigated the theoretical aspects of the Al₂O₃ ALD mechanism on LiMn₂O₄ surfaces using DFT calculations to investigate how near-surface manganese oxidation evolves with different Al precursor ligands and the consequences for electrochemical performance [92] in comparison to experimental observations.

Fluorides are thought to have higher electrical and ionic conductivity as well as greater resistance to hydrofluoric acid assaults. Many of them are stable and cannot be oxidized or reduced during cycling. Fluorides can also increase rate performance and cyclability while decreasing charge resistance [235]. Surface coating with AlF_3 , for example, can minimize the breakdown of the electrolyte salt LiPF_6 , restrict HF generation, and reduce Mn dissolution even more. Wu et al [236] found that surface coating with AlF_3 on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ resulted in an increased retention of around 94% after 50 cycles throughout the operating range of 3.5-4.9 V, which was greater than the uncoated spinel's retention of about 78% within the same operating voltage range. After coating with AlF_3 , a slow shift in impedance was observed, which might result in less resistant phases being formed on the surface. When the coating concentration was raised from 1wt% to 3wt% of LiCoO_2 with strong thermal stability, moderately high hardness, and a broad band gap, cycling performance deteriorated [237]. Coating LiCoO_2 with MgF_2 having good thermal stability, relatively high hardness and a wide band gap showed a deterioration of cycling performance when the coating content was increased from 1wt% to 3wt% [238]. This suggests that an excessive MgF_2 coating obstructs Li^+ channels, hence impeding lithium transport. Similarly, excessive ZrF_2 coating might obstruct Li^+ transport, even though it demonstrated a high discharge of 194 mAh/g at 4.8V with 1wt% ZrF_2 content [239].

Because of the strong chemical connection between the PO_4^{3-} and the metal ($\text{M} = \text{La}, \text{Y}, \text{Fe}, \text{Al}$, etc.), phosphates can reduce cathode-electrolyte interactions. Xiao et al [240] investigated the impact of FePO_4 as a coating for the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, finding that it may increase electrochemical performance and operate as a Li-ion reservoir during cycling, allowing for larger capacities when employing $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Furthermore, 1wt% LaPO_4 on $\text{Li}_{1.18}\text{Ni}_{0.15}\text{Mn}_{0.52}\text{Co}_{0.15}\text{O}_2$ demonstrated an enhanced discharge capacity of 272.5mAh/g at 0.4C compared to 248.6 mAh/g at 0.4C for the uncoated material [241]. However, increasing the coating thickness has an impact on electrochemical performance and impedes Li transfer.

Remarks

Lithium-ion batteries since their inception have played part to the development of electronics and currently electric vehicles. Despite their success, much work is still needed considering the current energy demand and depleting natural resources. Improving the cathode material greatly impacts the electronic performance and attaining high energy density. A vast amount cathode material has been considered as mentioned, Li-Mn-based cathode materials are widely considered currently, with the Li-rich Mn-based cathode materials having a superior highest energy density which exceed 250 mAh/g. LiMn_2O_4 spinel cathode has most advantages such as affordability, abundance, and thermal stability of the fully delithiated MnO_2 framework. Several limitations such as Jahn-Teller distortion and manganese dissolution limits its practical applications. Hence, strategies were introduced to reduce these limitations which stem from the electrolyte-cathode interactions. Noting the reactivity of the electrolyte towards the surface LiMn_2O_4 , it's important to zoom in their individual interactions and explore the effect of surface modifications (surface coating and doping) and electrolyte interactions on the morphologies, and surface stabilities.

CHAPTER 3

3. METHODOLOGY

This chapter gives a thorough discussion of the methodology used within this work. It goes over the essential concepts, equations, and expressions that form the basis of the characteristics covered in this work. This method is used to forecast real-world scenarios in solid-state physics, chemistry, and materials science by presenting physical systems as models of other systems. This approach, rather than trial and error, is commonly utilized to investigate and comprehend materials in their purest forms and after numerous alterations. Materials are often defined based on current data and the behaviour of their purest form. Most of this characterization is often undertaken experimentally, however, some data might not be accessible by experiments, thus theoretical modelling methods are used to further explain. As a result, this chapter covers the fundamentals of the time-independent nonrelativistic Schrödinger equation, which is used to explain many-body systems in a static nucleus. It also discusses the density functional theory's Hohenberg-Kohn theorems and Kohn-Sham equations, as well as the two approximations. It also specifies the number of electrons to be included in a periodic solids and atoms model using pseudopotentials and plane-wave basis sets. Finally, it covers how geometry optimization is performed, as well as a review of the features investigated, such as the Bader charge, vibrational frequencies, and so on.

3.1. Many-Body Schrödinger Equation

The primary difference between materials is their electrical activity, which is classified into ground and excited states. Ground state parameters regulate elastic constants, equilibrium crystal structures, and phase transitions, whereas excited state properties govern optical, thermal, and other excitations. As a result, to adequately explain the electrical structure, we must use quantum and statistical approaches. The Hamiltonian is the initial description of a system of electrons and nuclei [242]:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{|\vec{r}_i - \vec{R}_A|} + \sum_{i \neq j} \frac{e^2}{2|\vec{r}_i - \vec{r}_j|} - \sum_A \frac{\hbar^2 \nabla_A^2}{2M_A} + \sum_{A \neq B} \frac{Z_A Z_B e^2}{|\vec{R}_A - \vec{R}_B|} \quad (3.1)$$

where Z and M represent the nuclear charge and mass, respectively. Electronic and nuclear coordinates are $\vec{r}$, and $\vec{R}$, while the $\hbar$ and m are the Plank's constant and electronic mass, respectively. The lower and upper case denote the electrons and nuclei, respectively. Furthermore, the differential operator is $\nabla = \vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z}$. The terms in [equation 3.1](#) represent the kinetic energy of the electrons ($\hat{T}$), the kinetic energy of the nuclei, coulomb electron-electron repulsion ($\hat{V}_{\text{int}}$), the coulomb electron-nuclei repulsion ($\hat{V}_{\text{ext}}$) and classical nuclei-nuclei interaction (E_{II}), respectively. The nucleus kinetic energy factor, on the other hand, can be discarded because it is the inverse of the nucleus mass, and if the mass is set to infinity, the term becomes irrelevant. The Born-Oppenheimer approach [243] simplifies the Schrödinger equation by separating electronic and nuclear coordinates in the many-body wavefunction by ignoring nuclei kinetic energy and assuming nuclei repulsion to be constant. As a result, a simplified version of [equation 3.1](#) that represents electron mobility in static nuclei may be stated as:

$$\hat{H} = \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{ext}} + E_{\text{II}} \quad (3.2)$$

As a result, the time-independent Schrödinger equation for a non-relativistic quantum system is as follows:

$$E\psi(\{\vec{r}_i\}) = \hat{H}\psi(\{\vec{r}_i\}) \quad (3.3)$$

where E is the total energy, $\hat{H}$ Hamiltonian discussed above, and the $3N$ dimensional many-body wave function $\psi(\{\vec{r}_i\}) = \psi(\vec{r}_1, \dots, \vec{r}_N)$ for the electronic system considered. However, the precise solution to Schrödinger [equation 3.3](#) above is only for atoms of any size and a single electron, such as hydrogen, but further simplifications are required for systems with numerous atoms/electrons. This resulted in the creation of non-interacting Hartree-Fock (H-F) and independent electron approximation approaches. The approximations presume that the electrons in the system do not interact, but they do adhere to Pauli's exclusion principle, which states that no two or more electrons from the same atom may occupy the same electronic state. In the energy expression, H-F describes electron-electron Coulomb interactions but ignores electron correlation in the wave functions, resulting in substantial departures from experimental evidence. The non-interacting, on the other hand, has an effective potential that includes real interactions, but Hamiltonian does not include an explicit interaction term. The H-F method minimizes the total energy expression while taking into account all degrees of freedom in the wave function, with the caveat that it has an asymmetric shape (slater determinants). Although some refinements have been developed for the HF method to improve the difference of energies, the density functional theory (DFT) method is the one that is usually preferred in the context of solid-state modelling.

3.2. Density Functional Theory (DFT)

The Hohenberg-Kohn (H-K) theorems [244] and Kohn-Sham (K-S) equations [245] served as the foundation for the widely utilized density functional theory (DFT) technique. In 1964,

Hohenberg and Kohn offered two hypotheses for explaining the many-electron wave function of $3N$ variables as electron density [246]. The very first theorem states that:

“The external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particles ground state is a unique functional of $\rho(\vec{r})$ ”.

This theorem denotes that for a given system with interacting particles, the ground state density uniquely determines the external potential ($V_{ext}(\vec{r})$). The $V_{ext}(\vec{r})$ uniquely determines the many-body wave function once the ground state density $\rho(\vec{r})$ has been evaluated. The second theorem reads as follows:

“A universal functional for the energy $E[n(r)]$ in terms of the density $n(r)$ can be defined valid for any external potential $V_{ext}(\vec{r})$, and for any particular $V_{ext}(\vec{r})$ the ground state energy of the system is the global minimum value of this functional, and the density $n(r)$ that minimizes the functional is the exact ground state density $n_0(r)$ ”.

According to the second theorem, the ground state density uniquely determines the total energy of the system. The second H-K theorem energy functional is as follows:

$$E[n(r)] = \int V_{ext}(r)n(r)dr + F[n(r)] \quad (3.4)$$

where $F[n(r)]$ is the electronic part of the Hamiltonian comprised of the kinetic energy $T[n(r)]$ of the electrons and the electron-electron interactions V_{e-e} term. The $F[n(r)]$ is thus defined as:

$$F[n(r)] = \langle \psi | n | T + V_{e-e} | \psi | n \rangle \quad (3.5)$$

Even though the two theorems justify the problem of reducing the $3N$ dimensional into the ground state electronic density, they offer no way of computing $F[n(r)]$. Hence, no practical way of determining the ground state energy of the system.

Kohn and Sham, in 1965 came up with a way to reformulate the energy functional (third term noted in [equation 3.4](#)) to find an analytical solution for it. They initiated by separating the $F[n(r)]$ into three terms:

$$F[n(r)] = T[n(r)] + E_H[n(r)] + E_{xc}[n(r)] \quad (3.6)$$

The first term, $T[n(r)]$, being the kinetic energy functional for the imaginary system of non-interacting electrons giving the same density as $n(r)$, represented as:

$$T[n(r)] = \frac{1}{2} \sum_{i=1}^N \int \psi_i^*(r) \nabla^2 \psi_i(r) dr \quad (3.7)$$

The second term, $E_H[n(r)]$, represents the Hartree energy, which classically arises from the mutual coulomb repulsion of all electrons.

$$E_H[n(r)] = \frac{1}{2} \iint \frac{n(r)n(r')}{|r - r'|} dr dr' \quad (3.8)$$

The third term, $E_{xc}[n(r)]$, is the exchange-correlation functional which is a correction term that accounts for the many-body effect in $F[n(r)]$. The correctional term $E_{xc}[n(r)]$ is unknown, hence it is approximated.

3.2.1. Exchange Correlation Functions: LDA and GGA

Exchange correlation the energy contribution from the quantum effect that is not part of the coulomb repulsion, and the kinetic energy of a single particle is described by $E_{xc}[n(r)]$. Because the term is uncertain, approximations are used in the actual use of DFT. Local density approximation (LDA), generalized gradient approximation (GGA), and hybrid functionals are examples of such approximations.

2.5.2.1. Local density approximation (LDA)

Local density approximation is an exchange-correlation functional that employs the electron density $n(r)$ at each spatial point r . The exchange-correlation energy density is assumed to be the same as that of a homogeneous electron plasma. The exchange-correlation energy of LDA is computed as follows:

$$E_{xc}^{LDA} = \int n(r) \varepsilon_{xc}^{LDA} n(r) dr \quad (3.9)$$

where ε_{xc}^{LDA} is the exchange-correlation energy per particle of a uniform electron gas. For a homogeneous electron gas, the exchange-correlation energy can be represented as:

$$\varepsilon_{xc}^{LDA} = \frac{-e^2}{4\pi\epsilon} \left(\frac{3n}{\pi} \right)^{\frac{1}{3}} \quad (3.10)$$

The most common LDA approximation developed by fitting the results from a Quantum Monte Carlo calculation [247] to a mathematical expression [248] is the Vosko, Wilk and Nusair (VWN) functional. Other useful functionals are the Perdew-Zunger (PZ) [249], and Perdew-Wang (PW) [250]. This approximation applies to systems with a slow or moderate density

change over the space, such as metals. Perdew-Zunger (PZ) [249], and Perdew-Wang (PW) [250] are two others relevant functionals. This approximation applies to systems such as metals that have a modest or moderate density change across space.

2.5.2.2. Generalized gradient approximation (GGA)

In contrast to the LDA, the generalized gradient approximation (GGA) includes the gradient density ($|\nabla n(r)|$) as an independent variable in the approximation. The GGA is represented by:

$$E_{xc}^{LDA} = \int n(r) \epsilon_{xc}^{GGA}(n, |\nabla n(r)|) dr \quad (3.11)$$

The gradient density incorporates non-locality into the exchange-correlation description, which enhances functional performance by accounting for fast-changing variations in electron density that are not adequately characterized in LDA. Perdew-Wang 86(PW86) [251], Lee-Yang-Parr (LYP) [252], Perdew-Wang 91 (PW91) [253], Perdew-Burke-Enzerhof (PBE) [254], and revised Perdew-Burke-Enzerhof (RPBE) [255] are some of the existing GGA functionals. The computations in this thesis are performed using the PBE functional, which accurately represents the local spin density of atoms, molecules, and solids.

3.2.2. Hybrid Functionals

In systems with a tiny gap and structural features linked to the band gap, the usual LDA and GGA approximations underestimate the band gap. To address this, hybrid functionals were developed that integrate a component of the nonlocal exact exchange element from Hartree-fork theory while also offering some degree of self-interaction cancellation because the HF and the classical Coulombic interaction term have opposite signs. Such a functional often predicts

a bigger band gap than a regular DFT. The Becke, 3-parameter, Lee-Yang-Parr (B3LYP) functional [256] is the most prevalent hybrid functional.

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + E_c^{LDA} + a_c(E_c^{GGA} - E_c^{LDA}) \quad (3.12)$$

where $a_0 = 0.02$, $a_x = 0.72$ and $a_c = 0.81$, while the E_x^{LDA} , E_{xc}^{B3LYP} are the generalized gradient approximations {Becke 88 exchange functional [257], and correction functional of Lee, Yang and Parr (1988) [252] for B3LYP} and the E_c^{LDA} is the VWN local-density approximation.

3.3. Pseudopotentials and Basis Sets

The Plane-wave pseudopotential is a method for accurately calculating the variation of a self-consistent solution. Its developments and improvements allow it to anticipate the static and dynamic characteristics of crystalline solids and molecules [258]. The plane-wave pseudopotential approach is concerned with the weak pseudopotential and computes geometry optimization, namely the relaxation of internal parameters. It can also imitate metal, insulator, and semiconductor electrical ground states.

3.3.1. Basis Sets

The plane-wave approach, as described above, is more dependable and powerful for calculating material characteristics. It was created for periodic solids and was used to investigate the supercell technique for atoms and surfaces. Bloch's theorem asserts that the eigenstates of a one-electron Hamiltonian $H = -\frac{\hbar^2 \nabla^2}{2m} + V(r)$, where $V(r + T) = V(r)$ for all Bravais lattice translation vectors T can be selected to be a plane wave times a function with Bravais lattice periodicity. The electronic wave functions may be extended in terms of a discrete collection of plane waves using this theorem:

$$\psi_i = e^{ikr} F_i(r) \quad (3.13)$$

where $F_i(r)$ is the cell periodic term, described as:

$$F_i(r) = \sum_{\vec{G}} C_{i,G} e^{iGr} \quad (3.14)$$

where G is the reciprocal lattice vectors of the periodic cell. Each distinct electronic wavefunction $\psi_{k_i(r)}$ can be written as:

$$\psi_{k_i(r)} = \sum_{\vec{G}} C_{i,K+G} e^{-[i(K+G).r]} \quad (3.15)$$

where $C_{i,K+G}$ is the plane wave coefficient and it is fully dependent on the particular kinetic energy, $\left(\frac{\hbar^2}{2m}\right) |K + G_c|^2$ and plane waves with high kinetic energy are less relevant than plane waves with low kinetic energy. In order of finite basis set, the cut-off energy may be determined as follows:

$$E_{cut} > \frac{\hbar^2}{2m} |K + G_c|^2 \quad (3.16)$$

The size of the cut-off is increased until its total energy converges to the desired precision [259]. An increase in the number of plane waves, on the other hand, can express more quickly altering properties of an endlessly large number of basis sets. In a nutshell, the finite basis set is generated by introducing the finite cut-off energy to the discrete plane-wave basis set. Although this may result in computational mistakes, the cut-off energy should be increased

until it fully converges. A denser collection of k -points should also be used to decrease mistakes and ensure good convergence.

3.3.2. Pseudopotentials

The pseudopotential is a theory that seeks to make calculating energy density easier. The theory is built in such a way that the pseudo wavefunction has no radical nodes within the core areas and that the pseudo and potential agree well outside of some cut-off radius E_{cut} . Furthermore, the pseudopotential should retain the element's characteristics, including phase changes on scattering across the core, which will usually depend on the angular momentum. Due to the low reactivity of the core electrons, this theory replaces the Coulomb potential of the core electrons and nucleus with a potential operating on the valence electrons. The wavefunctions of the core electrons centred around the nucleus barely overlap with the wavefunctions of the nearby atoms' core electrons. As a result of the high Coulomb potential, the core wavefunctions fluctuate rapidly in the core area of an atom. The distribution of the core electrons is the same regardless of the atom's chemical surroundings. This is advantageous since the electrons must be addressed and fewer Kohn-Sham eigenstates must be determined. The lack of the core electrons in the computations, on the other hand, greatly reduces the overall energy, making energy difference estimates across atomic structures considerably more numerically stable. The introduction of pseudopotential approximation is an effort to restrict the very intricate effects of the core electrons in motion and their nucleus with the effective potential [260, 261]. The properties of the pseudopotential are further shown in [Figure 3.1](#)'s schematic illustration. Because of the high ionic potential, the valence wavefunctions fluctuate rapidly in the area inhabited by the core electrons. As a result of these oscillations, the orthogonality between the valence and core electrons is preserved. The pseudopotential should be non-local in general,

with no projectors for various angular momentum states. The general definition of the pseudopotential is as follows:

$$V_{ions} = \sum |lm\rangle V_l \langle lm| \quad (3.17)$$

where $|lm\rangle$ are the spherical harmonics and V_l is the pseudopotential for angular momentum.

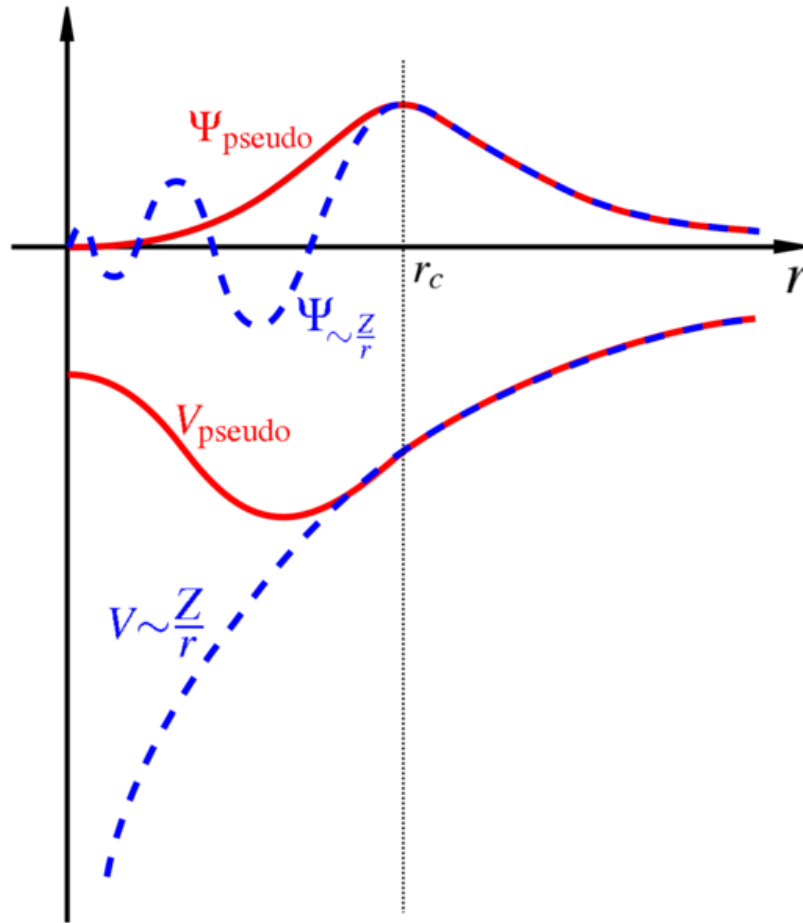


Figure 3.1: Schematic diagram for the illustration of an atomic all-electron wavefunction and the corresponding atomic pseudo wavefunction [258].

3.3.3. Projector Augmented Wave (PAW) method

In various areas of space, the wavefunction of materials has quite diverse characteristics. The wavefunction is smooth in the bonding area, but it oscillates fast near the nucleus due to the nucleus's high attractive potential. This is the disadvantage of using the electronic structure technique to accurately describe the bonding area while allowing for substantial differences in the atom centre. The augmented-wave approach was developed to partition the wave function into two parts: partial-wave expansions within atom-centered spheres and the envelope function beyond the spheres. The partial-wave expansions and the envelope function are linked by a term and derivative at the radius of the sphere. The projected augmented wave (PAW) method combines the linear augmented plane-wave (LAPW) method with the standard plane-wave approach's formal simplicity [262]. Its wavefunction is as follows:

$$\psi(r) = \tilde{\psi}(r) + \sum_{\Lambda} [\phi_{\Lambda}(r) - \tilde{\phi}_{\Lambda}(r)] \langle \tilde{p}_{\Lambda} | \tilde{\psi} \rangle \quad (3.18)$$

where $|\psi\rangle$ and $|\tilde{\psi}\rangle$ are the wavefunction and pseudo-wavefunction, respectively, $|\phi_{\Lambda}\rangle$ and $|\tilde{\phi}_{\Lambda}\rangle$ are the one-electron Schrodinger equations for isolated atoms and the pseudo partial wave, and $\tilde{p}_{\Lambda}$ are the projector functions. $|\psi\rangle$ behaves like an atom within an atom-centered sphere (augmentation area) and outside envelope function (interstitial region) in this formulation (see [equation 3.18](#)). $|\tilde{\psi}\rangle$ is cancelled out inside the augmented region by the growth of $|\tilde{\phi}_{\Lambda}\rangle$, which is in such a manner that it equals $|\phi_{\Lambda}\rangle$ interstitial regions. While the core electrons are assumed fixed in an atomic solution, the whole all-electron wavefunction is employed, and it relies on the full charge and spin density, such as the hyperfine [263].

3.4. Geometry Optimizations

Before any calculations, geometry optimization is performed, which is the relaxing of atomic locations and cell parameters. This technique seeks not just the structural minimum, but also the inter-nuclear Coulomb energy. [Figure 3.2](#) depicts the profile depiction of the local and global minima separated by the transitional stage. One of the most difficult problems in condensed matter physics is determining the lowest energy path for atom rearrangements from one stable configuration to the other. The activation energy (E_a) is computed as the total energy difference between the starting state and the saddle point. The activation energy (ΔE) of a reaction may alternatively be computed as the difference in energy between the end and beginning states.

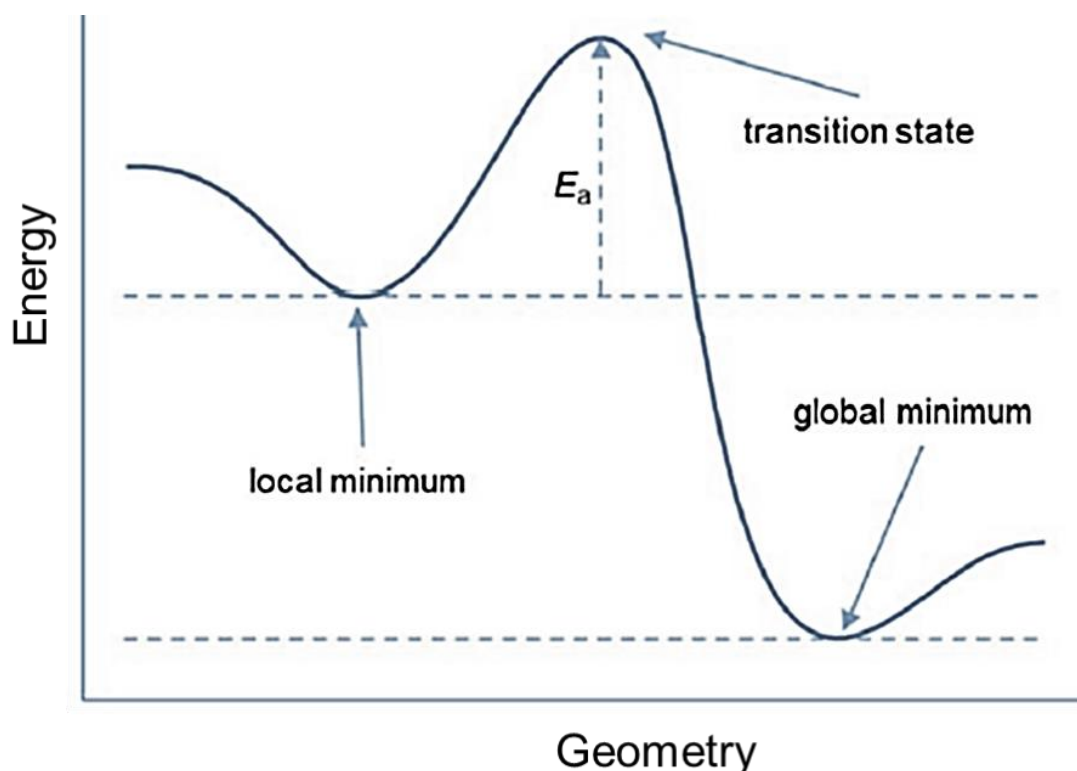


Figure 3.2: Representation of Local and global minima with the transition state [264].

3.5. Electronic Structure Analysis

3.5.1. Electronic Density of States (DOS)

The density of states (DOS) represents the number of states in specified energy. It explains in detail how chemical bonds are formed and how molecules interact with solid surfaces. Each k -point within the Brillouin zone defines energy levels that generate energy bands that may be depicted using a band diagram plot. The greater the DOS at an energy level, the more states are accessible for occupancy, whereas zero DOS implies that no states may be inhabited at that energy level. The Fermi level (E_F) is the energy level within the material's DOS that is particularly valuable for defining the material's electrical behaviour. In an insulator, E_F exists within a wide bandgap, far from any current-carrying states. In doped semiconductors, E_F is close enough to a band edge that there are a small number of thermally excited carriers present. E_F exists in a delocalized band in a metal or semimetal. The DOS can also be expressed as the volume that each ion occupies in each system. It may also be represented using the s , p , and d bands, which allows for the interpretation of the relative energies of distinct bands and their interactions in bonds.

3.5.2. Bader Charge Analysis

The determination of a material's charge can provide information about the bonding of the contributing atoms. Charge analysis can characterize the nature of the link between the interacting atoms based on the adsorbed systems. When the charge transfer between the contacting atoms is modest or insignificant, covalent bonds are formed, and this interaction is known as physisorption. There are several approaches for charge transfer analysis that provide varied findings [265]. We employ Bader charge analysis [266] in this study, which is implemented in the VASP code using the Henkelman technique [267]. The Bader technique is used to calculate the surface zero flux in the charge density surrounding an atom. The volume

encompassed by the surface is known as the Bader basin, and the electron densities inside are added to determine the atom's Bader charge. The Bader analysis underestimates the ionic charges due to DFT delocalization. Aside from DFT delocalization, the Bader is reliable in finding patterns in related systems.

3.5.3. Vibrational Frequencies

The force constant, which is the second derivative of the total energy affecting the displacements, is connected to vibrational frequencies. The approach entails calculating vibrational frequencies from the second derivatives of potential energy with respect to atomic locations that have been altered by tiny displacements to guarantee they lie inside the harmonic section of the potential well. They are required for a variety of reasons, including locating the steady state on the hypersurface and ensuring that the stationary optimum point is at the bottom of the potential energy surface. It is also possible to link it to the infrared (IR) or Raman spectra and compare it to experimental data. The vibrational frequencies (ω) are calculated from the eigenvalues of the Born-Oppenheimer energy Hessian, which is scaled by nuclear masses:

$$\det \left| \frac{1}{\sqrt{M_I M_J}} * \frac{\partial^2 E(R)}{\partial R_I \partial R_J} - \omega^2 \right| = 0 \quad (3.23)$$

If all of the second derivatives are positive and imaginary frequencies are detected, the stationary point can be designated as a saddle point. The finite difference method is used to calculate the Hessian matrix, which is specified by the equation:

$$H(f) = \begin{bmatrix} \frac{\partial^2 f}{\partial r_1^2} & \frac{\partial^2 f}{\partial r_1 \partial r_2} \cdots & \frac{\partial^2 f}{\partial r_1 \partial r_n} \\ \frac{\partial^2 f}{\partial r_2 \partial r_1} & \frac{\partial^2 f}{\partial r_2^2} \cdots & \frac{\partial^2 f}{\partial r_2 \partial r_n} \\ \frac{\partial^2 f}{\partial r_n \partial r_1} & \frac{\partial^2 f}{\partial r_n \partial r_2} \cdots & \frac{\partial^2 f}{\partial r_n \partial r_n} \end{bmatrix} \quad (3.24)$$

3.5.4. Scanning Tunnelling Microscopy (STM)

Scanning Tunnelling Microscopy (STM) is a technique which has been used for almost for four decades to offer insights into matter at the atomic level, allowing researchers to map the surface of a sample atom by atom with ultra-high resolution without the use of electron beams or light. Gerd Binnig and Heinrich Rohrer, two IBM scientists, invented STM in 1981 and five years later earned them a Nobel Prize in Physics [268]. STM operates by scanning a sharp conductive probe extremely close to the surface (less than 1nm) of a conducting material and causing electrons to pass through the space between them. When the tip gets close enough to the surface, the electron cloud of the tip's first atom and the surface begin to overlap. When a bias voltage is applied between the tip and the surface, electrons are induced to tunnel through the potential barrier from the tip to the surface via the overlapping electron cloud, resulting in a current. This tunnelling current is extremely sensitive to the gap between the probe tip and the surface, and it varies exponentially with the tip-sample distance. The intensity of the tunnelling current maps the sample's electrical density of states as the tip scans line by line across the sample's surface (see [Figure 3.3](#) below). Computationally, the STM pictures are obtained from a spatial dispersion of the valence band state around the surfaces' Fermi level. They are calculated using the Tersoff-Hamann approach's fundamental formulation [269], in which the tip of the STM is approximated to an infinitely tiny point source. For the creation of our

constant height STM topographic pictures, we employed the software HIVE [270], where the partial charge density was integrated in certain ranges.

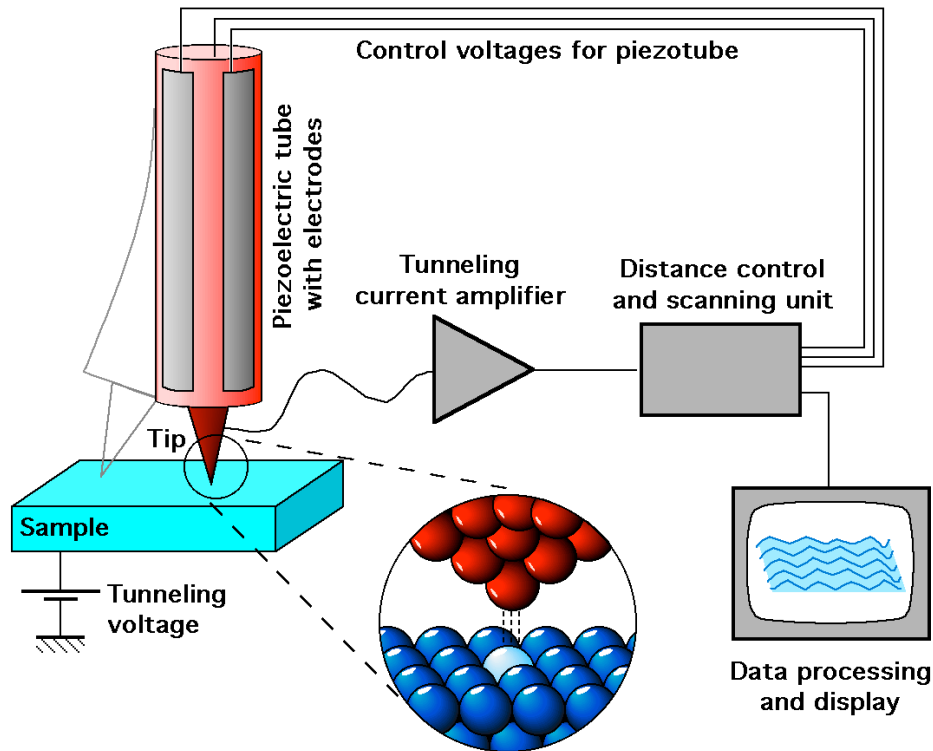


Figure 3.3: Schematic diagram showing the basic components of the scanning tunnelling microscopy (STM) [271].

3.6. Surface Modelling

3.6.1. Surface Model

Surfaces can be created by cleaving a bulk along distinct crystallographic planes known as Miller indices, which are lattice planes specified by three numbers known as h , k , and l (See [Figure 3.3a](#)). Based on the reciprocal lattice vectors, each index indicates a plane orthogonal to the direction and is denoted as (h, k, l) . Miller indices (001) denote a plane orthogonal to the l direction, whereas (011) represents a plane orthogonal to both the k and l directions. Some index planes can be orthogonal to the negative h , k , and l axes. (001) represents a plane

orthogonal to the negative l direction, for example. Atoms at simulated surfaces frequently show low coordination as compared to those in the bulk. Because of the existence of dangling bonds and changes in surface atom coordination, the surface geometry will relax or maybe rebuild to allow the atoms to find their equilibrium locations. There are two popular models in surface construction: the periodic model and the cluster model. The periodic slab model generates exposed surfaces with a vacuum on either side of the slab, whereas the cluster model treats the surface as a small, isolated cluster of atoms, with one of the resulting facets having the same symmetry and atomic arrangement as the crystal being studied. Most importantly when using the periodic slabs, the vacuum thickness should be large enough to avoid surface consecutive slabs from interacting with each other, and the thickness should be thick enough to avoid interactions of surfaces of one slab. The slabs in this work are modelled from a completely optimized virgin bulk. As seen in [Figure 3.3](#), the lowest atoms were frozen to simulate the bulk, while the highest atomic layers were relaxed. The slabs without fixed atomic layers were labelled as unrelaxed surfaces, whereas those having top atomic layers that might relax were labelled as relaxed surfaces.

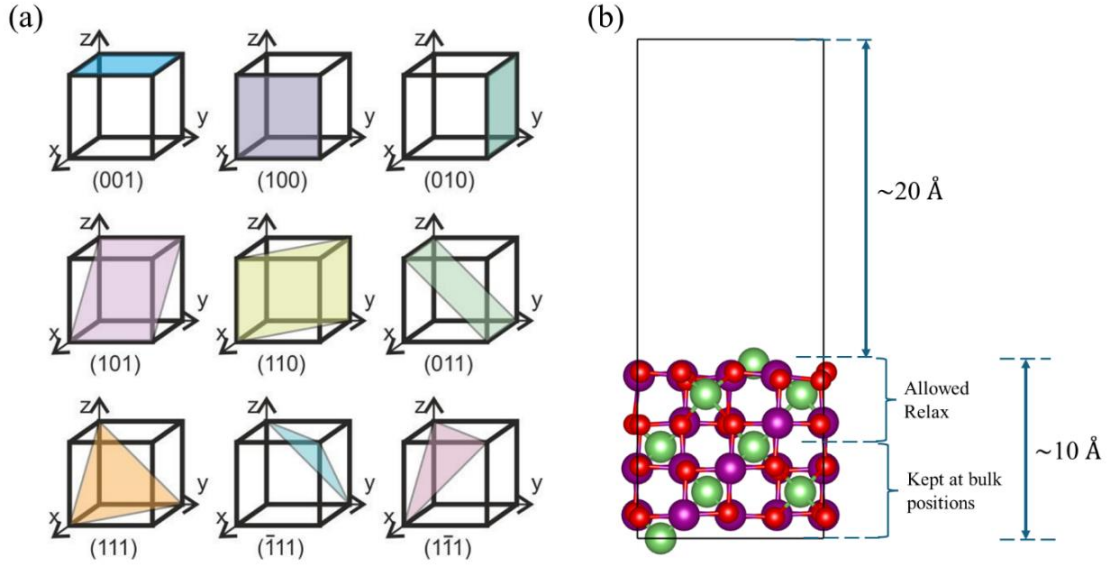


Figure 3.4: (a) Miller indices and how they are represented from a bulk structure [272]. (b) LiMn₂O₄ (001) surface showing a vacuum slab of approximately 20 Å and a slab thickness of ~10 Å. Additionally, (b) it shows the uppermost layers allowed to relax and the bottommost kept at bulk positions.

3.6.2. Surface Stabilities

The reactivity of the surface is influenced by its stability. The lower the surface stability, the more adsorbing species are attracted to it. For the relaxed and unrelaxed slabs, the surface energy of the simulated facets was computed. Static computations yielded the following unrelaxed surface energies (γ^{un}):

$$\gamma^{un} = \frac{E_{u,slab}^{DFT} - E_{bulk}^{DFT}}{2A_{slab}} \quad (3.19)$$

where $E_{u,slab}^{DFT}$ is the total energy of an unrelaxed slab, E_{bulk}^{DFT} is the total energy of the bulk with the same number of formula units as the slab and A is the surface area of the slab. The relaxed surface energies (γ^{rel}) were also calculated for the spinel following geometry optimization of

half of the slab, where the two bottommost layers were kept fixed at their relaxed bulk positions while the top layers were allowed to relax as shown in [Figure 3.3b](#) below. Hence, the relaxed surface energy is then calculated as:

$$\gamma^{rel} = \frac{E_{rel,slab}^{DFT} - E_{bulk}^{DFT}}{A_{slab}} - \gamma^{un} \quad (3.20)$$

$E_{rel,slab}^{DFT}$ denotes the total energy of the half-relaxed surface. For each surface, the degree of relaxation (R) was computed as follows:

$$R = \frac{\gamma_u - \gamma_r}{\gamma_u} \times 100 \quad (3.21)$$

The surface free energy of a particular plane is a measure of its stability, with the most stable surface having the lowest positive value.

3.6.3. Adsorption Energies

When studying the surface reactivity of materials, the adsorption of molecules on the surfaces of solids is an intriguing and useful phenomenon. Atoms and molecules interact with surfaces via forces derived from either “physical” Van der Waals interactions or “chemical” hybridization of their orbitals with those of the substrate’s atoms. We refer to physisorption or chemisorption depending on whose contribution predominates. These are limiting instances because hybridization occurs at all adsorption distances, even for adsorbed rare gases. The Van der Waals interactions between the adsorbate and the substrate, as well as between the adsorbed molecules, indicate physisorption. The binding energy varies depending on the number of atoms involved and ranges from a few meV (light gases) to a few eV (big organic compounds). The geometrical structure and electronic properties of the physisorbed molecule or atom, as

well as the surface, are virtually retained. After a given amount of time, a physisorbed molecule can depart the surface on its own. Chemisorption, on the other hand, happens when a chemical (typically covalent) connection forms between the adsorbate and the substrate. Binding energies of many eV are common. In comparison to physisorption, the geometrical structure and electronic properties of the chemisorbed molecule or atom are significantly altered. When molecules or atoms adsorb on a surface, the formed bond with the surface releases energy. Binding or adsorption energy (E_{ads}) is the entire energy of this formation. E_{ads} is determined by the coverage and distribution of adsorbates at the surfaces. The adsorption energy of a molecule adsorbed on a particular surface is computed as follows:

$$E_{\text{ads}} = E_{(\text{mol}+\text{slab})}^{\text{DFT}} - (E_{\text{mol}}^{\text{DFT}} + E_{\text{slab}}^{\text{DFT}}) \quad (3.22)$$

where $E_{\text{sys}(\text{mol}+\text{surf})}$ represents the total energy of the surface with the molecule adsorbed, E_{mol} represents the total energy of the isolated molecule, and E_{surf} represents the total energy of the pristine surface. A positive E_{ads} value denotes an endothermic and unfavourable adsorption process, whereas a negative number denotes an exothermic and favourable adsorption process.

3.6.4. Wulff Crystal Morphologies

The Wulff architecture for particle morphologies was inspired by J.W. Gibbs' classic study on heterogeneous substances [273]. He determined that a given amount of substance will have a form with a minimum total surface energy. This implies that the form of a crystalline solid will be a polyhedron with faces parallel to the hkl plane. Thus, facets with low surface energy will dominate surface morphologies. G Wulff [274] proposed decades later that the polyhedral form that corresponds to the lowest surface energy for a crystalline material can be as follows: A constant c and a Cartesian set of axes are chosen. Starting at the origin, O , draw a plane that is

normal to the $[hkl]$ vector and has a distance from O of $d_{hkl} = c \cdot \gamma_{hkl}$. Laue proposed the first proof of Wulff construction in 1943, which was later updated and discussed in detail [275]. It was also said that the polyhedral built utilizing the Wulff constructions: (i) is determined only by surface tension ratios rather than absolute values. (ii) Contains certain facets with a high Miller index, as they have a higher surface tension than low Miller index surfaces in most circumstances. (iii) Does not take edge- and vertex-energies into account, and (iv) has the same symmetry as the bulk structure. According to Wulff's theorem, the crystal in equilibrium has the height of the facet (h_i) directly proportional to its specific surface free energy (σ_i , where i = Miller index of the specific surface) and the ratio of the two is constant. These can be summarized by the expression:

$$\frac{\sigma_{(001)}}{h_{(001)}} = \frac{\sigma_{(011)}}{h_{(011)}} = \dots = \frac{\sigma_i}{h_i} \quad (3.23)$$

3.6.5. Work Function.

The work function is the amount of energy necessary to transfer one electron from a surface crystal to the vacuum. It can be used most essential crystal solid surface characteristic for understanding their physical, structural, and chemical reactivity [276]. Computationally, the work function (ϕ) for a specific solid material is calculated as the difference of the surface electrostatic potential energy (E_{vac}) and the Fermi level (E_{F}), through:

$$\phi = E_{\text{vac}} - E_{\text{F}} \quad (3.24)$$

[Figure 3.5](#) shows a schematic illustration of light shined on the surface, which ignites the release of an electron. The work function is calculated using the supercell technique in computational simulation. The vacuum zone chosen must be big enough to allow the

electrostatic potential to relax to its true vacuum level. Electrostatic potential and long-range image contribution therefore define the vacuum electron work function.

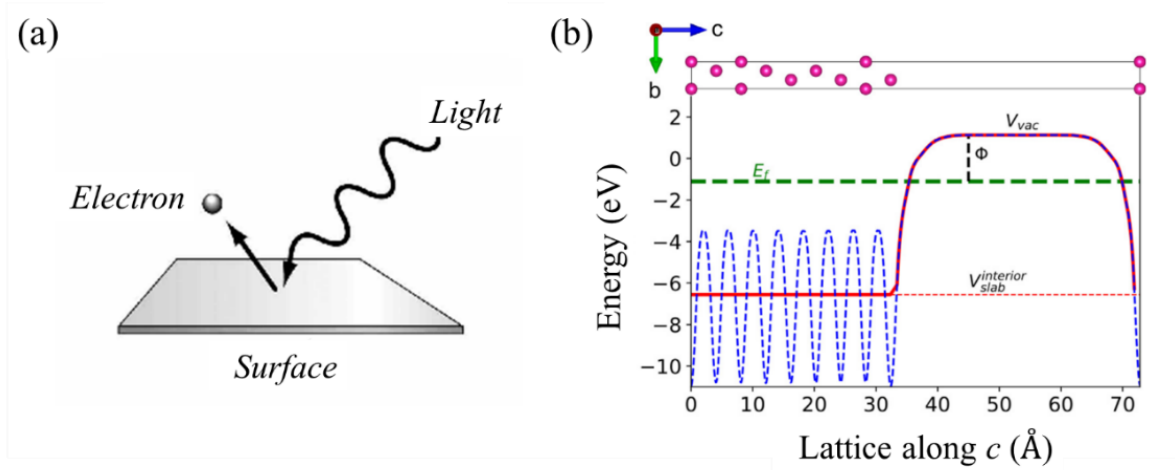


Figure 3.5: (a) A schematic illustration of a work function. (b) The electrostatic potential is depicted schematically, along with the slab model (where E_F , V_{vac} , $V_{slab}^{interior}$ and ϕ is Fermi energy, vacuum electrostatic potential, slab average electrostatic potential, and work function, respectively) [277].

Summary

In our work, the density functional theory (DFT) calculations were performed to obtain the bulk, surface and interface properties using the Vienna Ab-initio Simulation Package (VASP) [310]. The generalized gradient approximation (GGA) exchange correlation was used with the Perdew-Burke-Ernzerhof (PBE) [254] functional. The projector augmented wave (PAW) approach [312] in Kresse and Joubert's [313] implementation was used to describe the core electrons and their interactions. For the long-range dispersion correction, the Grimme semi-empirical approach with the Becke-Johnson damping [D3-(BJ)] [314, 315] was used. For the materials with localized 3d electrons, we have introduced a Hubbard correction [356] based on the formulation of Dudarev and co-workers [357]. The conjugate-gradient approach was used to accomplish geometry convergence, and the convergence condition was reached when the Hellmann-Feynman forces decreased below 0.01 eV/Å.

CHAPTER 4

4. Structural and Electronic Properties of Pristine LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$

This chapter describes the preliminary work performed for the pristine bulk structures of the cathode material LiMn_2O_4 , as well as the coating material $\alpha\text{-Al}_2\text{O}_3$. The convergence of both bulk structures, *i.e.*, the cut-off energy and k -point computations for both materials, is discussed. We then examine the bulk structure's equilibrium lattice characteristics and compare them to experimental results. Furthermore, examine and compare the individual average bond lengths within the structures to experimental data. The electronic density of states of each is then discussed, along with the average atomic Bader charges of each atom with the structures.

4.1. Convergence Test

Preliminary calculations are performed here to estimate the minimal cut-off energy and k -point mesh for both the LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ bulk structures. The values acquired here were utilized throughout the study as the cut-off and k -point.

4.1.1. Kinetic Energy Cut-off

A series of gamma calculations were performed to determine the cutoff energy of each material. These calculations were varied by 100 eV in the 100 - 900 eV range. The resulting total energies were plotted against the cutoff energies, as shown in [Figure 4.1](#). The kinetic energy cut-off for the plots was chosen at the point where the graph begins to show a minimal fluctuation in total energy. The curve for the spinel LiMn_2O_4 bulk begins to show a negligible change at roughly 560eV, which was therefore chosen as the lowest energy for use in further computations. The

energy cut-off for the α -Al₂O₃ bulk structure was changed from 100 to 900 eV and displayed versus total energies. From the plot, we observed a constant variation starting from 500 eV. Given our intention to build heterostructures out of the two materials, we set a cutoff energy of 560 eV for each.

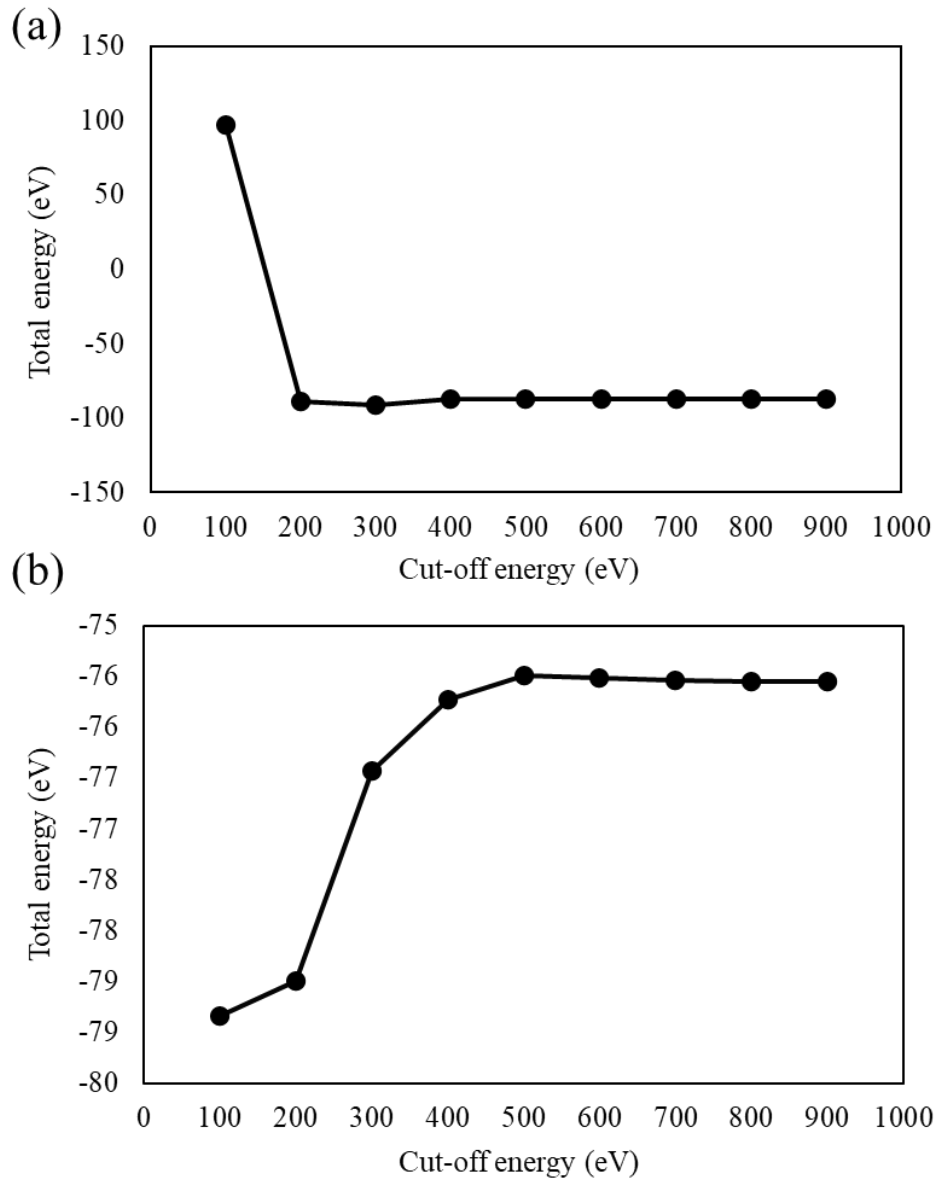


Figure 4.1: Total energy as a function of bulk (a) LiMn₂O₄ and (b) α -Al₂O₃ energy cutoff.

4.1.2. k -points Mesh.

We used a collection of k -point meshes that changed dependent on the bulk structures to sample the Monkhorst-Pack scheme of the Brillouin zone. We altered the k -points of cubic spinel LiMn_2O_4 from $1 \times 1 \times 1$ to $9 \times 9 \times 9$, increasing the same change. [Figure 4.2a](#) depicts the total energy collected regarding the k -point mesh. A minor variance began at $5 \times 5 \times 5$, which we chose as the k -point mesh for the LiMn_2O_4 . We changed k -mesh from $5 \times 5 \times 1$ to $13 \times 13 \times 9$ with the same difference for hexagonal $\alpha\text{-Al}_2\text{O}_3$ with lattice $a = b \neq c$. As demonstrated in [Figure 4.2b](#), a small difference begins to emerge around $9 \times 9 \times 5$.

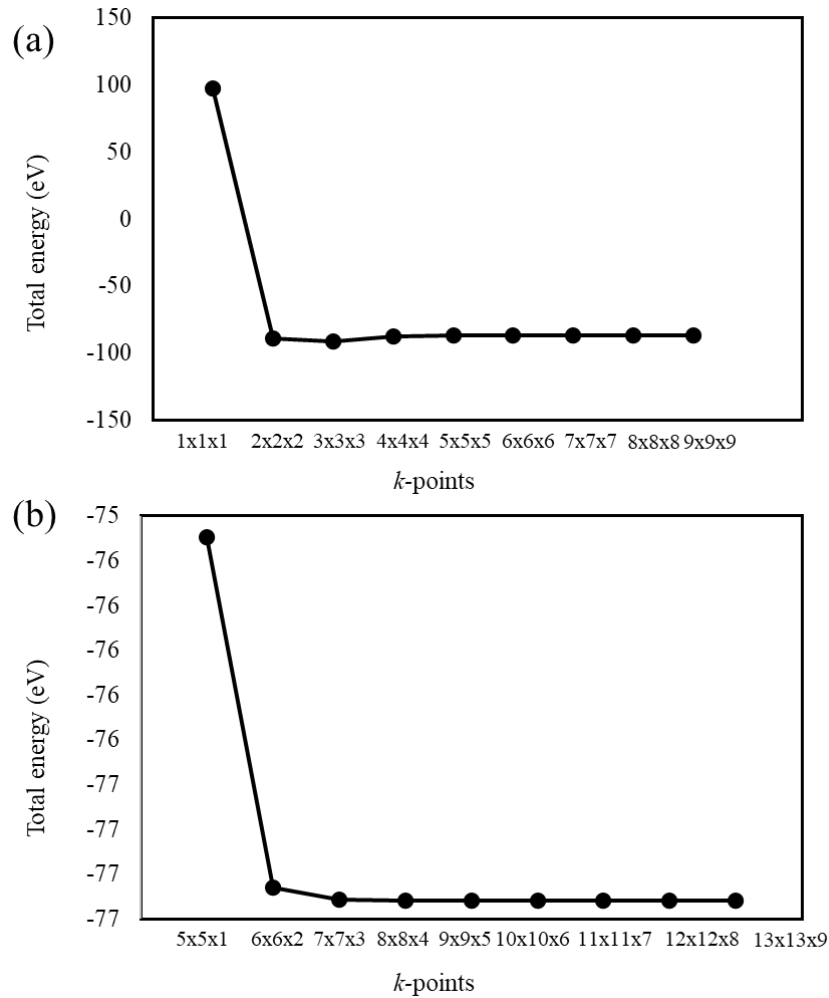


Figure 4.2: Total energy per atom as a function of energy k -point mesh of bulk (a) LiMn_2O_4 and (b) $\alpha\text{-Al}_2\text{O}_3$.

4.2. Structural Properties

[Table 4.1](#) presents the structural features of the spinel LiMn_2O_4 (including lattice parameters, space group, crystal symmetry, bond lengths between Li, Mn, and O atoms, and thermodynamic temperatures of formation in relation to the presented data). The cubic crystal structure of the bulk spinel LiMn_2O_4 cathode material is $Fd\bar{3}m$ (No. 227). The conventional unit cell consisting of 56 atoms, comprised of eight Li atoms occupying tetrahedral 8a sites, 16 Mn on the octahedral 16d with an equal amount of Mn^{3+} and Mn^{4+} ions averaging +3.5, and 32 oxygen (O) atoms orientated in a close-packed cubic array at the 32e sites, which forms a face-centred cubic crystal. The LiMn_2O_4 bulk structure illustrated in [Figure 4.3](#) has lattice parameters $a = b = c = 8.249 \text{ \AA}$ after geometry optimization, which is compatible with the published experimental results [62, 278, 279] of $a = 8.249 \text{ \AA}$ (a 1.18% difference). The estimated average Mn-O bond distance for Mn^{3+} and Mn^{4+} was $1.989 \text{ \AA}$, which agrees with the published actual value of $1.961 \text{ \AA}$ and theoretical value of $1.8665 \text{ \AA}$ [53]. The heats of formation (ΔH_f), computed as the energy difference of the pristine bulk's (E_{pris}) and the sum of the energies of the individual atoms (E_i) in a cubic (*bcc*) multiplied by the number of moles of each (x_i), are expressed as follows:

$$\Delta H_f = E_{\text{pris}} - \sum_i x_i E_i \quad (4.1)$$

A negative heat of formation -258.56 KJ/mol was calculated for the LiMn_2O_4 bulk, which indicates that the system is thermodynamically stable.

Table 4.1: The spinel LiMn_2O_4 structural properties.

Properties	Current work	Ref.
Lattice constant ($\text{\AA}$)	8.249	8.350 [36], 8.43 [280]
Space group	$Fd\bar{3}m$ (227)	
Crystal structure	cubic	
$\text{Mn}^{3+}-\text{O}$ ($\text{\AA}$)	1.760	1.961 $\text{\AA}$ [279], 1.875 [53]
$\text{Mn}^{4+}-\text{O}$ ($\text{\AA}$)	1.753	
ΔH_f (KJ/mol)	-258.56	

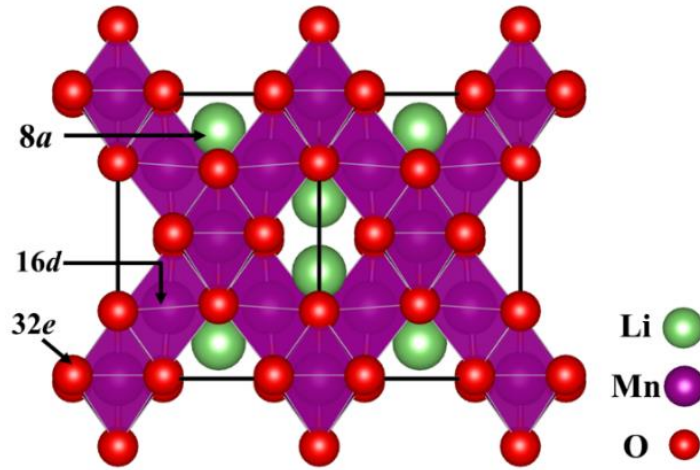


Figure 4.3: Schematic polyhedral model of the face-centred cubic (fcc) spinel LiMn_2O_4 conventional unit cell containing 8 formula units. The orientation expose the Li pathways and we indicated the Li $8a$, Mn $16d$ and O $32e$ Wyckoff positions.

Similarly, [Table 4.2](#) highlights the bulk $\alpha\text{-Al}_2\text{O}_3$ structural characteristics. Within the $R3c$ (No. 167) space group, the simulated $\alpha\text{-Al}_2\text{O}_3$ material possesses hexagonal bulk crystal symmetry. [Figure 4.4](#) depicts a unit cell made up of 30 atoms: 12 aluminium atoms occupying two-thirds of the octahedral $12c$ (0.000, 0.000, 0.148) locations and 18 oxygen atoms $18e$ (0.306, 0.000, 0.250) aligned in the $[001]$ direction. The $\alpha\text{-Al}_2\text{O}_3$ bulk structure has lattice parameters $a =$

4.776 Å and $c = 13.026$ Å after optimization, which correspond with reported experimental data [281, 282, 283, 284] that indicate values of $a = 4.751$ Å and $c = 12.868$ Å with variations of 0.52 and 1.22% for a and b , respectively. The estimated average Al^{3+} -O bond distance is 1.965, which is consistent with the known literature values of 1.9692 [285] and 1.969 [281].

Table 4.2: Structural properties of corundum α - Al_2O_3 .

Properties	This work	Ref.
Lattice Constant (Å)	$a = 4.776$	4.760 [281], 4.75 [283]
	$c = 13.026$	12.989 [281], 12.97 [283]
Space Group	$R3c$ (No. 167)	
Crystal Structure	Hexagonal	
Al^{3+} -O (Å)	1.965	1.9692 [285], 1.969 [281]
ΔH_f (KJ/mol)	-1665.30	

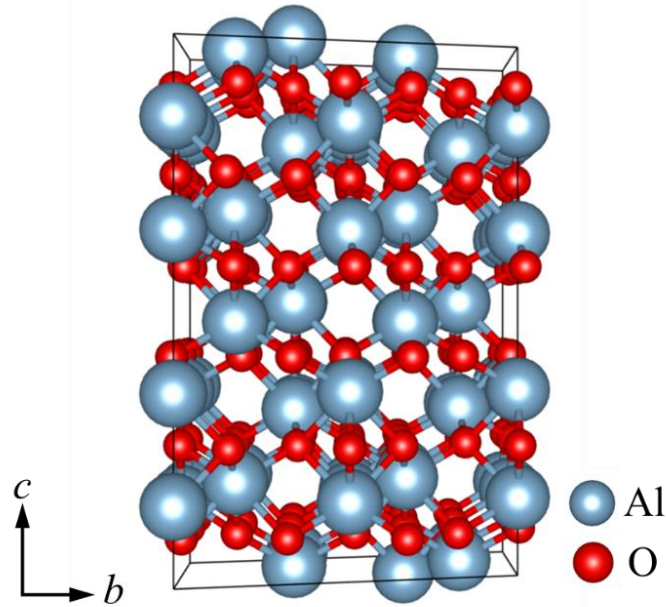


Figure 4.4: Schematic diagram of the corundum α - Al_2O_3 bulk unit cell.

4.3. Electronic Properties

By determining the density of states and average Bader charges of each atom inside the bulk structures, the electronic characteristics of two materials were investigated. First, we looked at the electrical density of states in bulk LiMn_2O_4 after optimizing the shape. The computed density of states demonstrates half-metallic behaviour (as stated in [278, 53]), with the Fermi level (E_F) cutting between spin-up e_g manganese (Mn^{3+}) ions and oxygen $2p$ orbitals. The occupied valence ranges between -8.5 and 2.3 eV, with Mn t_{2g} orbitals hybridized with O $2p$ orbitals and minor contributions from Mn, O, and Li atoms (See [Figure 4.5](#)). Furthermore, the computed average atomic charges for lithium, manganese, and oxygen are 0.88, 1.78, and -1.10 e^-/atom , respectively.

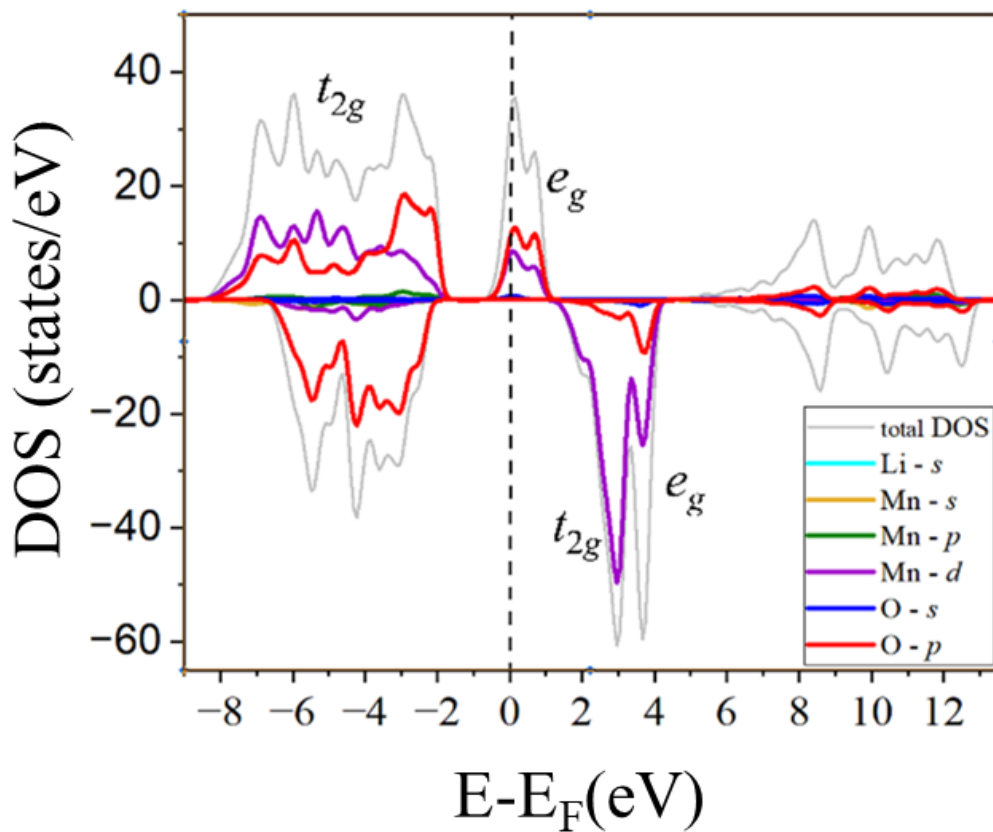


Figure 4.5: The density of states (DOS) for LiMn_2O_4 .

Similarly, as shown in [Figure 4.6](#), we calculated the density of states for the corundum α -Al₂O₃ bulk. The computed density of states suggests a broad band gap of 5.909 eV, which is within 1.02% of the experimental data [286] of 5.970 eV. This demonstrates that α -Al₂O₃ is an electrical insulator. The oxygen 2*p* orbitals dominate the valence band of α -Al₂O₃, with modest contributions from Al *s*, Al *p*, and O *s* orbitals spanning the range of -6.930 to 0.120 eV. The unoccupied conduction band, on the other hand, ranges from 0 to 6.10 eV. Our estimated Bader charges show that inside the bulk of α -Al₂O₃, $q(\text{Al}) = 2.480$ e⁻/atom and $q(\text{O}) = -1.650$ e⁻/atom.

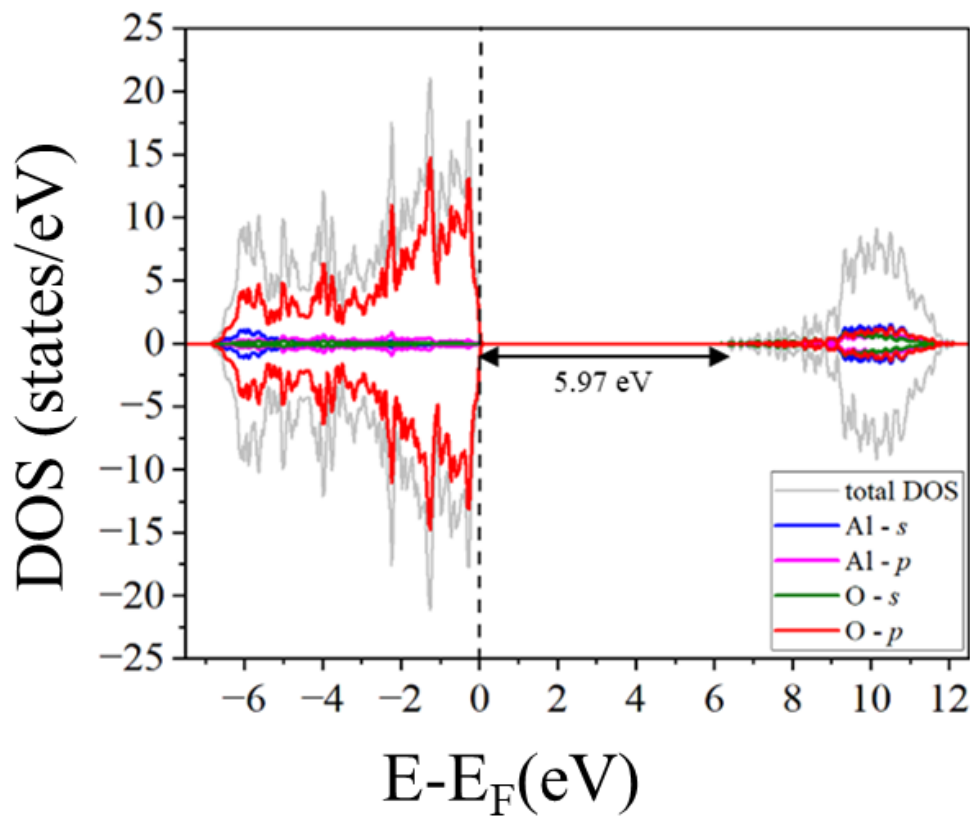


Figure 4.6: The density of states (DOS) for hexagonal α -Al₂O₃.

Summary

In summary, the bulk characteristics of spinel LiMn_2O_4 and corundum $\alpha\text{-Al}_2\text{O}_3$ were investigated using density functional theory (DFT+U). As a first step, we investigated the convergence of the two materials, discovering that the lowest kinetic energy cutoff for LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ was 560 eV and 500 eV, respectively. However, based on the aim of modelling heterostructures using surfaces of both materials, we have considered the energy cutoff for both structures to be 560 eV. The k -mesh was also estimated, and the obtained k -points for LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ were $5 \times 5 \times 5$ and $9 \times 9 \times 5$, respectively. The spinel LiMn_2O_4 with a cubic array of space group $Fd\bar{3}m$ (No. 227) and lattice parameters $a = 8.249 \text{ \AA}$ was compatible with the reported experimental results. The observed average $\text{Mn}^{3+}/\text{Mn}^{4+}$ -O bond distance was $1.989 \text{ \AA}$, which agreed well with the experimental and theoretical data. The predicted heats of formations were negative, indicating that the structures LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ are thermodynamically stable. The computed density of states demonstrates a half-metallic behaviour, with $\text{Mn}^{3+} e_g$ and $\text{O}^{2-} 2p$ crossing at the E_F level. Furthermore, the computed average atomic charges for Li, Mn, and O are 0.88, 1.78, and -1.10 e^-/atom , respectively. The simulated $\alpha\text{-Al}_2\text{O}_3$ possesses $R3c$ (No. 167) space group hexagonal crystal symmetry, with lattice $a = 4.776 \text{ \AA}$ and $c = 13.026 \text{ \AA}$ that are congruent with published experimental data. The computed average Al^{3+} -O bond lengths observed were $1.965 \text{ \AA}$, which is consistent with the given results. Corundum $\alpha\text{-Al}_2\text{O}_3$, an electrical insulator, with a large band gap of 5.909 eV in its density of states, which closely matches experimental data of 5.970 eV. The oxygen $2p$ orbitals dominate the valence band of $\alpha\text{-Al}_2\text{O}_3$, with modest contributions from Al s , Al p , and O s orbitals spanning the range of -6.930 to 0.120 eV. The unoccupied conduction band, on the other hand, ranges from 0 to 6.10 eV. The findings of this chapter clearly distinguish the precision of the parameters employed in comparison to prior investigations on both the LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ bulk structures.

CHAPTER 5

5. Electrolyte (ethylene carbonate) activity towards the major isolated (0001) Surface of Aluminium Oxide α -Al₂O₃

This chapter was published in the Journal of American Chemical Society (ACS) Omega.

Protective coating is one of the tactics used to increase performance and reduce electrode deterioration in LIBs. Experiments on the influence of α -Al₂O₃ coating on secondary lithium-ion batteries have not fully shown the material's reactivity with electrolyte components. This chapter investigated the adsorption of ethylene carbonate (EC) on the α -Al₂O₃ (0001) surface using density functional theory (DFT) calculations. The large (0001) surface terminations are simulated with their predicted surface energies and relaxation using the completely optimized bulk. Single and increased EC adoptions with the molecule engaging in different orientations (*i.e.*, parallel, and perpendicular contacts) have been studied. Adsorptions are further evaluated by computing adsorption energies, surface free energies, Bader charges, and vibration frequencies and presenting STM pictures for various EC coverage.

5.1. Background

Because of its strong electrochemical characteristics, surface coating with aluminium oxide (α -Al₂O₃) is regarded one of the best coating materials [287]. The α -Al₂O₃ significantly enhances the LiMn₂O₄ electrochemical performance at high temperatures, as initially mentioned by Kannan *et al.* [288], and Eftekhari [289]. Numerous later research found that α -Al₂O₃ improves

cycle capacity by lowering Mn transition metal dissolution [290, 291, 292, 293, 294]. In other technological applications, α -Al₂O₃ is widely employed due to its strong thermal conductivity, resilience to severe temperatures and corrosion, and good electrical insulation qualities [295, 296, 297, 298]. Several investigations have documented the adsorption of different molecules onto the α -Al₂O₃, including H₂O [299, 300, 301], HCl [302, 303, 304], CO₂ [305] and methanol [306], since they are of interest for diverse applications.

Despite various experimental research discussing surface coating with α -Al₂O₃, the material's reactivity towards the electrolyte components remains unknown. Quan *et al.* [307] used first principle (DFT) calculations to investigate the interactions of hydrofluoric acid - HF on α -Al₂O₃ (0001) surface and discovered that relaxation resulted in the creation of Al-F bond. Subsequently, the interaction with the HF with α -Al₂O₃ forms an additional AlF₃ artificial layer on the cathode [308].

As it is vital to understand the interaction of the electrolyte on the cathode LiMn₂O₄ surfaces [309], the organic solvent reactivity towards the major coating layer (0001) surface will provide an understanding of the interaction of the coating layer with the electrolyte content. Hence, this chapter employed DFT+U computations to study the EC reactivity on major α -Al₂O₃ (0001) surface, even at high coverages. Because it is critical to understand the electrolyte reactivity on the cathode LiMn₂O₄ surfaces, the organic solvent reactivity towards the major coating layer (0001) surface will offer insight into the coating layer's interaction with the electrolyte content.

5.2. Calculation Details

Vienna Ab-initio Simulation Package (VASP) [310] was used to perform the spin-polarized DFT computations. The Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional was used in the generalized gradient approximation (GGA) [311]. The core electrons and their interactions with the valence electrons were modelled using the projector augmented wave

(PAW) approach [312] in Kresse and Joubert's [313] implementation. The frozen core electrons included values as high as $2p$ for Al and $1s$ for O and C, with the electron of the H atom regarded as a valence electron. To describe the long-range dispersion interactions, the Grimme semi-empirical approach with the Becke-Johnson damping [D3-(BJ)] [314, 315] was used. For the growth of the Kohn-Sham (KS) valence states, the kinetic energy cut-off was set at 560 eV. The Γ -centred Monkhorst-Pack grids with $9 \times 9 \times 5$ and $5 \times 5 \times 1$ k -points were employed for the reciprocal space integration of the α -Al₂O₃ bulk and its two (0001) surface terminations, respectively. To avoid spurious interactions, the position of the Brillouin zone was collected during energy reduction of the isolated EC molecule using a cell of size $10 \text{ \AA} \times 11 \text{ \AA} \times 12 \text{ \AA}$. Gaussian smearing with a width of 0.05 eV was set for all geometry optimization computations to increase the convergence of the Brillouin integrations [315]. To get precise total energies and electronic properties, the tetrahedron approach with Blöchl adjustments was applied [316].

5.3. Results and Discussion

5.3.1. Pristine (0001) α -Al₂O₃ Surface

Terminations of α -Al₂O₃ (0001) surface were investigated were modelled by cleaving a fully optimized (2×2) supercell using the approach described in the METADISE package [317] for creating non-dipolar surface models. We picked the α -Al₂O₃ (0001) surface to simulate since it has been shown to be the dominating plane in α -Al₂O₃ nanoparticles [318, 319, 320]. The (0001) surface consists of 120 atoms (48 aluminum and 72 oxygen) spread in 6 formula unit (f.u.) atomic layers in both Al and O-terminations with a surface area of $90.3 \text{ \AA}^2$. To eliminate interactions between the periodic images, a $15 \text{ \AA}$ vacuum zone was perpendicularly added to the slabs. The atoms in the top layers (3 f.u.) were permitted to move during relaxation, while the lower layers (3 f.u.) remained fixed at bulk locations. Along the z -axis, the two slabs were stoichiometric, symmetric, and non-polar (see [Figure 5.1](#)).

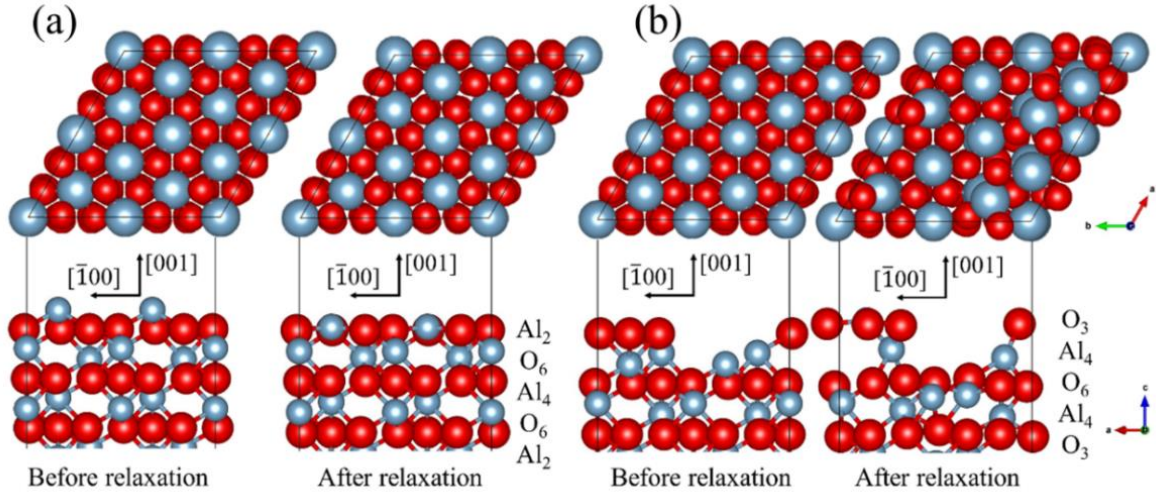


Figure 5.1: Top and side view of the (a) Al- and (b) O-terminated α - Al_2O_3 (0001) surface. The stacking sequence of both are shown on the far right and crystallographic direction are shown.

The stacking pattern for the two terminations alternates between Al and O layers, which are Tasker type III surfaces [321]. The sequence for Al-terminated surface is Al_2 , O_6 , Al_4 , O_6 , ..., O_6 , Al_4 , O_6 , Al_2 , while the O-terminated show O_3 , Al_4 , O_6 , Al_2 , ..., Al_4 , O_6 , Al_4 , O_3 sequence. The surface energies of the α - Al_2O_3 (0001) surfaces before (γ^{un}) and after (γ^{rel}) relaxation, together with their respective relaxation (R) percentages using [equations 3.19](#), [3.20](#), and [3.21](#), respectively. Static calculations we performed to study the stability of the slabs before relaxation, while the surface energies of the half-relaxed slabs were calculated upon full geometry optimization.

Table 5.1: Surface energies before (γ^{unrel}) and after (γ^{rel}) relaxation of the α - Al_2O_3 (0001) facets together with their relaxation percentage (R).

(0001) Surface	γ^{un} (eV/Å ²)	γ^{rel} (eV/Å ²)	R (%)
Al-termination	0.25	0.11	57.0
O-termination	0.38	0.13	65.8

[Table 5.1](#) summarized the calculated surface energies, and the lowest unrelaxed and relaxed surface energies were obtained for the Al-terminated slab with $\gamma_r = 0.11 \text{ eV}/\text{\AA}^2$, which accounts for the most stable termination. The predominant stability of the Al-terminated (0001) surface is consistent with previously reported studies [305, 322, 323, 324, 325, 301] and the experimental work by McHale et al. [326], who found $\gamma = 0.16 \text{ eV}/\text{\AA}^2$. For both Al- and O-terminated surfaces, we observed a large geometry relaxation, with the largest $R = 65.8\%$ obtained for the O-terminated slab. The substantial difference between the unrelaxed and relaxed surface energies was caused by the exposed ions moving inwards in the Al-terminated facet and outwards in the O-terminated slab. We found a substantial relaxation during energy reduction, with the Al---O interlayer distance decreasing from $1.85 \text{ \AA}$ to $1.69 \text{ \AA}$, and from $1.70 \text{ \AA}$ to $1.97 \text{ \AA}$ for the Al-terminated and O-terminated slabs, respectively. This drop was coupled with vertical Al-O relaxation, with the Al-terminated slab experiencing an inward relaxation of $0.75 \text{ \AA}$ along the z -axis, bringing it closer to the O layer underneath, while the O-terminated slab had an outward relaxation of $0.99 \text{ \AA}$. Previously, both experimental and theoretical studies demonstrated that Al-terminated surfaces display a substantial lattice contraction along the z -direction to limit the high electrostatic attractions [327, 328, 329]. The rebuilt surface termination of $\alpha\text{-Al}_2\text{O}_3$ is unstable because it leaves naked surface Al^{3+} ions or dangling O-bonds [322, 330, 331, 332, 333]. The molecular adsorption of EC and the assessment of the physicochemical characteristics are exclusively done in this study on the most stable Al-terminated surface, which is more likely to emerge in the corundum crystal morphology in the absence of water [301].

5.3.2. Molecular Adsorption

The adsorption of ethylene carbonate on the major Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface is investigated in this section. Given the availability of one top layer Al site on the (1×1) Al-

terminated surface, the Al terminated surface sites on our (2×2) Al-terminated surface are all similar. The earliest surface EC binding configurations incorporate EC coordination through carbonyl (O_c) and ethereal oxygen (O_e), in parallel, perpendicular, and bridging/bidentate binding orientations. As described in our prior work [309], where the structural characteristics of our optimized and isolated EC molecule were compared to known experimental and theoretical data, our computational settings can adequately reflect the molecule's major attributes (see [Table 5.2](#) and the molecule in [Figure 5.2](#)).

Table 5.2: The equilibrium bond distances and angles of the electrolyte components, ethylene carbonate compared to the reported data.

Parameters	This work	Ref.
$d(C=O)/\text{\AA}$	1.20	1.20 [334], 1.15 [335]
$d(C-O)/\text{\AA}$	1.37	1.39 [334], 1.33 [335]
$d(C-C)/\text{\AA}$	1.50	1.54 [334], 1.52 [335]
$d(C-H)/\text{\AA}$	1.10	1.09 [334]
$\angle(O-C-O)/^\circ$	110.5	125.2 [334], 124.1 [335]
$\angle(C-O-C)/^\circ$	108.9	109.5 [334], 109.0 [335]

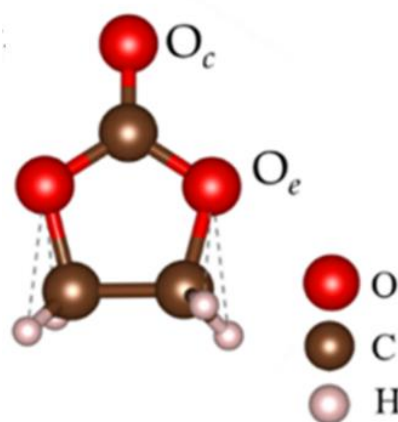


Figure 5.2: Representation of ethylene carbonate (EC) molecule, showing the carbonyl (O_c) and ethereal (O_e) oxygen.

The average adsorption energy per EC molecule on the α -Al₂O₃ (0001) surface were calculated using the equation:

$$E_{\text{ads}} = \frac{1}{N_{\text{EC}}} [E_{\text{EC+slab}} - (N_{\text{EC}}E_{\text{EC}} + E_{\text{r,slab}})] \quad (4.1)$$

where $E_{\text{slab+EC}}$, E_{EC} , and $E_{\text{r, slab}}$ are the total energies of the slab, the isolated molecule, and the clean surface, respectively. The number of adsorbed EC molecules is represented by N_{EC} .

5.3.2.1. *Single ethylene carbonate molecule adsorption*

The adsorption of a single EC molecule parallel and perpendicular to the surface, interacting through the carbonyl (O_c), ethereal (O_e) oxygen, and both on the top-layer Al locations of α -Al₂O₃ (0001) surface, was then investigated. The EC molecule was first positioned at 2.0 Å from the surface in all orientations to favour the attractive forces between the adsorbate and the facet. During relaxation, however, the molecule and surface were free to move. The adsorption energies determined for the α -Al₂O₃ (0001) surface with the EC molecule situated parallel, perpendicular, and in a bridging/bidentate binding are summarized in [Figure 5.3](#). With $E_{\text{ads}} = -1.69$ eV, the molecule had the highest adsorption energy when positioned parallel to the surface. The projecting Al atom engaging with the molecule moved upward out of the surface by 0.035 Å to make a bond with the EC molecule in all adsorptions. When the bridging/bidentate conformation was relaxed, the EC molecule preferred to engage with the surface via the carbonyl oxygen.

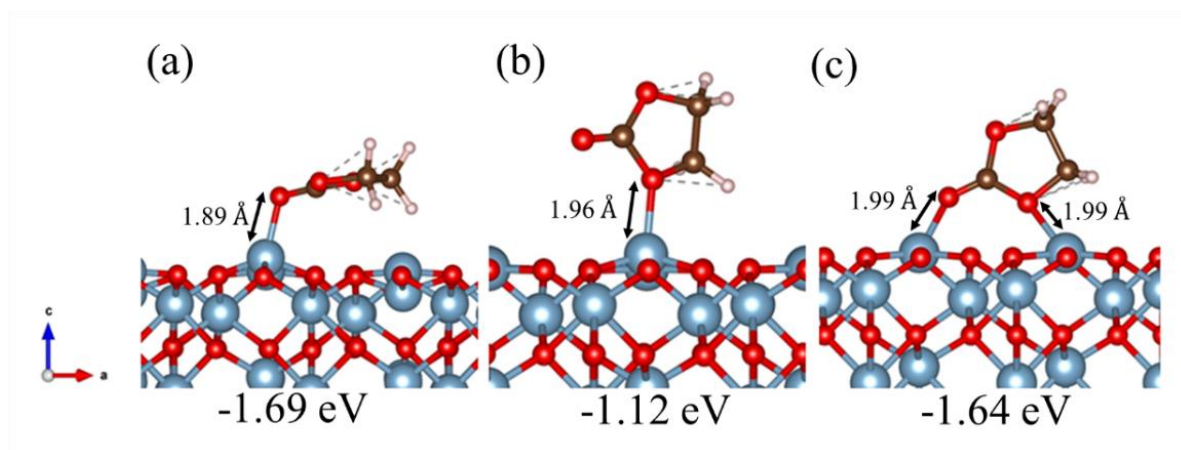


Figure 5.3: Adsorption energies (E_{ads}) calculated for a single EC molecule place (a) parallel, (b) perpendicular and (c) in a bridging/bidentate binding.

5.3.2.2. Varying surface coverages

To investigate the effect of varied surface coverages, the number of adsorbed EC molecules (N_{EC}) on the Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface was raised gradually until a complete monolayer was produced. The surface coverage (θ) was determined as the ratio of the number of adsorbed EC molecules (N_{EC}) to the total number of accessible adsorption sites (N) as $\theta = \frac{N_{\text{EC}}}{N}$, where $\theta = 0$ implies that no adsorption occurs on the surface and $\theta = 1$ indicates that surface adsorption has reached a complete monolayer. The influence of surface coverage on the average adsorption energy of the EC molecule was investigated for parallel and perpendicular surface contacts, as shown in [Figure 5.4](#). In general, the value of $E_{\text{ads}}/N_{\text{EC}}$ declines with N_{EC} for parallel binding modes, whereas the average adsorption energy increases for perpendicular orientations at $\theta_{\text{EC}} \leq 0.75$, but it somewhat reduces again at $\theta_{\text{EC}} = 1.00$. The drop in $E_{\text{ads}}/N_{\text{EC}}$ seen for parallel contacts suggests that for $\theta_{\text{EC}} > 1$, the steric effects caused by lateral interactions between EC molecules, which occupy a significant surface area, destabilize the system. As there are attractive Van der Waal forces between the parallelly stacked molecules, the value of $E_{\text{ads}}/N_{\text{EC}}$ grows with respect to single EC molecule adsorption up to θ_{EC}

≤ 0.75 for perpendicular contacts. However, when we achieved a complete monolayer ($\theta = 1$), the repulsive steric interactions between the closely packed EC molecules were stronger than the attractive Van der Waal forces, causing the average adsorption energy ($E_{\text{ads}}/N_{\text{EC}}$) to decrease. According to our findings, the EC molecule prefers to connect to the surface in a parallel way up to $\theta_{\text{EC}} \leq 0.75$, however a whole monolayer is energetically more beneficial if all the molecules move to a perpendicular orientation. We justify the shift in adsorption configuration based on steric parameters, since parallel molecules oppose each other and must thus become perpendicular to the surface to accommodate the whole monolayer. Adsorption at larger coverages resulted in the removal of the fifth molecule from the surface due to severe steric hindrance induced by EC-EC interactions.

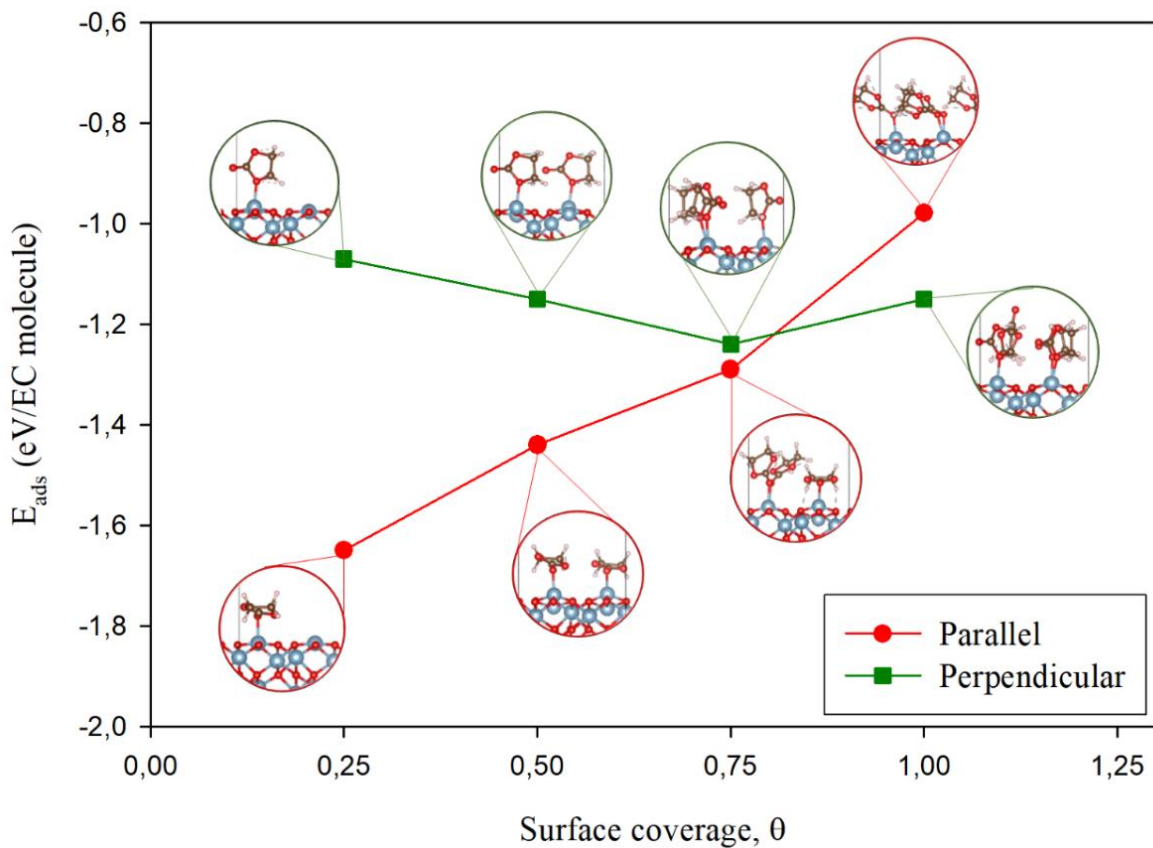


Figure 5.4: Average adsorption energy as a function of the surface coverage for the EC molecules adsorbed parallelly and perpendicularly to the surface.

We also investigated the influence of surface coverage (θ) on the work function (ϕ) of EC molecules placed on the surface in parallel and perpendicular configurations. The work function (ϕ) is a measurement of the energy required to transport a surface electron into the vacuum, and it is known to be bigger for denser surface crystals than for open lattices [336, 337]. In general, increasing the surface coverage (θ_{EC}) increased the work function for both parallel and perpendicular interactions, as seen in [Figure 5.5](#). The entire monolayer of perpendicularly arranged EC molecules had the highest value of $\phi = 6.37$ eV.

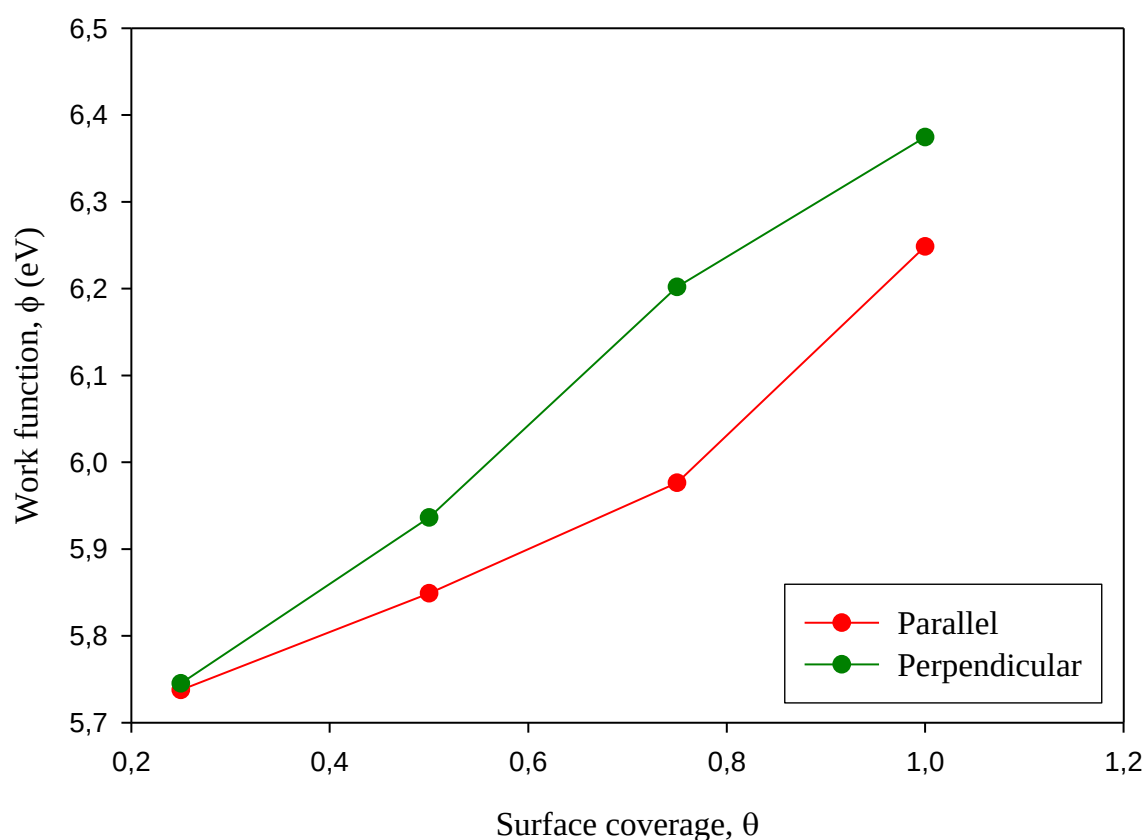


Figure 5.5: Work function (ϕ) as a function of the surface coverage for the EC molecules adsorbed parallelly and perpendicularly to the surface.

5.3.3. Surface Free Energies

We then calculated the surface free energy (σ) for the surfaces following adsorption of various EC coverages using:

$$\sigma = \gamma_r + \frac{E_{\text{EC}+ \text{slab}}^{\text{DFT}} - E_{u,\text{slab}}^{\text{DFT}} - N_{\text{EC}} \times E_{\text{EC}}^{\text{DFT}}}{A} \quad (4.7)$$

The influence of surface coverage (θ) on surface free energies (σ) is summarized in [Figure 5.6](#). The computed surface free energy decreases in general when compared to the clean surface ($\theta = 0$), suggesting that the system is stabilized during EC adsorption, with the most stable surface when we achieve a complete monolayer ($\theta = 1$). Surface free energies drop with respect to the surface energy of the pristine (0001) facet up to $\theta \leq 0.75$, when it stabilizes at roughly 0.06 eV/Å for parallel interactions. At $\theta = 1$, repulsive steric forces between closely placed EC molecules become stronger than attractive Van der Waal forces, causing the fourth molecule to detach from the surface upon relaxation of the entire monolayer covered surface, resulting in the same surface energy for $\theta = 0.75$ and $\theta = 1$ for the parallel EC molecules.

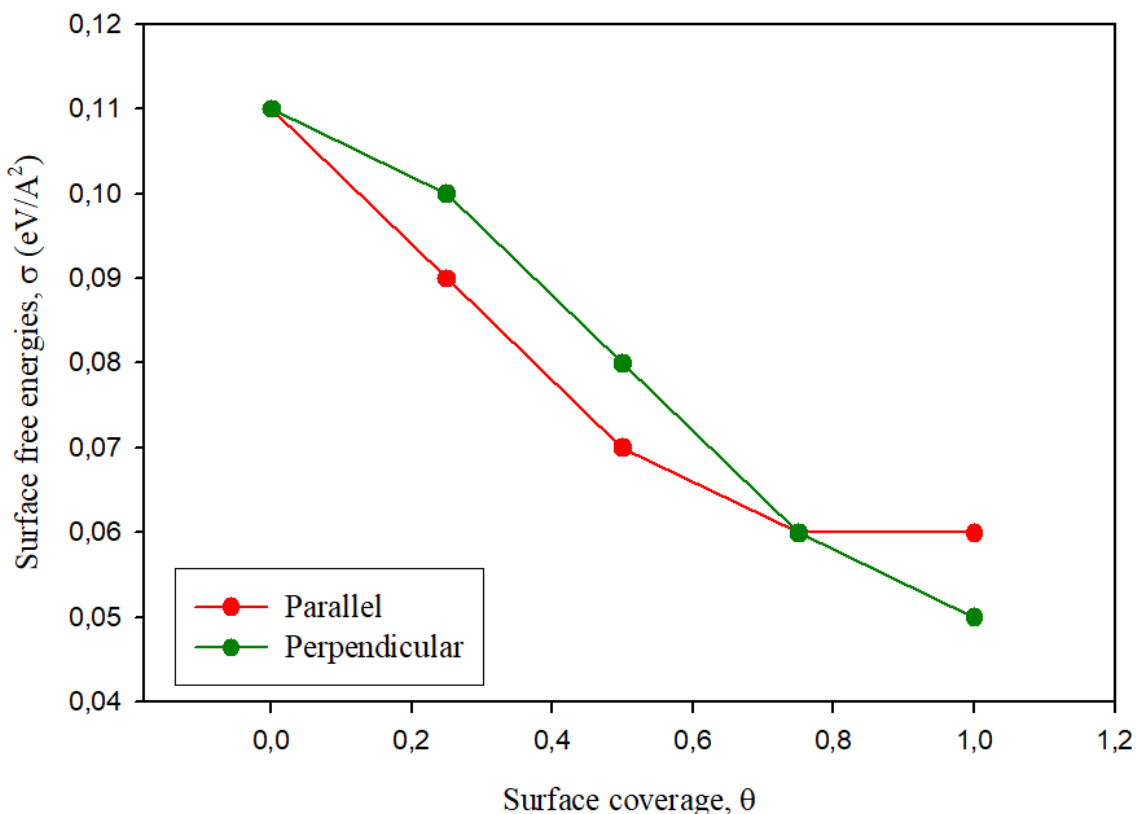


Figure 5.6: Surface free energies (σ) for the Al-terminated α -Al₂O₃ (0001) surface as a function of the surface coverage for the EC molecules adsorbed parallelly and perpendicularly to the surface.

5.3.4. Bader Charge Analysis

To study the electronic charge transfers between the EC molecules and the surface, we performed a Bader charge analysis on the most favourable adsorption configurations discovered on the α -Al₂O₃ (0001) surface. To do the Bader analysis of charges [266], we utilized the algorithm written by Henkelman and colleagues [267]. Atoms are defined in this manner as the areas contained inside surfaces of zero flow of charge density. [Table 5.2](#) summarizes the charge exchanges between the surface and the adsorbed EC molecules. Minor charge exchanges between the surface and the adsorbate are often observed during the adsorption of a single EC molecule. Similar results were obtained in our earlier investigation,

in which we evaluated EC adsorption on the main surfaces of the LiMn_2O_4 spinel [309]. When the EC molecule was placed on the surface in parallel and perpendicular modes, it gained minor charges of $-0.094 e^-$ and $-0.071 e^-$. When the surface coverage is increased to $\theta = 0.50$, the charge transfer stays constant in both orientations. However, due to interactions between the closely packed adsorbate molecules, we discovered a decrease in charge transfer for $\theta \geq 0.75$ compared to lower surface coverages of the EC molecule. We also estimated the charge accumulation/depletion between the interacting atoms, which were the EC molecule's carbonyl or ethereal oxygen atoms and the surface's Al atom. When the coverage is extended up to $\theta = 0.50$, our calculations show that there is modest charge buildup for parallel interactions and negligible charge depletion for parallel interactions. However, for $\theta = 0.75$ and complete monolayer coverage, we detect a substantial charge buildup of $0.761 e^-$ and $0.836 e^-$ on the interacting oxygen atom.

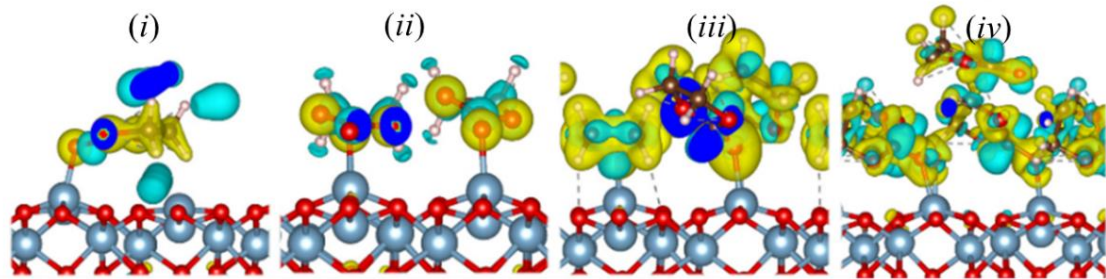
We further examined the differential electron density ($\Delta\rho$) to acquire a better understanding of electronic charge exchanges. The isosurfaces of the electron density differential between the $\alpha\text{-Al}_2\text{O}_3$ (0001) surface and the EC molecule at different coverages are shown in [Figure 5.7](#). The charge density difference was calculated by subtracting the sum of the electron charge densities of the clean surface (ρ_{surf}) and an isolated EC molecule (ρ_{EC}), which had the same structure as the adsorbed form, from the electron density of the total system (ρ_{sys}), using the equation $\Delta\rho = \rho_{\text{sys}} - (\rho_{\text{surf}} + \rho_{\text{EC}})$. [Figure 5.7](#) demonstrates that, while a single EC molecule adsorbs with a minor charge transfer, the electronic charge flow implies an internal charge rearrangement inside the molecule. We see partial oxidation of the carbon atom and partial reduction of the interacting oxygen because of an intramolecular electronic rearrangement from the $\text{C}=\text{O}$ π -bond to the newly created $\text{Al}-\text{O}$ σ -bond, which is consistent with prior work [309]. The charge density iso-surfaces also show electronic buildup on the hydrogen atoms generated by interactions with the surface oxygen atoms.

Table 5.3: Bader Charge between the EC molecule and the surface (Δq_{EC}) as well as the average value for the charge accumulation/depletion within the interacting EC atom ($\Delta q_{Oc/Oe}$), *i.e.*, carbonyl or the ethereal oxygen atom as a function of the surface coverage (θ_{EC}). Average stretching mode for the carbonyl group $\nu(C=O)$, as well as the asymmetric ν_{asy} (CH_2) and symmetric stretching mode ν_{sys} (CH_2) and the bending mode for the methylene group $\delta(CH_2)$.

Adsorption orientation	θ	Δq_{EC} (e ⁻)	$\Delta q_{Oc/Oe}$ (e ⁻)	$\nu_{C=O}$ (cm ⁻¹)	CH ₂		
					ν_{sys} (cm ⁻¹)	ν_{asy} (cm ⁻¹)	δ (cm ⁻¹)
Isolated EC molecule				1829	2952	2990	1341
Liquid film EC [338, 339]				1803	2928	2955	1397
Parallel	0.25	-0.094	-0.053	1654	3087	3022	1482
	0.50	-0.094	-0.049	1665	2991	3112	1474
	0.75	-0.021	0.743	1704	3015	3064	1455
	1.00	-0.010	0.766	1753	3054	3053	1468
Perpendicular	0.25	-0.071	0.056	1619	3024	3059	1432
	0.50	-0.072	0.054	1851	3026	3086	1456
	0.75	-0.019	0.617	1819	3091	3040	1465
	1.00	-0.019	0.631	1823	3120	3054	1474

^aNegative charge transfer values indicate a charge accumulation on the adsorbate while positive values indicate charge transfers to the surface.

(a)



(b)

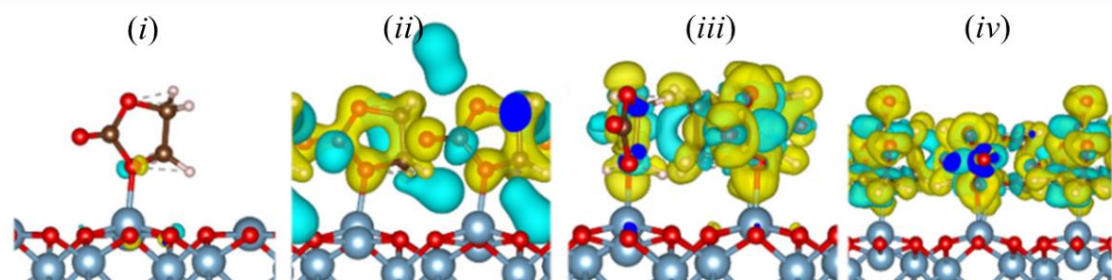


Figure 5.7: Side view of the charge density flow ($\Delta\rho$) for different coverages of the EC molecule adsorbed (a) parallel and (b) perpendicularly on the α -Al₂O₃ (0001) surface. Density gains and depletion regions are represented in yellow and blue, respectively. Isosurfaces display a value of $\pm 0.099 e/\text{\AA}^3$, $\pm 0.190 e/\text{\AA}^3$, $\pm 0.018 e/\text{\AA}^3$, and $\pm 0.009 e/\text{\AA}^3$ for (i) a single EC, (ii) 2 EC, (iii) 3 EC and (iv) 4 EC molecules.

5.3.5. Vibrational Modes

The simulated vibrational mode wavenumbers are directly related to the intramolecular bond force constant, calculated as the 2nd derivatives of the total energy to the atomic positions [340, 341], which were allowed to move by small displacements to ensure that they fall within the harmonic part of the energy potential well. The asymmetric (ν_{asy}), symmetric stretching mode (ν_{sys}), and bending mode (δ) vibrational modes for the carbonyl group $\nu(\text{C=O})$ and methylene group $\nu(\text{CH}_2)$ are summarized in [Table 5.2](#). The stretching modes shown are the modes for individual EC molecules as well as the average vibrational modes at different EC coverages on the Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface. The wavenumbers of an isolated EC molecule's vibrational modes accord quite well with the observed modes for liquid films [342], thus we are confident in our predictions for the interacting molecules. The average stretching modes estimated for EC as surface coverage increases stay in the same range as for single EC adsorption, demonstrating that the increase in coverage has no effect on the vibrational modes. For example, for single adsorptions and with higher coverage, our estimated vibrational modes for the carbonyl group $\nu(\text{C-H})$ were within the range 2850 - 3300 cm^{-1} described in prior research [343, 344]. When compared to the solitary adsorbate, the carbonyl (C=O) stretching modes are red shifted, indicating that the carbonyl double bond weakens during adsorption. Because of the steric effect and the more limited mobility of the hydrogen atoms, the stretching vibrational modes of the methylene $\nu(\text{CH}_2)$ groups are blue shifted with respect to the solitary EC molecule.

5.3.6. Scanning Tunnelling Microscopy (STM) Images

We then generated topographical scanning tunnelling microscopy (STM) images from a spatial distribution of the valence band state around the Fermi level on surfaces with varying EC molecule coverages. The STM pictures were generated using the Tersoff-Hamann approach's fundamental formulation [269], with the STM tip approximated to an endlessly tiny point source. For the generation of our constant height STM topographic pictures, we utilized the software HIVE [270], with the partial charge density integrated between the ranges -2.5 - 0 eV [345, 346, 347]. STM images for a clean surface and after adsorption with varying coverages of parallel and perpendicular EC molecules are shown in [Figure 5.8](#).

The STM for a pristine corundum α -Al₂O₃ surface was achieved at 0.1 Å and a density of $\rho = 0.0017 \text{ e}/\text{\AA}^3$, revealing alternating rows of well-defined Al and O atoms. The corundum α -Al₂O₃ material has the same hexagonal arrangement as the isostructural haematite α -Fe₂O₃ mineral, and the STM pictures are identical [348, 349, 350]. STM pictures of surfaces with adsorbed EC molecules vividly reveal the array and orientation of the molecules on the surface, allowing us to differentiate the EC molecules' orientation and surface coverage. However, due to the molecule's size, the molecule(s) in the adsorbed surfaces appear as bright spots, as seen by the insets. The pictures become less distinct as coverage increases because the molecules grow more densely packed and closer together.

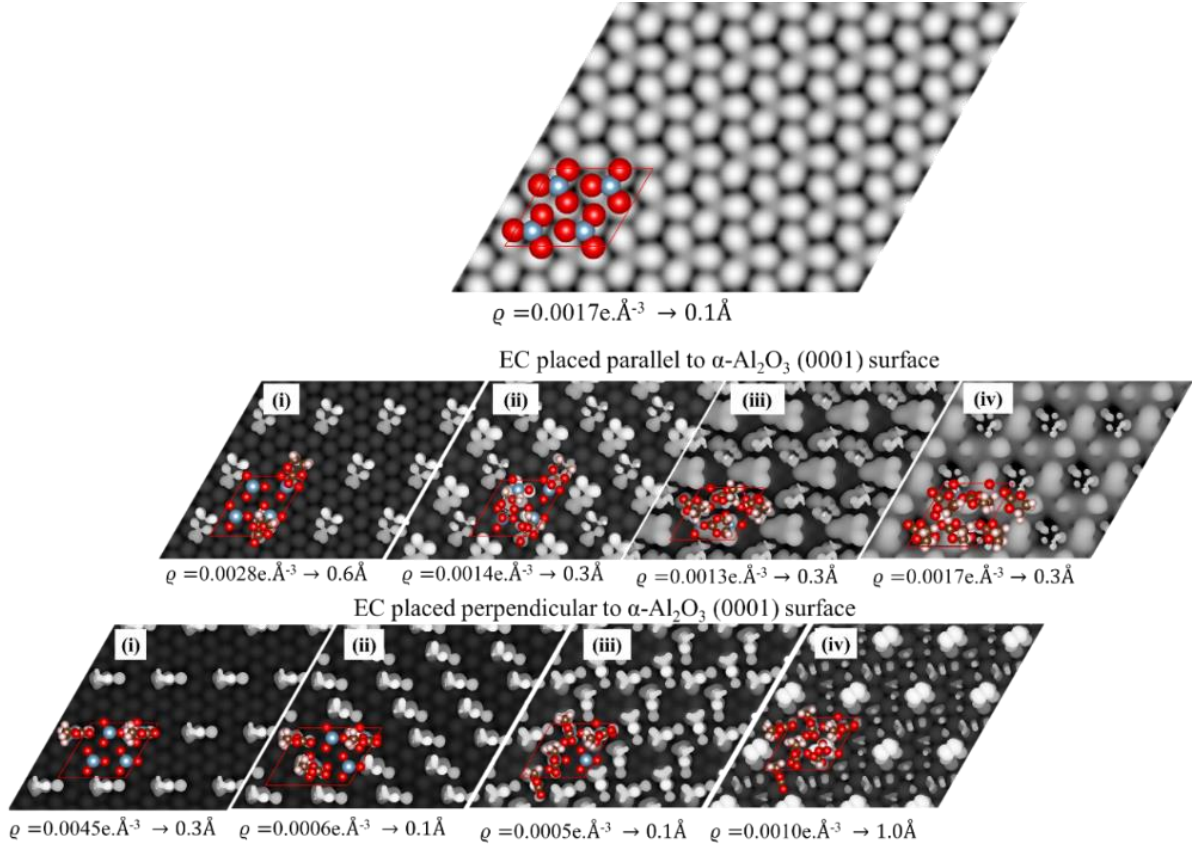


Figure 5.8: Simulated scanning tunnelling microscopy (STM) images of (a) a clean Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface, and after adsorption with different coverages of parallelly and perpendicularly placed EC molecules a sample bias of -2.5 eV. Density (ρ) and tip distance (d) are also indicated. Insets show the adsorbed EC molecules and atoms on the top surface layer.

Summary

DFT simulations were used to study the adsorption of a variety of ethylene carbonate coverages onto the major $\alpha\text{-Al}_2\text{O}_3$ (0001) surface. Our surface energy estimates show that the Al-terminated (0001) surface is the most stable facet, which is consistent with earlier research. A single EC molecule prefers to attach to the Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface in a parallel orientation, with relatively negligible charge transfer happening during adsorption. When the surface coverage was extended to a complete monolayer, the $E_{\text{ads}}/N_{\text{EC}}$ for parallel contacts fell

while the average adsorption energy rose for perpendicular orientations relative to the initial adsorption of an isolated EC molecule. When parallel or perpendicular EC molecules interact with the surface, the surface free energy fall as the EC coverage increases, indicating enhanced surface stability. Even with increasing surface coverage, minor charge transfers between the surface and EC molecules were seen in both directions. However, we discovered a rise in charge accumulation on the interacting atom (either carbonyl or ethereal oxygen). At greater coverages, we also observed steric hindrance caused by the EC-EC interaction, which resulted in the separation of EC molecules. Our simulations reveal a growing redshift for $\nu(\text{C=O})$ with respect to an isolated EC molecule as the surface coverage increases, implying that the carbonyl bonds weaken during adsorption. The symmetric and asymmetric (CH_2) modes' blue shifts suggest steric hindrance. The simulated scanning tunnelling microscopy (STM) pictures for a clean corundum $\alpha\text{-Al}_2\text{O}_3$ (0001) surface and surfaces with absorbed molecules at various EC coverages are also displayed. The STM picture for the clean corundum $\alpha\text{-Al}_2\text{O}_3$ (0001) surface contrasts favourably with the image for the same facet of the isostructural hexagonal haematite $\alpha\text{-Fe}_2\text{O}_3$ structure, which can be employed for future experiments.

CHAPTER 6

6. Delithiation Thermodynamics, Electronic Properties, and Structures of the Heteroepitaxial Interfaces α -Al₂O₃/LiMn₂O₄ (001) and (111)

This chapter has been published in the Surface and interfaces Journal.

As previously noted, α -Al₂O₃ surface coating plays a critical role in improving the performance of secondary lithium-ion batteries by reducing undesired electrolyte activity towards cathode materials. However, the complex interaction between the coating layer and the cathode substrate is yet unknown. Thus, density functional theory calculations with a Hubbard Hamiltonian and long-range dispersion corrections (DFT+U-D3) are used in this study to investigate the interfacial geometry, stability, and electronic properties of α -Al₂O₃ coated LiMn₂O₄ (001) and (111) surfaces at varying coating thicknesses. Before creating the interfaces, the individual surfaces were thoroughly modelled. We determine their respective misfit percentages using the specific lattice parameters of α -Al₂O₃ as compared to the LiMn₂O₄ (001) and (111) surfaces, while also considering the expansions of the α -Al₂O₃ surfaces to the LiMn₂O₄ facets. Because only interfacial topologies with misfits of less than 5% may occur experimentally, their stabilities were examined using adhesion energy estimates. The electronic characteristics of the substrate as contrasted to the isolated slab, as well as their individual atom interactions at the heterojunction, were investigated using Bader charge calculations. Finally, the delithiation thermodynamics of the interfaces

were computed and compared to the isolated surfaces, and their vacancy formation energies were determined and analysed.

6.1. Background

Because of its abundance, less poisonous, and cost-effective manganese content, Thackeray et al [58] discovered spinel LiMn_2O_4 as an efficient alternative for LiCoO_2 . LiMn_2O_4 is a three-dimensional structure with diffusion routes that allow unrestricted Li^+ movement while conserving the integrity of the parent Mn_2O_4 material after complete delithiation [59, 60]. Nonetheless, as a cathode material, LiMn_2O_4 experiences capacity fading owing to electrolyte activity, which causes Jahn-Teller distortion of Mn^{3+} ions [51, 52, 53], cathode-electrolyte interphase (CEI) production [49, 50], and dissolution of Mn^{2+} ions into the electrolyte [54, 61, 56, 57]. To address these concerns, researchers have investigated protective coating materials [65, 66, 67], cation/anion doping [62, 63, 64], and increasing the fraction of the LiMn_2O_4 (111) surface on the morphology [68, 69, 70]. Among these, surface coating appears as a powerful method for inhibiting electrolyte-cathode interactions while keeping the structural composition of LiMn_2O_4 .

Various coating materials, including metallic oxides (e.g., TiO_2 [89, 90], Al_2O_3 [91, 92], ZnO [93, 94, 95], MgO [96, 97]), fluorides (such as AlF_3 [98, 99], SrF_2 [100] and LaF_3 [101]), and phosphates (*i.e.* LaPO_4 [102, 103]), YPO_4 [104], FePO_4 [105], AlPO_4 [106]), have been studied. Because of its outstanding mechanical and thermal stability, corrosion resistance, and low electrical conductivity [107, 108], $\alpha\text{-Al}_2\text{O}_3$ stands out as a possible contender among them. As noted by Myung et al [109], the surface coating with alumina greatly improve the electrochemical performance of Li-Ni-Co-Mn-O cathode materials and scavenge the acidic electrolyte medium (hydrofluoric acid -HF), resulting in an additional protective layer (AlF_3) via the chemical equation: $\text{Al}_2\text{O}_{3(s)} + 6\text{HF}_{(aq)} \rightarrow 2\text{AlF}_{3(s)} + 3\text{H}_2\text{O}_{(l)}$. As we also discussed in our

previous chapter, the organic electrolyte physically interacts with the surface and can detach at higher coverages as a result of their steric hindrances [108].

Next, it is crucial to also understand closely the cathode-coating interactions between the LiMn_2O_4 and the alumina. Experimentally, several synthesis methods for Al_2O_3 coating encompass sol-gel, hydrothermal, solvothermal, chemical vapour deposition, atomic layer deposition (ALD), pulsed laser deposition, etc [225, 226, 227, 228]. ALD has emerged as an effective technique for Al_2O_3 coating synthesis, enabling precise thickness and control at the atomic scale on the LiMn_2O_4 surface [229, 230, 91]. ALD entails a binary reaction involving trimethylaluminum ($\text{TMA} = \text{Al}(\text{CH}_3)_3$) and water vapour producing methane (CH_4) as a by-product through the reaction: $2\text{Al}(\text{CH}_3)_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4$. A few studies have investigated Al_2O_3 coating on LiMn_2O_4 using ALD. Warburton et al [230, 233, 234] have extensively delved into the theoretical aspects of the Al_2O_3 ALD mechanism on LiMn_2O_4 surfaces using DFT calculation to investigate how the near-surface manganese oxidation evolves with different Al precursor ligands and the consequences for electrochemical performance [92] in comparison with experimental observations. Here, we employ DFT calculations to discern the heteroepitaxial interface stability of $\alpha\text{-Al}_2\text{O}_3$ -coated LiMn_2O_4 (001) and (111) surfaces with distinct coating thicknesses throughout cycling.

6.2. Calculation Details

The pristine and partially-delithiated $\alpha\text{-Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ heterostructures were simulated using spin-polarized density functional theory (DFT) computations performed in the Vienna Ab-initio Simulation Package (VASP) [351]. The Perdew, Burke, and Ernzerhof (PBE) functional inside the generalized gradient approximation (GGA) was used to explain the exchange-correlation energy [352]. For the growth of the Kohn-Sham (KS) valence states, a kinetic energy cut-off of 560 eV was used. For the bulk structures of LiMn_2O_4 and Al_2O_3 , the

Monkhorst-Pack k -point meshes were used at $5 \times 5 \times 5$ and $9 \times 9 \times 5$, respectively. The k -points of the LiMn_2O_4 and Al_2O_3 surfaces, as well as the $\alpha\text{-Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ interface, were fixed at $5 \times 5 \times 1$ and $1 \times 1 \times 1$, respectively. The projected augmented wave (PAW) formalism [353] developed by Kresse and Joubert [313] was used to model treat Li ($2s^1$), Mn ($3d^5 4s^2$), O ($2s^2 2p^4$) and Al ($3s^2 3p^1$) valence electrons and their interactions with core electrons. To account for long-range dispersion interactions, the Grimme semi-empirical approach with the Becke-Johnson damping [D3-(BJ)] [354, 355] was used. To get precise total energies and electrical characteristics, the tetrahedron approach with Blöchl adjustments was applied [316]. To increase the convergence of the Brillouin zone integrations, all geometry optimization computations were subjected to a Gaussian smearing approach with a width of 0.05 eV [355]. To improve the description of the localized 3d manganese electrons, we introduced a Hubbard correction [356] based on the formulation of Dudarev and co-workers [357], where we used the effective parameter, $U_{\text{eff}} = 4.0$ eV, as in previous reports [358, 359, 280, 360]. To improve the convergence of the electronic energy, dipole adjustments were made perpendicular to the surface plane. The conjugate-gradient approach was used to accomplish geometry convergence, and the convergence condition was reached when the Hellmann-Feynman forces decreased below 0.01 eV/Å.

6.3. Results And Discussions

6.3.1. Low Miller Index Surfaces

We imitate by modelling the low Miller index surfaces of both the substrate LiMn_2O_4 and overlayer $\alpha\text{-Al}_2\text{O}_3$. We discuss the surface models, stability, relaxation, average Bader charges of each atom within the surfaces and their respective work functions. Finally, construct the morphologies of both materials using their surface energies as inspired by J.W. Gibbs' classic study on heterogeneous substances [273].

6.3.2. Spinel LiMn_2O_4

We modelled the spinel LiMn_2O_4 surfaces which are non-polar, stoichiometric, and symmetric as discussed [361]. We established a vacuum region of ~ 20 Å perpendicular to the slabs to aid the accommodation of the $\alpha\text{-Al}_2\text{O}_3$ coating layers on these surfaces while preventing interactions among vertical periodic images. We evaluated eight formula units (f.u.) for each of the simulated (001), (011), and (111) surfaces illustrated in [Figure 6.1](#), with corresponding unit cell areas of 8.72, 6.16 and 7.55 Å², respectively. The four bottommost atomic layers were retained fixed in their relaxed bulk locations, whereas the highest atomic layers were allowed to move throughout the geometry optimization.

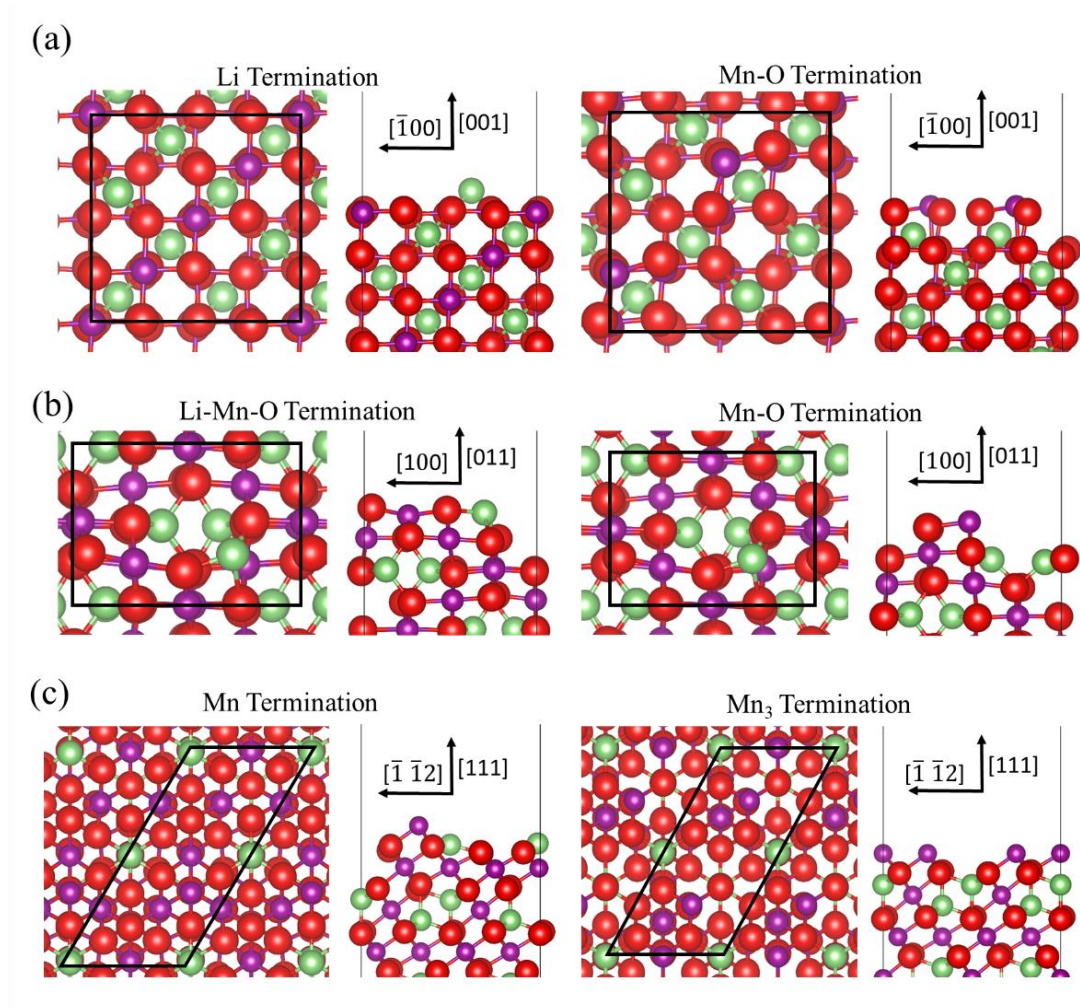


Figure 6.1: Top and side view of the (a) (001) (b) (011) and (c) (111) surface terminations after geometry optimization. The crystallographic directions and stacking sequences of the atomic layers are indicated.

The surface energies of the low Miller indices indicated in [Figure 6.1](#) before (γ^{un}) and after (γ^{rel}) relaxation, together with their respective relaxation (R) percentages were calculated using [equations 3.19](#), [3.20](#), and [3.21](#), respectively. The Li-terminated (001) surface has the lowest estimated surface energy of $0.037 \text{ eV/\AA}^2$, which is consistent with previously published findings [280, 362, 363]. According to our calculations, the (011) surface has the highest relaxation percentage $R = 50.0\%$ when compared to the unrelaxed surface slab. The computed average atomic charges observed for these stable terminations show congruence with the charges calculated for the bulk of LiMn_2O_4 [278], with the Mn atoms of the Li-terminated (001) surface showing the highest divergence of 2.6%. We also computed the work function (ϕ) for each surface, which reflects the energy required to remove one electron from the solid and place it in the vacuum. The work function was determined by subtracting the electrostatic potential energy of the vacuum (E_{vac}) from the Fermi energy (E_{F}). Our computed work function values indicate that the (011) surface is less reactive than the (001) and (111) surfaces, with the (111) surface being the most reactive.

Table 6.1: Surface energies before (γ^{un}) and after (half-relaxed (γ^{rel})), percentage of relaxation (R), average atomic charge (q) and work functions (ϕ) for LiMn_2O_4 low Miller index surfaces.

Property	Bulk [278]	Surfaces					
		(001)		(011)		(111)	
		-Li-	-MnO-	-LiMnO-	-MnO-	-MnO-	-Mn-
$\gamma^{\text{un}} (\text{eV/\AA}^2)$		0.066	0.154	0.100	0.104	0.208	0.085
$\gamma^{\text{rel}} (\text{eV/\AA}^2)$		0.037	0.110	0.050	0.066	0.087	0.052
R (%)		43.7	28.7	50.0	37.2	57.9	38.0
$q(\text{Li})$ (e/atom)	0.88	0.897	0.902	0.897	0.891	0.890	0.892
$q(\text{Mn})$ (e/atom)	1.78	1.734	1.680	1.739	1.738	1.604	1.744
$q(\text{O})$ (e/atom)	-1.11	-1.091	-1.065	-1.094	-1.092	-1.025	-1.095
ϕ (eV)		4.531	4.215	4.740	4.263	3.171	3.658

6.3.3. Corundum α -Al₂O₃

Similarly, we modelled all the corundum α -Al₂O₃'s seven low-Miller index surfaces. The optimized surface structures of the most stable α -Al₂O₃ terminations are shown in [Figure 6.2](#), and [Table 6.2](#) provides their computed surface energies before and after relaxation, relaxation percentage, average atomic charges, and work function. As previously noted [108], the lowest surface energy of $\gamma^{rel} = 0.11$ eV/Å² for the Al-terminated (0001), which is projected to be the most stable system, which is consistent with prior research [364, 365, 366]. The O-terminated (11 $\bar{2}$ 0) facet is the second most stable, with the lowest surface energy of $\gamma^{rel} = 0.15$ eV/Å². The alumina surfaces' surface energy increases in the following order: (0001) < (11 $\bar{2}$ 0) < (01 $\bar{1}$ 0) < (11 $\bar{2}$ 1) < (10 $\bar{1}$ 1) < (01 $\bar{1}$ 1) < (10 $\bar{1}$ 0). The highest relaxed layers experienced a considerable modification during the optimization of all surfaces to their most stable configurations, according to the determined percentage of relaxation. The Al-terminated (0001) surface has the highest relaxation percentage of 56.9%, which is mostly due to the inward relaxing of dangling bonds along the z-axis. We also estimated the Bader charges for each atom on the surfaces, which showed that they were somewhat lower than the values reported for their completely coordinated corresponding ions in the bulk.

For example, on the (0001) surface, we got an average charge depletion of $q(\text{Al}) = 2.45$ e⁻/atom and an accumulation of $q(\text{O}) = -1.63$ e⁻/atom, with a difference of 1.22% in comparison to the bulk (noted in chapter 4). The work function (ϕ) shows that the (01 $\bar{1}$ 1) surface is 0.22 eV more reactive than the most stable (0001) surface.

Table 6.2: Surface energies before (γ^{un}) and after relaxation (γ^{rel}), the percentage of relaxation (R) and work function for α -Al₂O₃ surfaces. The average charge (q) of the exposed atoms is also reported.

Property	Surfaces						
	(0001) [108]	(10 $\bar{1}$ 0)	(01 $\bar{1}$ 0)	(01 $\bar{1}$ 1)	(10 $\bar{1}$ 1)	(11 $\bar{2}$ 0)	(11 $\bar{2}$ 1)
Unit cell Area ($\text{\AA}^2$)	3.26	5.18	5.44	5.18	5.44	4.49	4.49
γ^{urel} (eV/ $\text{\AA}^2$)	0.25	3.96	0.24	1.99	1.98	0.19	0.30
γ^{rel} (eV/ $\text{\AA}^2$)	0.11	3.88	0.16	1.95	1.94	0.15	0.23
R (%)	56.9	2.0	33.4	2.3	1.9	22.3	24.8
$q(\text{Al})$ (e/atom)	2.45	2.34	2.43	2.37	2.47	2.46	2.35
$q(\text{O})$ (e/atom)	-1.63	-1.52	-1.61	-1.55	-1.65	-1.64	-1.57
ϕ (eV)	4.30	5.45	4.52	4.25	5.43	5.60	5.92

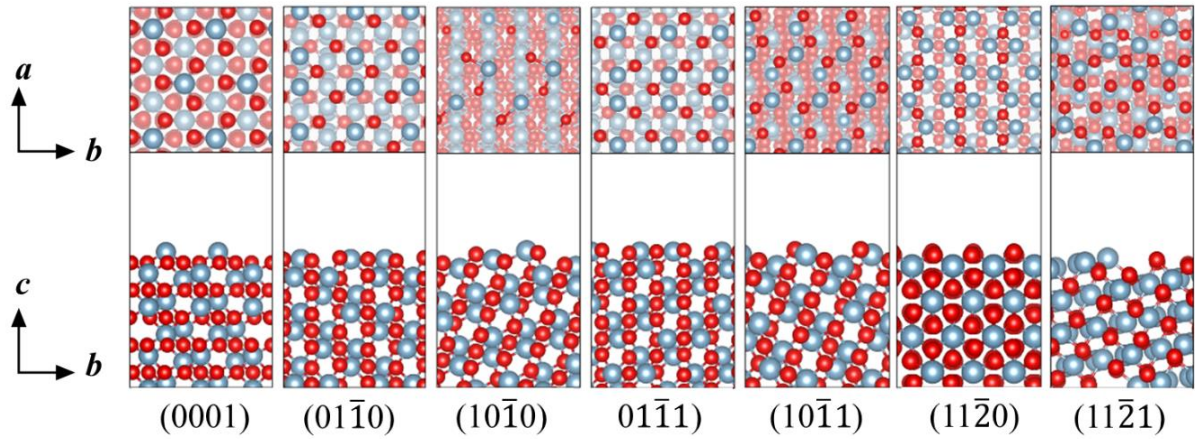


Figure 6.2: (Top panels) top views and (bottom panels) side views of the seven low-Miller index surfaces of the α -Al₂O₃. Al is in blue, and O is in red.

6.3.3.1. Wulff morphologies

We then utilised the surface energies of their respective low-Miller index surfaces and built particle morphologies for both materials. The crystal in equilibrium has the height of the facet (h_i) precisely proportional to its surface free energy (σ_i , where i = Miller index of the specific surface), and the ratio of the two is constant, according to Wulff's theorem. These can be summed up as follows:

$$\frac{\sigma_{(001)}}{h_{(001)}} = \frac{\sigma_{(011)}}{h_{(011)}} = \dots = \frac{\sigma_i}{h_i} \quad (6.1)$$

[Figure 6.3a](#) depicts the Wulff morphology of LiMn_2O_4 as a cuboctahedral particle with the (001) dominating plane. This morphology also reveals a diminishing stability trend with (001) > (011) > (111). We discovered that after delithiation, the (111) plane acquired prominence whereas the (011) surface lost relevance in the morphology [309]. As a result, we are concentrating our efforts on modelling $\alpha\text{-Al}_2\text{O}_3$ -coated LiMn_2O_4 (001) and (111) surfaces. We got a hexagonal-prism form for $\alpha\text{-Al}_2\text{O}_3$ with a dominating Al-terminated (0001) plane and a lesser fraction of the (11 $\bar{2}$ 0) and (01 $\bar{1}$ 0) surfaces. The other low-Miller index surfaces are obscured by their high surface energy in comparison to the dominating (0001) surface (see [Figure 6.3b](#)).

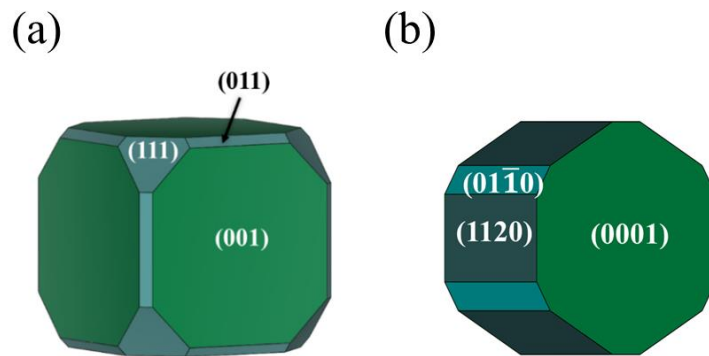


Figure 6.3: Wulff morphologies of the pristine (a) LiMn_2O_4 and (b) $\alpha\text{-Al}_2\text{O}_3$ surfaces.

6.3.4. Heteroepitaxial Interface Geometry

We analyze the scenario involving the deposition of $\alpha\text{-Al}_2\text{O}_3$ onto the major LiMn_2O_4 (001) and (111) surfaces using the surfaces of the two materials that are more prominent in the Wulff crystal shape. Given the incompatibility of the surface lattices of these two materials, we first investigate several possible configurations of the $\alpha\text{-Al}_2\text{O}_3$ overlayer over the LiMn_2O_4 substrate surfaces to achieve good surface-to-surface alignment. To create these arrangements, we used integers to extend the unit lattices of both the substrate and the overlayer along the a and b axes, as shown in [Figure 6.4a-b](#). In particular, l and k indicate the numbers used to extend the spinel LiMn_2O_4 lattice in the a and b directions, respectively, while m and n represent the equivalent expansion factors for the $\alpha\text{-Al}_2\text{O}_3$ overlayer surfaces. To assess the alignment of the surfaces, we employed the misfit (μ) calculation method introduced by Carter et al [367, 368, 369, 370]:

$$\mu = \left(1 - \frac{2\Omega}{A_{\text{LMO}} + A_{\text{Al}_2\text{O}_3}} \right) \times 100 \quad (6.2)$$

where A_{LMO} and $A_{\text{Al}_2\text{O}_3}$ are the surface areas of the LiMn_2O_4 substrate and $\alpha\text{-Al}_2\text{O}_3$ overlayer in each interface and Ω is the overlap area between the surfaces of the two materials, see [Figure 6.4c](#).

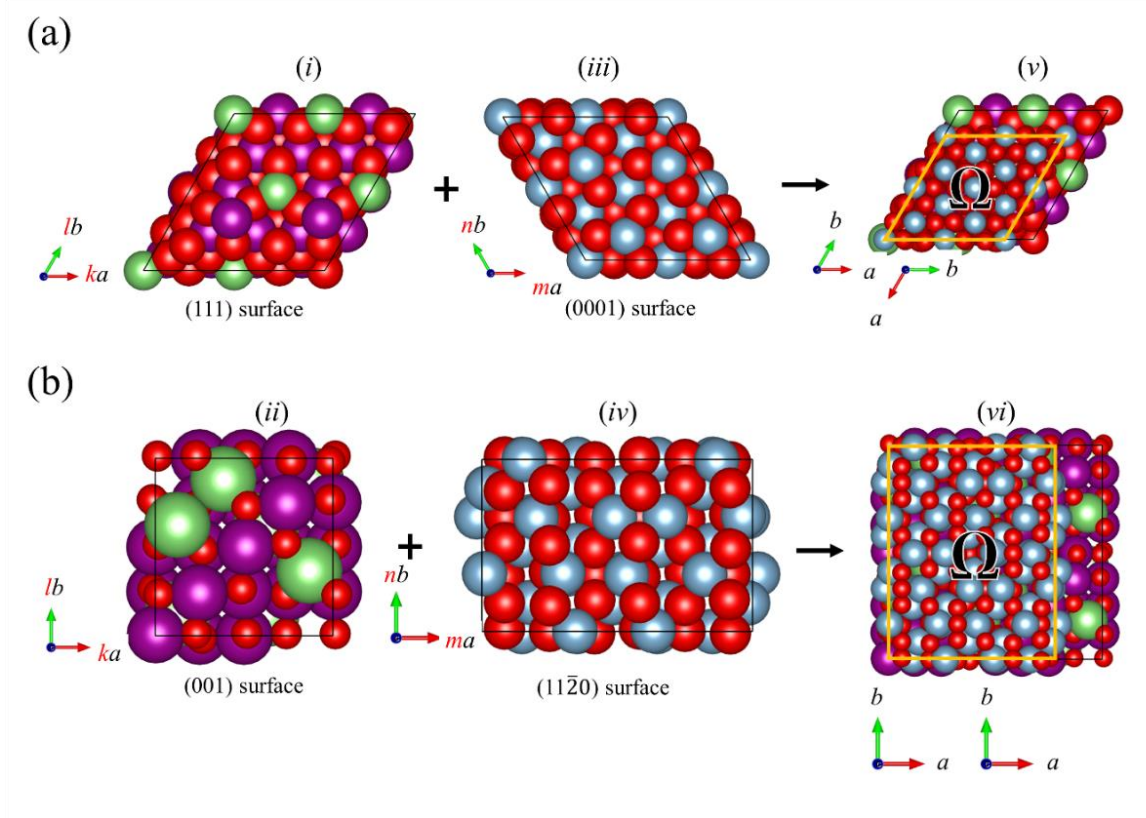


Figure 6.4: Top views of the unit cells of the isolated (*i-ii*) LiMn_2O_4 substrate and (*iii-iv*) $\alpha\text{-Al}_2\text{O}_3$ overlayer surfaces. Both surfaces are supercells of a surface unit cell expanded along the a and b directions by the k, l, m, n integers shown in red. The overlap area (Ω) of both (v) $\alpha\text{-Al}_2\text{O}_3$ (0001)// LiMn_2O_4 (111) and (vi) $\alpha\text{-Al}_2\text{O}_3$ (11 $\bar{2}$ 0)// LiMn_2O_4 (001) interfaces before coherence is outlined in orange.

Since low misfit and lattice strain values can always be achieved at extremely large interface areas and our standard *ab initio* calculations cannot handle large systems, we have limited our interface lattice area to $450 \text{ \AA}^2$. Furthermore, since our simulations require boundary conditions, we imposed a degree of interfacial coherence, by adjusting the $\alpha\text{-Al}_2\text{O}_3$ overlayer to accommodate the mismatch. We quantified this enforced strain on the overlayer with the variables δ_1^{nl} and δ_2^{km} calculated as:

$$\delta_1^{nl} = \frac{la_1 - nb_1}{nb_1} \quad (6.3)$$

$$\delta_2^{km} = \frac{ka_2 - mb_2}{mb_2} \quad (6.4)$$

where a_1 and a_2 denote the lengths of the basis vectors spanning the unit cell of the α -Al₂O₃ overlayer while b_1 and b_2 correspond to the unit cell of the LiMn₂O₄ substrate. Experimentally, the feasibility of forming an epitaxial interface between the α -Al₂O₃ (0001) and LiMn₂O₄ (111) surfaces has been discussed [371, 372]. However, the understanding of the compatibility between the α -Al₂O₃ surfaces and the LiMn₂O₄ (001) surface is limited. Consequently, our purpose is to model the α -Al₂O₃ (0001)/LiMn₂O₄(111) interface and identify the α -Al₂O₃ surface that best aligns with the substrate (001) surface. To achieve this, we compared the lattices of the seven low-Miller indices surfaces of α -Al₂O₃ with the lattice of the LiMn₂O₄(001) surface, aiming to find an overlayer surface that fits with minimal strain. Three potential surfaces were examined, *i.e.*, the α -Al₂O₃ (10 $\bar{1}$ 0), (01 $\bar{1}$ 0) and (11 $\bar{2}$ 0) facets (see the highlighted surface in [Table 6.3](#)).

Table 6.3: Equilibrium lattice parameters for the spinel LiMn_2O_4 surfaces and corundum $\alpha\text{-Al}_2\text{O}_3$ created from their corresponding optimized bulk structures.

Material	Surface	a (Å)	b (Å)	α (°)	β (°)	γ (°)
LiMn_2O_4	(001)	8.34	8.34	90	90	90
	(011)	8.35	5.90	90	90	90
	(111)	5.90	11.81	90	90	120
$\alpha\text{-Al}_2\text{O}_3$	(0001)	4.77650	4.77650	90	90	120
	(10 $\bar{1}$ 0)	4.77650	13.02467	90	90	90
	(01 $\bar{1}$ 0)	4.77650	13.02467	90	90	90
	(01 $\bar{1}$ 1)	4.77650	13.02467	90	90	90.9130
	(10 $\bar{1}$ 1)	4.77650	13.02467	90	90	90.9130
	(11 $\bar{2}$ 0)	13.02467	8.27314	90	90	90
	(11 $\bar{2}$ 1)	8.27314	13.02467	90	90	72.6519

6.3.4.1. The $\alpha\text{-Al}_2\text{O}_3$ (0001)// LiMn_2O_4 (111) interface

For the $\alpha\text{-Al}_2\text{O}_3$ (0001)// LiMn_2O_4 (111) interface, we have presented the misfit percentages relative to the matching area in [Figure 6.5](#). A summary of the four configurations with the lowest misfits is provided in [Table 6.4](#). Given that interfaces with lattice mismatches exceeding 5% are unlikely to exist, we have considered only geometry configurations with μ below that value. The lowest calculated misfit percentage was 2.75% for the interface with the configuration $klmn = \{1132\}$. The calculated strain of $\delta_1^{nl} = \delta_2^{km} = -0.57$ suggests that the $\alpha\text{-Al}_2\text{O}_3$ overlayer should be compressed along both a and b to accommodate the (111) surface of the substrate.

Table 6.4: Geometry misfit percentages (μ) and strain parameters ($\delta_1^{nl}, \delta_2^{km}$) for various configurations of α -Al₂O₃ (0001) surfaces on the major (111) surfaces of LiMn₂O₄

LiMn ₂ O ₄		α -Al ₂ O ₃		δ_1^{nl}	δ_2^{km}	Area (Å ²)	μ (%)
k	l	m	n				
1	1	3	2	-0.59	-0.59	112.81	2.75
1	1	3	3	-0.73	-0.73	120.76	16.14
1	1	2	2	-0.38	-0.38	79.03	17.91
2	1	3	3	-0.45	-0.45	146.54	27.14

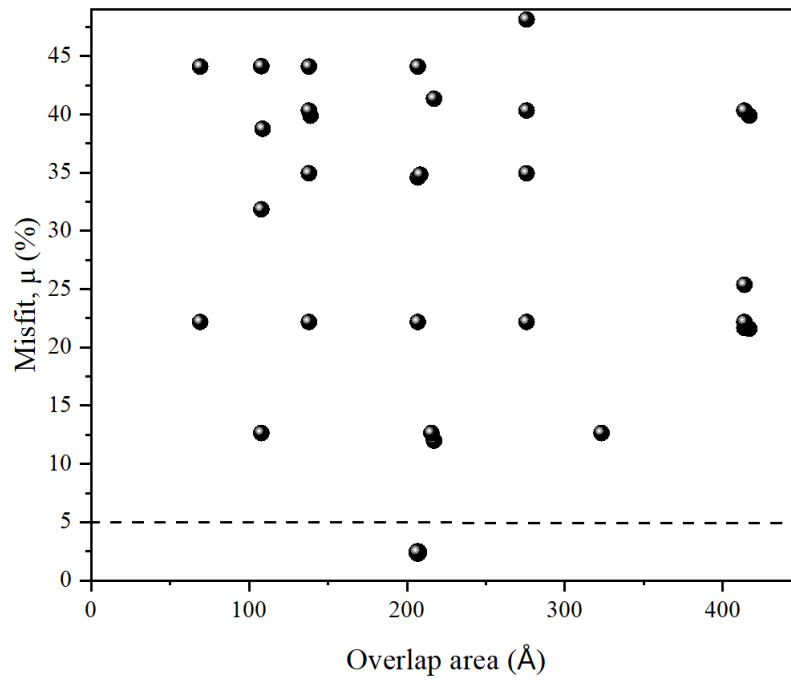


Figure 6.5: Plot of the interfacial geometry misfits for the LiMn₂O₄ (111) substrate and the α -Al₂O₃ (0001) overlayer for different overlap areas.

For validation, we also calculated the interfacial geometry misfits for the α -Al₂O₃ (0001)//LiMn₂O₄ (111) interface considering similar $klmn$ configurations using the near coincidence site lattice (NCSL) theory [373, 374]. The misfit percentages we computed as:

$$F = \frac{2[a_{\text{LMO}}\sqrt{\sum \text{LiMn}_2\text{O}_4} - a_{\text{alumina}}\sqrt{\sum \text{Al}_2\text{O}_3}]}{a_{\text{LMO}}\sqrt{\sum \text{LiMn}_2\text{O}_4} + a_{\text{alumina}}\sqrt{\sum \text{Al}_2\text{O}_3}} \quad (6.5)$$

where a_{LMO} and a_{alumina} are the lattice parameters of the LiMn_2O_4 substrate and $\alpha\text{-Al}_2\text{O}_3$ overlayer, respectively. $\Sigma \text{LiMn}_2\text{O}_4$ and $\Sigma \text{Al}_2\text{O}_3$ are defined as the planar reciprocal coincidence density at the interface, calculated as:

$$\Sigma \text{LiMn}_2\text{O}_4 = k^2 + l^2 + kl \text{ and } \Sigma \text{Al}_2\text{O}_3 = m^2 + n^2 + mn \quad (6.6)$$

where the k , l , m , and n are the integers multiplying the unit cells of LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$, respectively. The rotational angle of the overlayer with respect to the substrate was calculated as:

$$\theta = \sin^{-1} \left[\frac{k\sqrt{\frac{3}{2}}}{\sqrt{k^2 + l^2 + kl}} \right] \pm \sin^{-1} \left[\frac{m\sqrt{\frac{3}{2}}}{\sqrt{m^2 + n^2 + mn}} \right] \quad (6.7)$$

[Table 6.5](#) lists the calculated rotational angles (θ) and geometry misfits (F) of the $\alpha\text{-Al}_2\text{O}_3$ (0001) surface on the LiMn_2O_4 (111) substrate. The lowest calculated interfacial misfit was observed for the configuration $\{1132\}$ ($\Sigma \text{LiMn}_2\text{O}_4 / \Sigma \text{Al}_2\text{O}_3 = 3/19$) with $F = -1.9\%$. Note that the negative misfit indicates that the $\alpha\text{-Al}_2\text{O}_3$ overlayer is compressed when enters coherence with the substrate. The $\{1132\}$ configuration was also found to have negative strain values, indicating compression of the overlayer to accommodate over the substrate. The $\{1133\}$ configuration has the second lowest misfit of -19.4% for a rotation angle of 0° .

Table 6.5: Calculated geometry misfit for the α -Al₂O₃ (0001) surface on the LiMn₂O₄ (111) substrate using the near coincidence site lattice (NCSL) theory.

LiMn ₂ O ₄ substrate			α -Al ₂ O ₃ overlayer			θ		F
$\sum$ LiMn ₂ O ₄	k	l	$\sum$ Al ₂ O ₃	m	n	(°)		(%)
3	1	1	27	3	3	30.5	0.0	-19.4
3	1	1	19	3	2	23.9	-6.6	-1.9
3	1	1	12	2	2	30.5	0.0	21.0
7	1	2	19	3	2	36.9	17.5	40.0
3	1	1	7	1	2	19.6	-10.9	47.2
7	1	2	13	1	3	14.2	-5.2	57.8

3.1.1.1. The α -Al₂O₃ (11 $\bar{2}$ 0)//LiMn₂O₄(001) interface

We initially compared the misfit percentages of the α -Al₂O₃ (10 $\bar{1}$ 0), (01 $\bar{1}$ 0) and (11 $\bar{2}$ 0) surfaces on the substrate LiMn₂O₄ (001) surface (see [Table 6.6](#)). The lowest misfit percentage of 2.40% indicates that the (11 $\bar{2}$ 0) surface fits on the (001) substrate surface with the geometry configuration $klmn = \{3121\}$. The calculated strain variables $\delta_1^{nl} = -0.04$ and $\delta_2^{km} = 0.51$ suggest that the (11 $\bar{2}$ 0) The surface should be compressed and expanded along a and b , respectively, to achieve coherence between the two materials. Also, we have considered only geometry configurations with μ below that value since interfaces with lattice mismatches exceeding 5% are unlikely to exist experimentally.

Table 6.6: Interfacial geometry misfit (μ) for α -Al₂O₃ (10 $\bar{1}$ 0), (01 $\bar{1}$ 0) and (11 $\bar{2}$ 0) on the LiMn₂O₄ (001) substrate surface (μ values are restricted to less than 60%). The calculated overlayer area (Ω) and strain variables ($\delta_1^{nl}, \delta_2^{km}$) are also reported.

Interfaces overlayer//substrate	$klmn$	Ω ($\text{\AA}^2$)	δ_1^{nl}	δ_2^{km}	μ (%)
(10 $\bar{1}$ 0)//(001)	1322	208.44	0.31	-0.52	8.8
	1211	79.63	-0.13	-0.68	17.9
	1211	79.63	2.49	0.28	20.8
	1222	138.96	-0.13	-0.68	28.3
	1231	108.57	0.16	-0.57	33.3
(01 $\bar{1}$ 0)//(001)	1312	208.44	0.31	-0.04	8.8
	1211	108.57	0.75	0.28	17.6
	3221	248.85	1.62	0.92	25.2
	1111	69.48	-0.13	-0.36	28.3
	3121	159.26	0.31	-0.04	30.3
(11 $\bar{2}$ 0)//(001)	3121	206.88	-0.04	0.51	2.4
	2111	107.75	0.28	1.02	12.6
	1111	68.96	-0.36	0.01	22.2
	3111	107.75	0.92	2.02	31.8
	2131	137.92	-0.57	-0.33	40.3

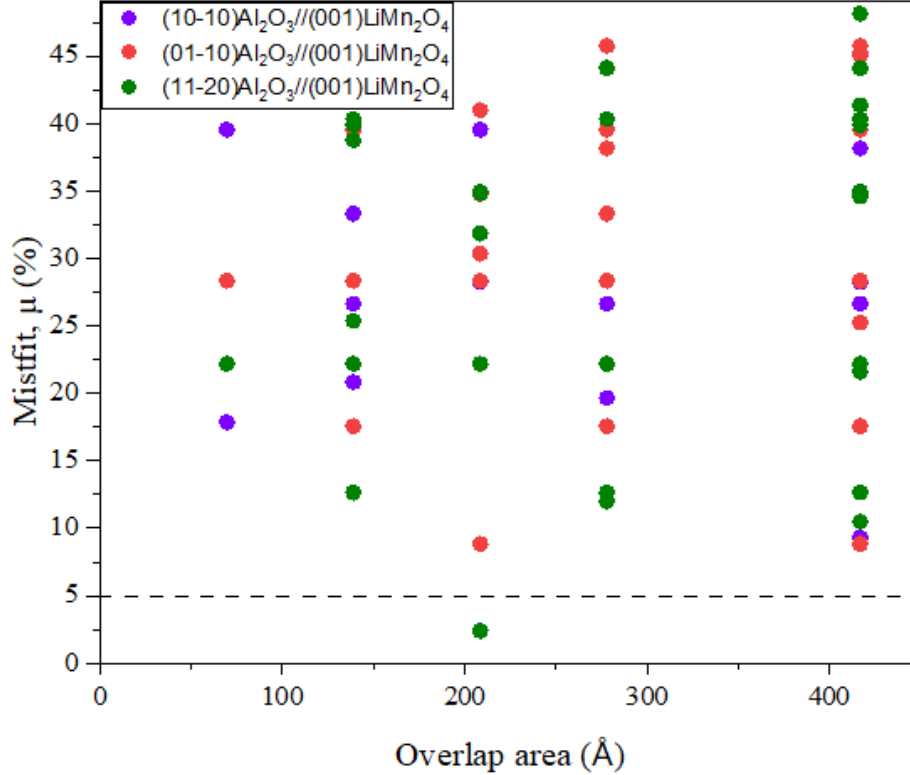


Figure 6.6: Plot of the interfacial geometry misfits for the LiMn₂O₄ (001) substrate and α -Al₂O₃ overlayer for different overlap areas.

6.3.5. Adhesion Energies and Interplanar Distances

To obtain insight into the interfacial stability, we calculated the adhesion energy (E_{adh}), which quantifies the energy acquired when the interface barrier between the two materials forms, as follows:

$$E_{\text{adh}} = \frac{E_{\text{Inter}}^{\text{DFT}} - (E_{\text{Al}_2\text{O}_3}^{\text{DFT}} + E_{\text{LMO}}^{\text{DFT}})}{A} \quad (6.8)$$

where $E_{\text{Al}_2\text{O}_3}^{\text{DFT}}$, and $E_{\text{LMO}}^{\text{DFT}}$ represent the total energies of an unsupported α - Al_2O_3 overlayer and a relaxed major surface of the LiMn_2O_4 substrate. The term $E_{\text{Inter}}^{\text{DFT}}$ stands for the total energy of the relaxed heteroepitaxial interface while A denotes the interface area. Taking into account the effect of coating thickness on Li^+ intercalation during cycling [375], we investigated heterostructures with varying α - Al_2O_3 thicknesses (n_1 , n_2 , and n_3). To create the most stable configurations during relaxing, all interfaces were adjusted. The interfaces with varied overlayer thicknesses and their accompanying adhesion energies are summarized in [Figure 6.7](#). Positive interfacial energies indicate stability, while negative values indicate unstable heterostructures. Notably, the monolayer α - Al_2O_3 (n_1) had the highest predicted energies, with the most stable $\{11\bar{3}2\}$ structure providing $E_{\text{adh}} = 0.16 \text{ eV}/\text{\AA}$. E_{adh} drops as thickness increases, implying that increasing thickness contributes to system instability. In contrast to experiments [221, 376, 377] with amorphous coating thicknesses of up to 15 nm on an $\sim 500 \text{ nm}$ LiMn_2O_4 substrate, our computational method was unable to model such large systems due to the prohibitive computational cost of our DFT method for a large number of atoms. Our calculations also revealed that overlayer-surface interactions at the boundary form Al-O, Mn-O and Li-O bonds, while subsequent α - Al_2O_3 overlayers exhibit disorder, except for the more crystalline $\{3121\}n_3$ configuration.

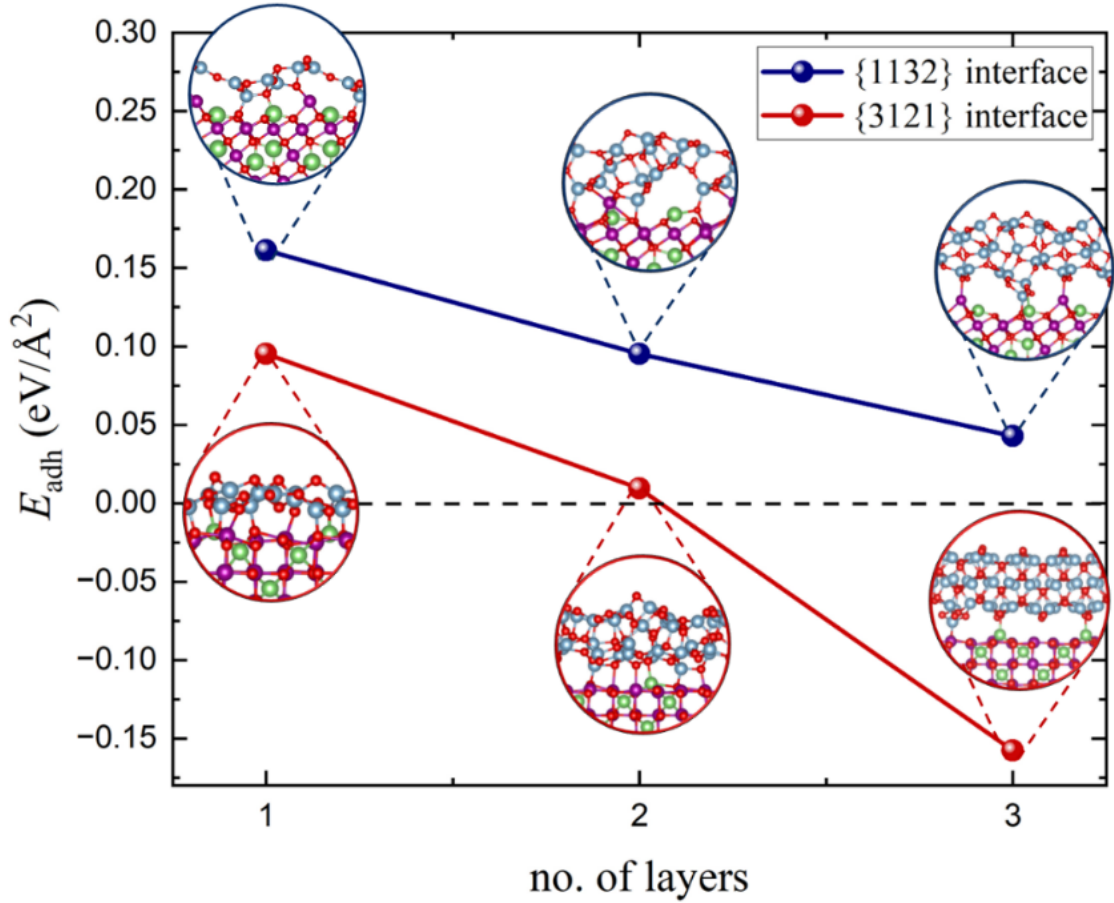


Figure 6.7: Calculated adhesion energies for potential interfaces α -Al₂O₃ (0001)// LiMn₂O₄ (111) and α -Al₂O₃(11 $\bar{2}$ 0)//LiMn₂O₄(001) with geometry configurations {1132} and {3121}, respectively, for various overlayer thicknesses.

We also investigated the interplanar distances (Δ_{ij}) of both the substrate and coating layers within the α -Al₂O₃ (0001)// LiMn₂O₄ (111) and α -Al₂O₃(11 $\bar{2}$ 0)//LiMn₂O₄(001) interfaces with respect to their equivalent distances in the relaxed pristine surfaces (see Figure 6.8). The interplanar distances of the α -Al₂O₃ and LiMn₂O₄ surfaces in the interfaces formed with varying number of coating layers were calculated as $\Delta_{ij} = \left(\frac{d_{ij} - d_{ij}^0}{d_{ij}^0} \right) \times 100$, where d_{ij} represents the separation distance between the relaxed i and $j = i + 1$ layers, and d_{ij}^0 is the corresponding distance in the pristine LiMn₂O₄ surfaces or the unsupported α -Al₂O₃ overlayer. As shown in Figure 6.8 (a-b), it was evident that the dangling atoms of the (001) and (111)

substrates were slightly displaced outward towards the interacting atoms of α -Al₂O₃ within the LiMn₂O₄ surfaces upon interface relaxation. The dangling bonds of Mn in configuration {1132} moved outward in response to the formation of Mn-O and Al-O bonds with the α -Al₂O₃ coating, with the maximum shift of 3.8% observed for n_3 . Similarly, on the Mn-terminated (111) surface, the dangling bonds in the first atomic layer of the interface with configuration {3121} exhibited significant outward relaxation of 3.8% for both n_3 and n_2 . In both cases, the subsequent (MnO) layer experienced inward shifts of 1.1 and 1.9% for n_1 {1132} and n_3 {3121}, respectively, during relaxation. Additionally, we noted minor relaxation in the subsequent layers of both interface models as we moved towards the lower planes where the atoms were fixed at their bulk positions. Similarly, as shown in [Figure 7 \(c-d\)](#), we analysed the shifts of the interplanar distances of the overlayer within the {3121} heterostructures in relation to the pristine unsupported α -Al₂O₃ surfaces. Our results show that the Al and O atoms are displaced inwards and outwards, respectively, upon formation of the Al-O and Mn-O interfacial bonds. However, a different trend was observed for the 1132 n_2 interface, where the Al ions moved outwards, suggesting a steric repulsion between the Mn/Li and Al atoms. The largest displacements were observed at 15.2% and 12.4% for 1132 n_2 (O)-6 and 3121 n_1 (Al)-9, respectively, due to the formation of Al-O interfacial bonds. As the thickness of the coating layers was increased, we observed smaller interplanar relaxation, showing that the system tends to remain crystalline.

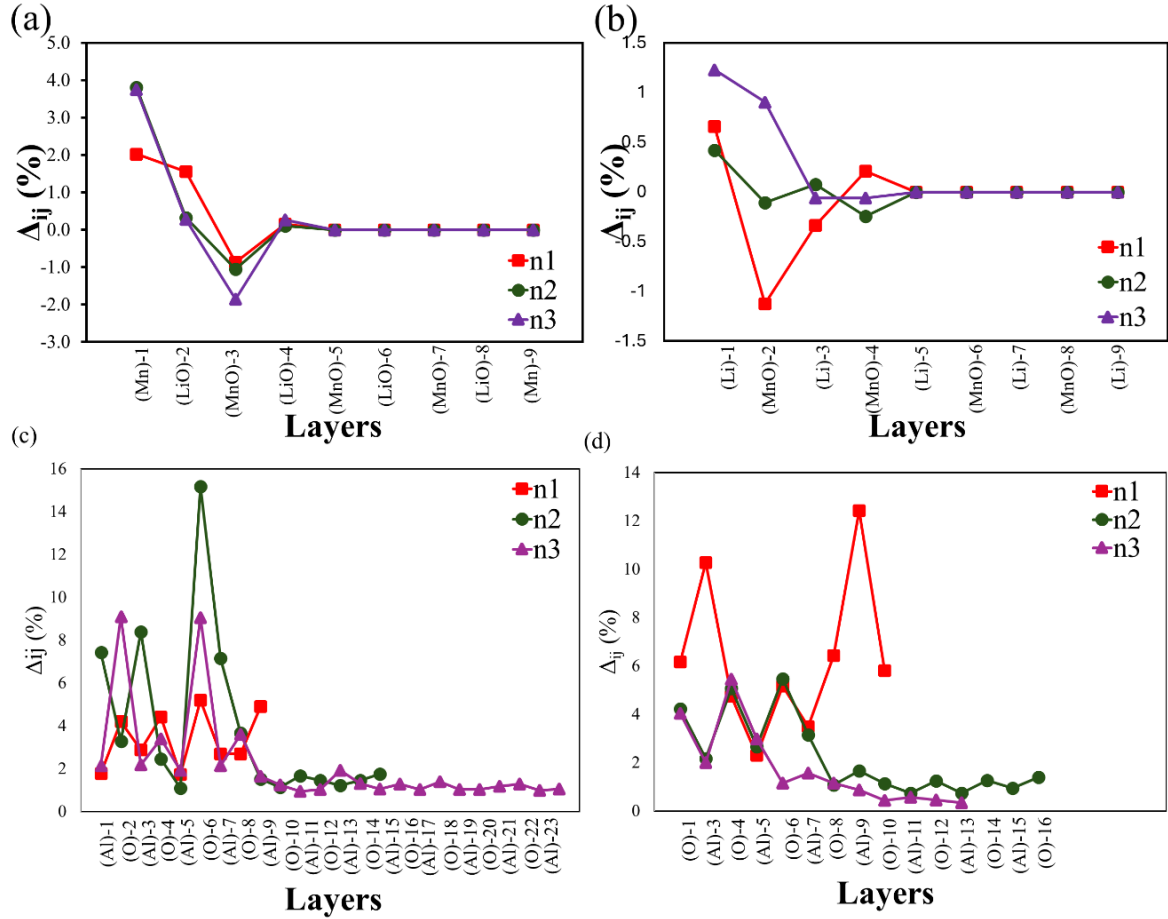


Figure 6.8: Interplanar distance relaxation (Δ_{ij}) of the (*a-b*) LiMn_2O_4 (001) and (111) substrate surfaces and (*c-d*) $\alpha\text{-Al}_2\text{O}_3$ (0001) and ($11\bar{2}0$) overlayer surfaces in heterostructures compared to their isolated pristine counterparts for $\alpha\text{-Al}_2\text{O}_3(0001)/\text{LiMn}_2\text{O}_4(111)$ and $\alpha\text{-Al}_2\text{O}_3(11\bar{2}0)/\text{LiMn}_2\text{O}_4(001)$ with the configurations {1132} and {3121}, respectively, for various overlayer thicknesses.

6.3.6. Electronic Properties

We now quantify the electron charge accumulation/depletion on the LiMn_2O_4 substrate within the interface and compare it to the pristine surface, see [Table 6.7](#). In general, we observed a minor electronic charge gain on the substrate, which was provided by the $\alpha\text{-Al}_2\text{O}_3$ overlayer in both $\alpha\text{-Al}_2\text{O}_3(0001)/\text{LiMn}_2\text{O}_4(111)$ and $\alpha\text{-Al}_2\text{O}_3(11\bar{2}0)/\text{LiMn}_2\text{O}_4(001)$ heterostructures with varying $\alpha\text{-Al}_2\text{O}_3$ layers. The largest charge difference of $\Delta q = -0.90 e^-$ was noted for the {3121}

configuration with a single $\alpha\text{-Al}_2\text{O}_3$ layer. However, a slight charge depletion of $0.06 e^-$ in the overlayer was observed for $n_3\{3121\}$, attributed to the formation of Al-O and Li-O bonds, which contributed -0.28 and $-0.002 e^-$, respectively. With the increase in the number of $\alpha\text{-Al}_2\text{O}_3$ layers, the charge transfer tended to decrease except for $n_2\{1132\}$, which exhibited $\Delta q = -0.71 e^-$. We further analysed the average charge transfer on the exposed Mn, Li, and O atoms of LiMn_2O_4 interacting with the overlayer and forming the Al-O, Mn-O and Li-O bonds. A consistent trend emerged of charge depletion from the interacting Mn atom to the overlayer O atom, reaching a maximum of $0.41 e^-/\text{atom}$ for $n_2\{1132\}$. As for the interacting Li atoms in the top layer, we observed a negligible charge accumulation from the overlayer O atom, with a minimal charge gain of $\Delta q = -0.002 e^-/\text{atom}$. Similarly, a general charge accumulation was observed on the interacting oxygen in the top layer forming the Al-O bond, with a negligible charge gain of $\Delta q = -0.01 e^-/\text{atom}$ observed in the case of $n_1\{1132\}$. Notably, the charge transfer for Al-O interactions increased with the number of $\alpha\text{-Al}_2\text{O}_3$ layers for $\{1132\}$, while the opposite trend was observed for $\{3121\}$.

Table 6.7: Electronic charge transfers on the LiMn_2O_4 substrate ($\Delta q(\text{LiMn}_2\text{O}_4)$) and individual interacting atoms ($\Delta q(\text{Li})$, $\Delta q(\text{Mn})$, and $\Delta q(\text{Al})$). Positive charge transfer values indicate depletion while negative indicate accumulation. The work functions (ϕ) calculated for different numbers of $\alpha\text{-Al}_2\text{O}_3$ layers are also reported.

Interface $\alpha\text{-Al}_2\text{O}_3//\text{LiMn}_2\text{O}_4$	$klmn$	No. of layers	$\Delta q(\text{LiMn}_2\text{O}_4)$ (e^-)	$\Delta q (e^-/\text{atom})$			ϕ (eV)
				$q(\text{Mn})$	$q(\text{Al})$	$q(\text{Li})$	
(0001)//(111)	1132	n_1	-0.17	0.28	0.02	-0.023	5.78
		n_2	-0.71	0.83	-1.09	-0.015	5.87
		n_3	-0.08	0.28	-0.66	-0.004	5.39
(11 $\bar{2}$ 0)//(001)	3121	n_1	-0.90	0.03	-0.25	-0.041	5.84
		n_2	-0.13	0.04	-0.26	0.019	6.31
		n_3	0.06	-	-0.28	-0.002	5.76

[Figure 6.9](#) provides a visual representation of the charge density difference ($\Delta\rho$) between the two materials within the heterostructure. The $\Delta\rho$ values are depicted as the charge difference between the total charge density of the interfaces (ρ_{int}) and the sum of the electronic charge densities of the isolated LiMn_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ surfaces in the same geometry of the heterojunction, *i.e.*, $\Delta\rho = \rho_{\text{inter}} - (\rho_{\text{LMO}} + \rho_{\alpha\text{-Al}_2\text{O}_3})$. These visualizations were generated using VESTA (Visualization for Electronic and Structural Analysis) [376], with yellow indicating charge accumulation and blue representing charge loss. Notably, the interaction involving Mn atoms exhibits charge depletion, which is offset by the accumulation of charge on the interacting O atoms within the $\alpha\text{-Al}_2\text{O}_3$ overlayer. Additionally, we observed minor charge fluctuations on the neighbouring Al atom within the overlayer. The interacting O atom has a propensity for charge accumulation at the expense of the interacting Al atom. Conversely, there is a minimal charge gain observed on the Li-O bond, which is further observed on the neighbouring O atoms in the substrate LiMn_2O_4 . In conjunction with the charge transfer analysis, we also investigated the energy required to remove an electron from the Fermi level into the vacuum, known as the work function (ϕ). In both interface configurations, we noted the largest work function values for $n = 2$, with the peak value reaching 6.31 eV for the {3121} heterojunction. This trend of increasing work function values relative to the pristine surfaces implies that the coated surfaces exhibit reduced reactivity.

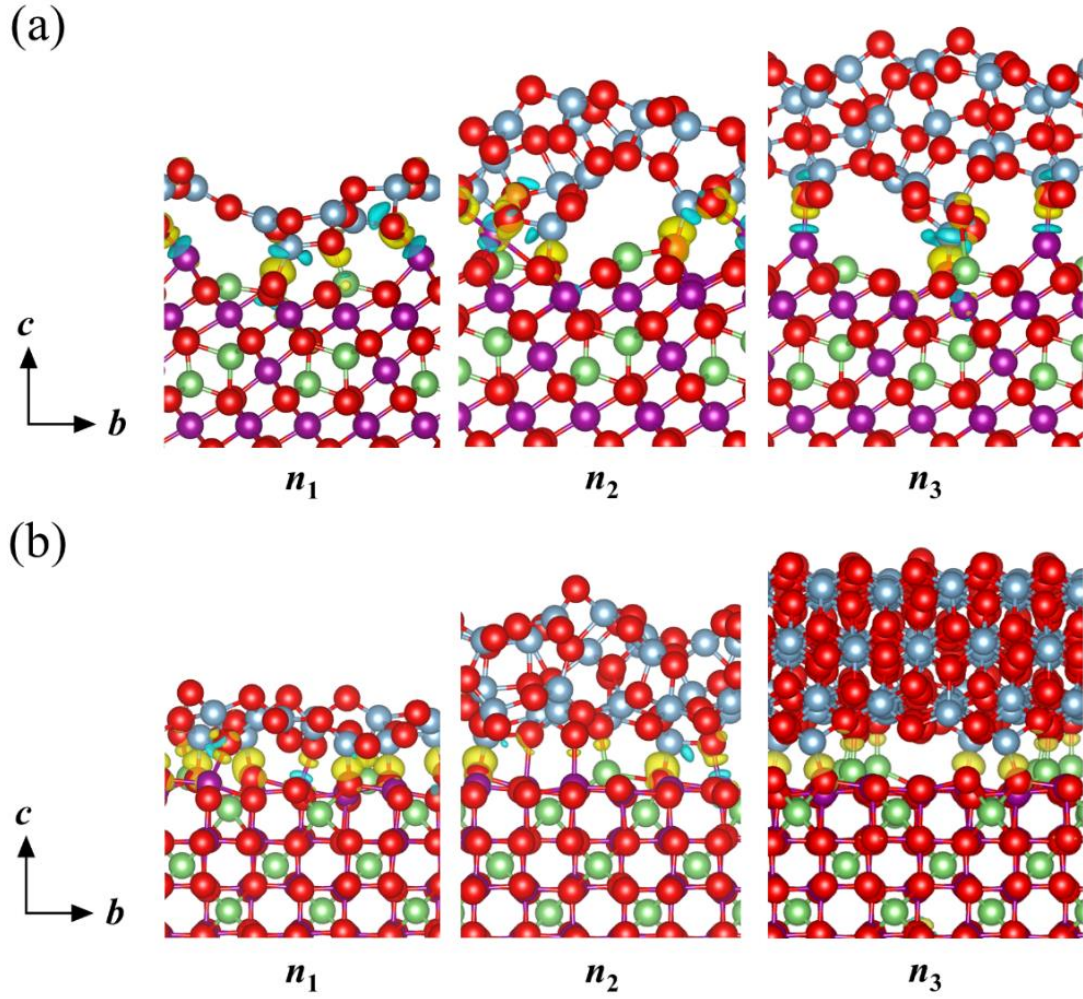
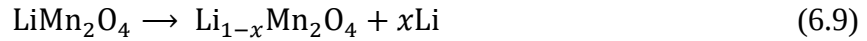


Figure 6.9: Charge density difference (Δq) in the α -Al₂O₃//LiMn₂O₄ heterostructures with the (a) {1132} and (b) {3121} configurations and a varying number of overlayers (n_1 , n_2 , n_3). The iso-surfaces are displayed at ± 0.0068 , and ± 0.0076 e/Å³, respectively. Accumulated charge is represented in yellow and charge depletion is indicated in blue.

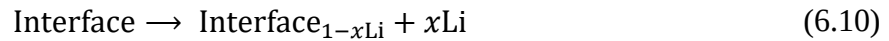
6.3.7. Partial Delithiation Thermodynamics

The mobility of lithium ions during cycling significantly impacts a battery's performance, encompassing its capacity, energy density and cycle life. To delve into the effect of partial delithiation on the coated LiMn₂O₄ surfaces relative to isolated surfaces, we explored a sequential Li removal from the top layers of the (001) and (111) surfaces of the spinel substrate within the α -Al₂O₃//LiMn₂O₄ interface, with varying α -Al₂O₃ thicknesses. The Li vacancy

formation energies ($\Delta E_{\text{inter-Li}}$) for the partially delithiated pristine/interface models were calculated and plotted against the number of Li atoms removed (see [Figure 6.10](#)). For the pristine (001) and (111) surfaces, we consider the half-reaction during cathode during cycling as follows:



In this process, lithium ions are extracted from the cathode and migrate through the electrolyte to the anode while traversing the external circuit to the anode, forming Li atoms. We simulated the Li atom removal from the surfaces of the $\alpha\text{-Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ heterostructures as:



The vacancy formation energies for both processes were calculated using:

$$\Delta E_{\text{LMO}-x\text{Li}}^f = (E_{\text{LMO}-x\text{Li}} + xE_{\text{Li}}) - E_{\text{LMO}} \quad (6.11)$$

$$\Delta E_{\text{inter}-x\text{Li}}^f = (E_{\text{inter}-x\text{Li}} + xE_{\text{Li}}) - E_{\text{Inter}} \quad (6.12)$$

where $E_{\text{LMO}-x\text{Li}}$, $E_{\text{inter}-x\text{Li}}$ and E_{LMO} , E_{Inter} are the total energies of the surfaces/interfaces with and without Li defects, while E_{Li} is the total energy of an isolated Li atom in a *bcc* unit cell and x is the number of removed lithium atoms. Positive values suggest that Li removal from the interfaces is an endothermic process, while an exothermic and favourable process would have negative energy. [Figure 6.10](#) indicates that the removal of Li from the pristine spinel requires energy, as the calculated vacancy formation energies are all positive for both the (001) and (111) surfaces. This coincides with Li-ion battery operation since the charging

process requires energy to move the Li^+ ions from the cathode to the anode material. Relative to the pristine (001) and (111) surfaces of LiMn_2O_4 , the lower vacancy formation energies in the $\alpha\text{-Al}_2\text{O}_3//\text{LiMn}_2\text{O}_4$ heterostructures suggest that surface delithiation on the coated surfaces demands less energy.

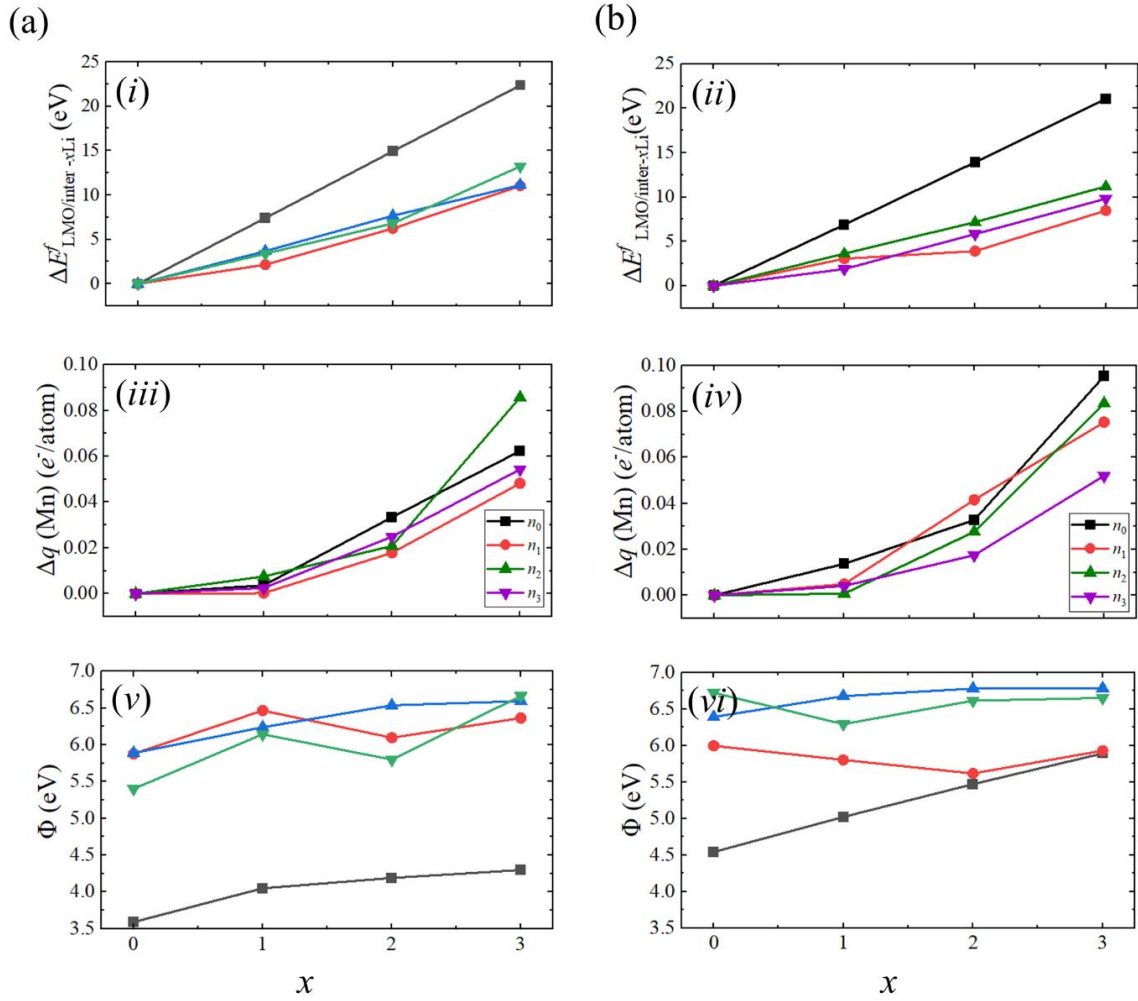


Figure 6.10: Partial delithiation thermodynamic properties for (a) $\{1132\}$ $\alpha\text{-Al}_2\text{O}_3(0001)//\text{LiMn}_2\text{O}_4(111)$ interface and (b) $\{3121\}$ $\alpha\text{-Al}_2\text{O}_3(11\bar{2}0)//\text{LiMn}_2\text{O}_4(001)$ interface. The calculated properties include (i – ii) Li vacancy of formation ($\Delta E_{\text{LMO}/\text{Inter}-x\text{Li}}^f$), (iii–iv) atomic Bader charges of Mn atoms near the vacancy ($\Delta q(\text{Mn})$), and the (v – vi) work function (ϕ) as a function of a number of lithium atoms removed (x).

For the $\alpha\text{-Al}_2\text{O}_3(0001)/\text{LiMn}_2\text{O}_4(111)$ interface, the monolayer (n_1) shows the lowest energy with n_2 and n_3 showing approximately the same energy for $x = 1$ and 2. However, at $x = 3$, n_2 shows relatively higher vacancy energy. At $x = 1$, the $\alpha\text{-Al}_2\text{O}_3(11\bar{2}0)/\text{LiMn}_2\text{O}_4(001)$ interface containing a monolayer (n_1) and three layers (n_3) of $\alpha\text{-Al}_2\text{O}_3$ with the $\{3121\}$ configuration exhibit the lowest vacancy formation energies of 2.16 and 1.89 eV, respectively. For the $\{3121\}$ configuration, we found that n_3 has the lowest Li vacancy formation energy, although the monolayer n_1 becomes less endothermic with increased lithium removal. Bader charge analysis of neighbouring Mn atoms generally shows increased charge depletion, escalating with more Li vacancies. Neighboring Mn atoms lose charge to the oxygen atoms compensating for the defects. The calculated work functions (ϕ) for the pristine surfaces rise with greater Li removal, signifying reduced reactivity upon partial delithiation. Similar trends emerge for the heterostructures, with ϕ decreasing for the $\{1132\}$ n_1 and n_2 configurations between $x = 1$ and 2, and for the $\{3121\}$ n_1 configuration from $x = 0$ to 2, slightly declining for n_2 between $x = 0$ and 1. However, compared to the pristine surfaces, lithium removal from the heterostructures results in less reactive systems, except in the case of the $\{3121\}$ n_1 configuration.

Summary

We have used density functional theory (DFT+U) calculations to simulate the $\alpha\text{-Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ (001) and (111) interfaces to mimic the spinel LiMn_2O_4 cathode material coated with corundum $\alpha\text{-Al}_2\text{O}_3$. We have considered the near coincidence site lattice (NCSL) theory method and determined that the $\{1132\}$ and $\{3121\}$ configurations provided the best alignment, with the lowest calculated misfit of 2.75 and 2.40% for the $\alpha\text{-Al}_2\text{O}_3$ (0001)/ LiMn_2O_4 (111) and $\alpha\text{-Al}_2\text{O}_3$ ($11\bar{2}0$)/ LiMn_2O_4 (001) interfaces, respectively. The calculation of the adhesion energies for one (n_1), two (n_2) and three (n_3) $\alpha\text{-Al}_2\text{O}_3$ overlayers suggest that the heterostructures become less stable as the coating thickness increased. The

relaxation of the α -Al₂O₃ overlayer resulted in disorder at the boundaries for n_1 , and n_2 , but showed limited surface-surface changes at the boundaries for n_3 . We observed a minor electronic charge gain on the substrate, with a negligible charge depletion on the overlayer α -Al₂O₃ for both heterostructures at different coating thicknesses. Notably, the largest charge transfer of $\Delta q = -0.90 e^-$ was calculated for {3121} n_1 , which was attributed to electronic density gain on the interacting O and Li atoms, forming Al-O and Li-O, and partial depletion on the Mn atoms. For both interfaces, we observed the largest work function and smallest reactivity for $n = 2$. Finally, we investigated the effect of Li vacancy formation to simulate the charged surfaces/interfaces. Our findings aligned with the theoretical understanding of Li-ion battery operation, as we observed an increase in vacancy formation energies corresponding to the number of Li atoms removed from both pristine LiMn₂O₄ (001) and (111) surfaces. This trend was consistent for the heterostructures as well. Furthermore, our analysis of work functions suggested that the incorporation of an overlayer and partial delithiation led to a decrease in reactivity in most cases, except for {3121} n_1 . These findings collectively contribute to our understanding of how α -Al₂O₃ coatings impact the properties and behaviour of LiMn₂O₄ surfaces in the context of lithium-ion batteries. In future work, we aim to explore the effects of temperature and the formation of an amorphous Al₂O₃ deposition using molecular dynamics techniques. In addition, we will aim to provide a clear understanding of the kinetics and thermodynamic properties of the deposition of amorphous Al₂O₃ films and their effect on the electrolyte.

CHAPTER 7

7. LiMn_2O_4 Nb-doping and Electrolyte (Hydrogen Fluoride and Ethylene Carbonate) Surface Adsorptions

This chapter has been published in the Journal of the Electrochemical Society (JES).

Cation/anion doping is another proposed modification approach for reducing the quantity of trivalent manganese (Mn^{3+}) ions that undergo a disproportionation process in lithium manganese oxide-based (LiMn_2O_4) lithium-ion batteries. The impact of surface doping on the primary LiMn_2O_4 surfaces and their interactions with the electrolyte components, on the other hand, is not entirely known. As a result, this chapter used density functional theory (DFT) simulations to study the influence of surface Nb-doping on the principal LiMn_2O_4 (001), (011), and (111) surfaces. The Nb elements are replaced on the Mn-sites of the first (Nb_{first}), second ($\text{Nb}_{\text{second}}$), and top and bottom (Nb_{both}) layers. The stability of Nb-doped surfaces was investigated by computing surface-free energies in comparison to pure LiMn_2O_4 surfaces. In addition, we studied the effect of electrolyte adsorptions (ethylene carbonate (EC) and hydrogen fluoride (HF)) on Nb-doped surfaces. Adsorptions are investigated by estimating the binding energies of the electrolyte components to the major surfaces, performing Bader charge analysis, vibrational frequencies, and constructing Wulff morphologies.

7.1. Introduction

Cation doping [72] in LiMn_2O_4 has been proposed as one of the most successful techniques for lowering the quantity of trivalent manganese (Mn^{3+}) ions that can undergo Hunter's [71] disproportionation reaction, namely: $2\text{Mn}^{3+}_{(\text{solid})} \rightarrow \text{Mn}^{4+}_{(\text{solid})} + \text{Mn}^{2+}_{(\text{solution})}$. The use of dopants to replace Mn^{3+} restricts the development of Mn^{2+} , which is prone to dissolution. Many dopants, including Al^{3+} [76, 203, 204], Co^{2+} [205], Ni^{2+} [377, 206, 74, 207], Ti^{4+} [78], Nb^{5+} [77, 85], Na^+ [208, 209, 73], F^- [210, 75], have previously been examined and demonstrated better structural stability and capacity retention in diverse cathode materials. Zhang et al [85] investigated the element doping of a spinel LiMn_2O_4 cathode material and summarized a few Mn^{3+} replacement rules. (i) The dopant radius should be close to the Mn^{3+} radius of 0.645 Å to ensure compatibility. (ii) Dopant can increase the average oxidation of the state of Mn to limit the Jahn-Teller distortion. (iii) The guest TM element should have a larger TM-O bond energy than Mn-O to enhance stability, and most importantly. (iv) The dopant content should be suitable since excessive doping can negatively impact the capacity.

Nb^{5+} was chosen as one of the best dopants because it has a higher Nb-O binding energy than Mn-O [79]. Furthermore, the ionic radius of Nb^{5+} is equivalent to that of $\text{Mn}^{4+/3+}$ and Li^+ ions, allowing doping on either the lithium or transition metal (TM) sites [80]. Li et al [81] discovered that doping with modest levels of Nb affects crystal volume and lattice parameters without impacting Li^+ transport while studying the influence of Nb doping on the structure and electrochemical characteristics of LiMn_2O_4 spinel. They also showed that for varying Nb concentrations, the diffraction peaks are fully spinel, despite the presence of minor LiNbO_3 impurities. Li et al [82] later highlighted how Nb doping in spinel LiMn_2O_4 might boost capacity and electrochemical performance while also strengthening crystal development along

the (111) and (400) planes. Nb doping, like Cr doping, enhances Li diffusion in lithium manganese-based cathode materials, according to later research [83, 84, 85, 77, 86].

Doping the bulk spinel with atoms of varying sizes and charges, on the other hand, can result in varying amounts of cation order, resulting in changes in capacity and cycle stability [87, 88]. As a result, surface doping is currently regarded as the more effective way of spinel cathode stabilization [378, 379, 380]. We use spin-polarized density functional theory calculations in this work to investigate the influence of Nb doping on the main surfaces of the LiMn_2O_4 spinel material and their interactions with the electrolyte components, ethylene carbonate (EC) and hydrogen fluoride (HF). The influence of Nb doping on the first (Nb_{first}), second ($\text{Nb}_{\text{second}}$), and both first and second (Nb_{both}) layers, as well as surface free energies, morphologies, and Bader charges, is discussed. We also compare single molecule EC and HF adsorption onto the pristine and most stable Nb-doped setups.

7.2. Calculation Details

The spin-polarized density functional theory (DFT) calculations performed with the Vienna Ab initio Simulation Package (VASP) [310] were used to produce the computational findings given in this chapter. The computations were performed using the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional [311] within the generalized gradient approximation (GGA). For the growth of the Kohn-Sham (KS) valence states, a kinetic energy cutoff of 560 eV was used. For all surfaces, the Monkhorst-Pack k -point meshes were set to $5 \times 5 \times 1$. Gaussian smearing was incorporated with a width of 0.05 eV to increase the convergence of the Brillouin zone integrations during geometry improvements [315]. To appropriately characterize the long-range dispersion interactions and define the surfaces, the Grimme semi-empirical approach with the Becke-Johnson damping [D3-(BJ)]] [314, 315] was used. The projector augmented-wave (PAW) approach [312] in Kresse and Joubert's [313]

implementation was used to characterize the core electrons: Li ($2s^1$), Mn ($3d^5 4s^2$), O ($2s^2 2p^4$), and Al ($3s^2 3p^1$), as well as their interactions with the valence electrons. To strengthen the description of the localized $3d$ manganese electrons, a Hubbard correction [356] in the formulation of Dudarev and co-workers [357] was used. We selected the effective parameter, $U_{eff} = 4.0$ eV, based on the range of values given in the literature [358, 359, 280, 360] and consistent with our prior findings [207, 278, 361]. The Bader approach, implemented in the Henkelman code, was used to investigate charge distributions [381, 382, 383]. The convergence test was performed by raising the cutoff energies in the plane wave expansion of the pseudo-wavefunctions repeatedly until a constant total energy change was found.

7.3. Results And Discussions

7.3.1. Niobium Doping and Surface Stability.

Three doping scenarios were studied and compared with the normal spinel surfaces simulated to mimic the LiMn_2O_4 (001), (011), and (111) surfaces doped with Nb on the manganese positions [361]. The three situations investigated were: (i) Nb atoms integrated in the first (Nb_{first}) (iii) second (Nb_{second}) layers, and (iii) Nb atoms inserted in both the first and second layers (Nb_{both}). Various Mn locations were explored in each situation, as indicated in [Figure 7.1 \(a-c\)](#). There are four Mn locations on the Nb_{first} sites of the (001) surface, namely bridging, two hollow, and one corner, whereas three and one Mn positions were examined for the (011) and (111) surfaces, respectively. There were multiple Mn sites accessible for Nb_{second} , namely four, two, and six Mn locations in the (001), (011), and (111) surfaces, respectively. We investigate tiny amounts of Nb doping on the surfaces, namely $x = 0.125$ for Nb_{first} and Nb_{second} , and $x = 0.25$ for Nb_{both} (two Nb atoms were replaced at Mn locations in the first and second layers). The surface atoms were free to migrate and modify their shape after Nb substitution.

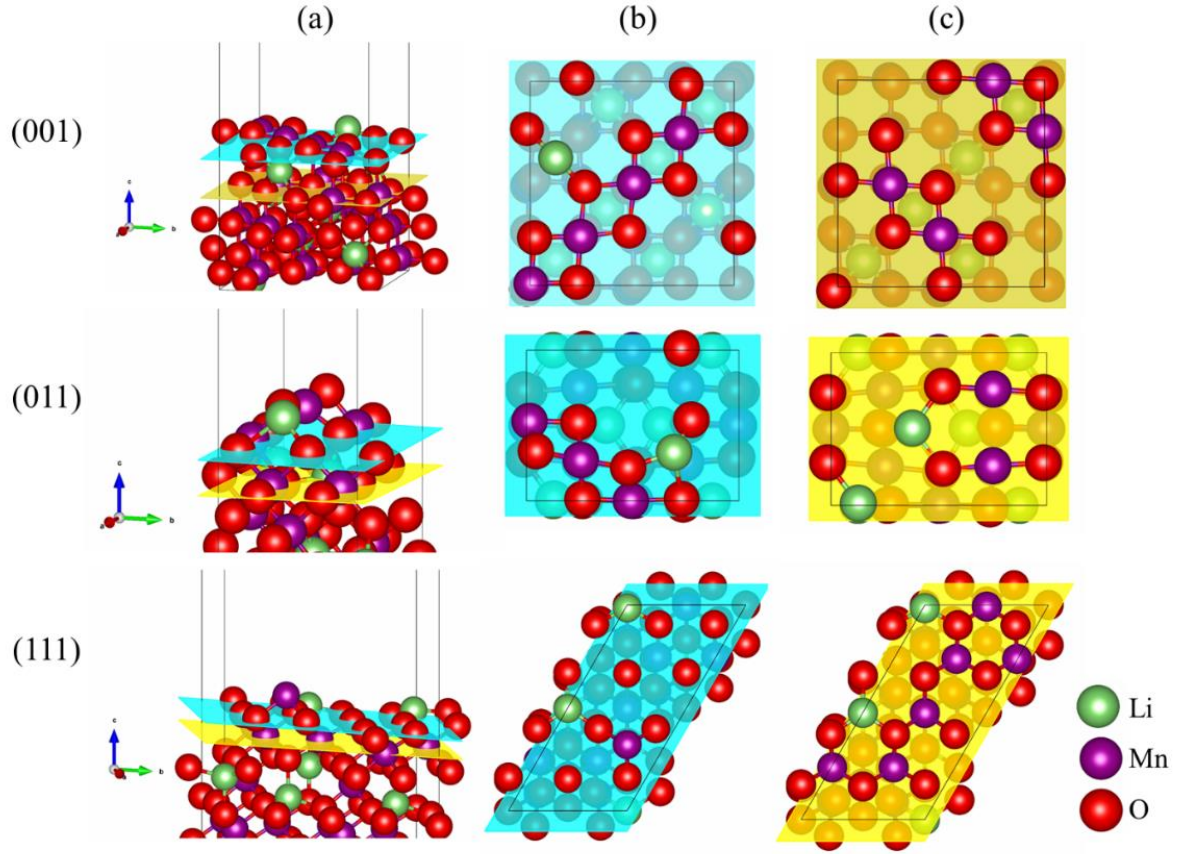


Figure 7.1: (a) Side and top views of the two top layers chosen for niobium doping on the LiMn_2O_4 (001), (011), and (111) surfaces. The first (Nb_{first}) and second ($\text{Nb}_{\text{second}}$) atomic layers are coloured blue and yellow, respectively.

[Figure 7.2](#) summarizes the calculated surface free energies (σ) for doping the Nb_{first} , $\text{Nb}_{\text{second}}$, and Nb_{both} sites as compared to the surface energies previously calculated for the undoped spinel surfaces [361]. Upon doping, it was generally observed that the calculated σ increased as compared to the pure facets, suggesting that this process requires energy input. For example, the σ increased from 0.037 to 0.210 eV/Å² after doping the Nb_{first} sites of the (001) surface to the pristine facet, which was the smallest change observed. The incorporation of Nb on the Nb_{first} layer maintained the same stability trend as the pure pristine surfaces (*i.e.*, (001) < (011) < (111)), but different results were obtained when doping the $\text{Nb}_{\text{second}}$ and Nb_{both} sites. The surface free energies of the (011) facets are larger following doping on the $\text{Nb}_{\text{second}}$ and Nb_{both}

sites, resulting in a new stability trend, namely $(001) < (111) < (011)$. As a result, the (111) surface is stabilized for Nb_{second} and Nb_{both} doping, notably in the former instance, even though the (001) facet remains the most stable.

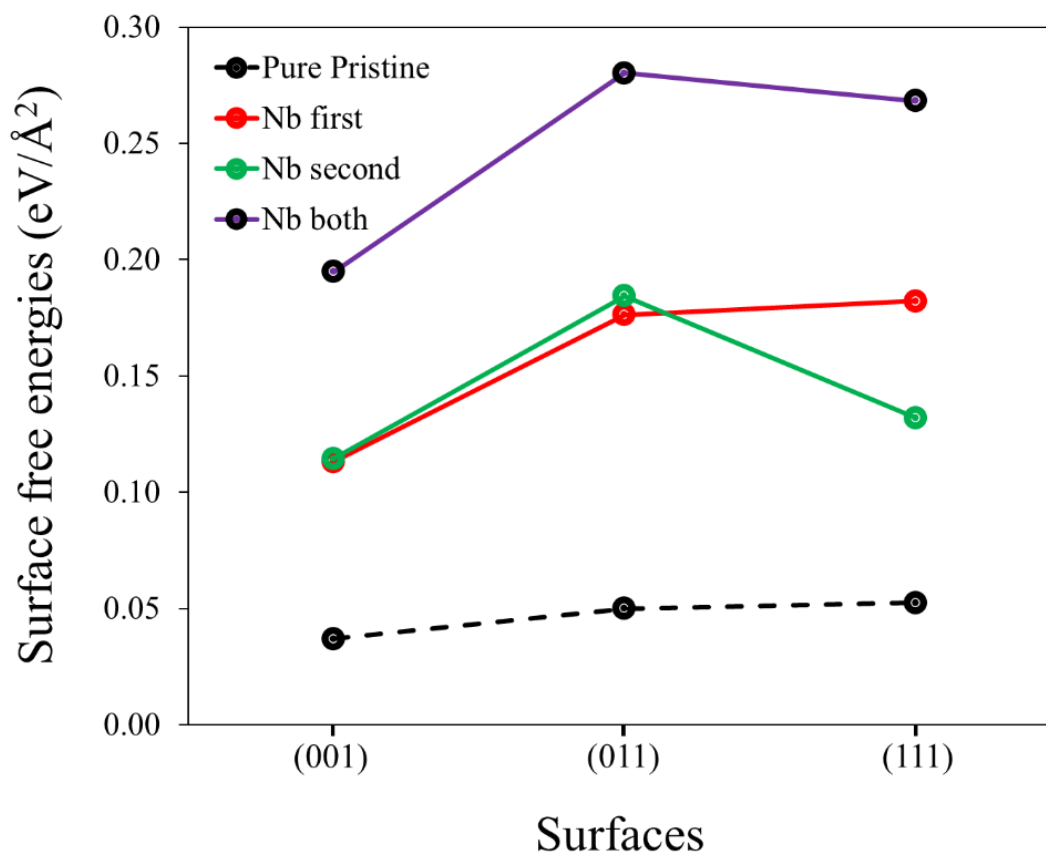


Figure 7.2: Surface free energies of the facets with Nb replaced at various Mn locations, *i.e.*, Nb_{first}, Nb_{second} and Nb_{both}, were compared to the surface energies of pure immaculate slabs.

7.3.2. Electrolyte Interactions

In this section, we compare the adsorption of the electrolyte components ethylene carbonate (EC) and hydrogen fluoride (HF) on niobium doped LiMn₂O₄ facets to pure pristine facets. [Figure 7.3a](#) shows the binding sites studied, which include the bridging and hollow Mn/Nb sites for the (001) surface, as well as on-top accessible Mn/Nb locations for the (011) and (111) surfaces. The first EC contacts with the surface were through the carbonyl (O_c) and ethereal (O_e) oxygen atoms, whereas the HF interactions were through the fluoride atom. Although the

atoms in the surfaces and the EC/HF were allowed to migrate and adjust their adsorption geometry upon relaxing, the molecules were originally set at 2.0 Å to favour the attractive interactions between the molecule and surface over the repulsive ones. Following our prior chapter 3 [361] the EC structural parameters were compared to the existing experimental and theoretical data, which were found to be in good agreement. Similarly, with $d(\text{H-F}) = 0.937\text{Å}$, the computed internal bond distance for HF coincides with the known literature values of $\sim 0.91\text{Å}$ [384, 385, 386].

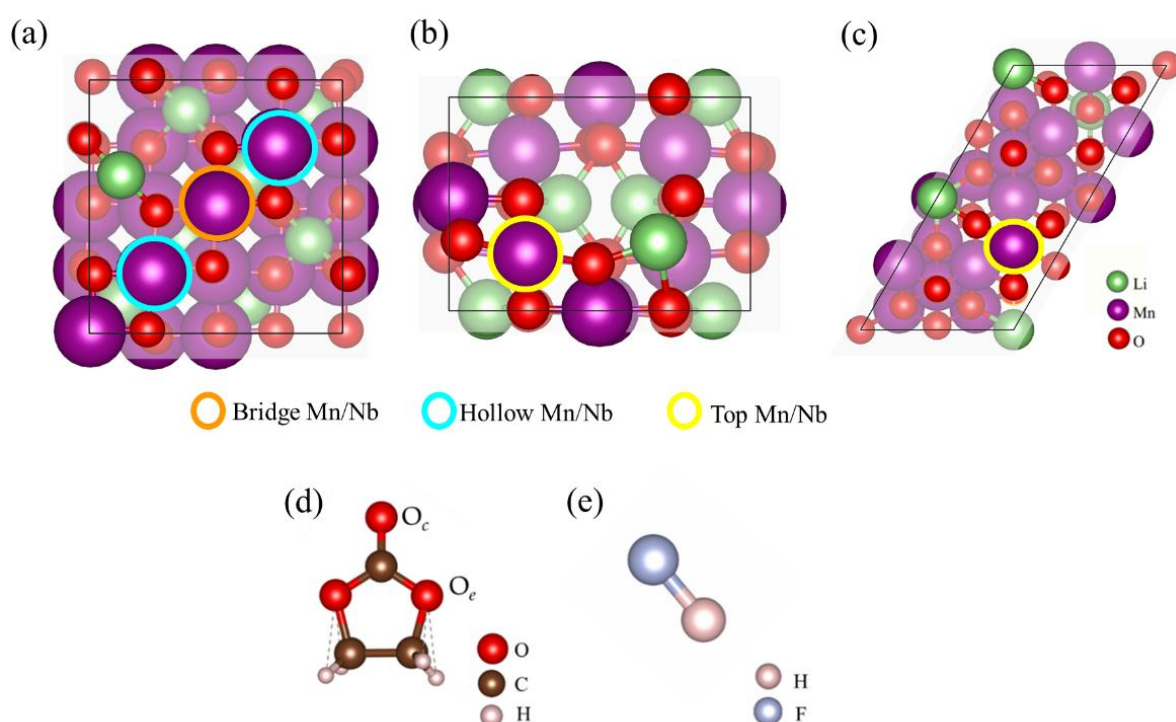


Figure 7.3: Adsorption Mn/Nb positions on the (a) (001), (b) (011) and (c) (111) surfaces and molecular representation of (d) ethylene carbonate (EC) and (e) hydrogen fluoride (HF) molecules, showing carbonyl (O_c) and ethereal (O_e) oxygen.

7.3.2.1. Ethylene carbonate adsorptions

The structures and binding energies (E_{ads}) of the most stable EC contact configurations at Nb-doped surfaces are shown in [Figure 7.4](#). The EC adsorption energies for Nb-doped surfaces were compared to undoped surfaces. The EC molecule was permitted to bond to the surfaces at the manganese or niobium atoms in a variety of adsorption positions. After relaxing, the molecule chose to connect to the surface via the Nb atoms rather than the Mn atoms, due to the higher dissociation energy of the Nb-O bond (753 kJ/mol) compared to the Mn-O (402 kJ/mol) [387]. When arranged parallelly and interacting with the slabs via the O_c , the EC molecule favoured binding on the surfaces. In general, the Nb_{second} site of the (011) surface had the highest adsorption energy, with $E_{\text{ads}} = -5.13$ eV at 2.25 Å. The EC molecule preferred to interact through the Nb atom rather than the Mn atom when adsorbing on surfaces containing Nb atoms, and the most favoured configuration was on the LiMn_2O_4 (011) and (001) surfaces with Nb on the Nb_{first} and Nb_{both} sites, respectively. In general, interactions with Nb-doped surfaces resulted in higher EC adsorption energies than interactions with pure pristine surfaces [361].

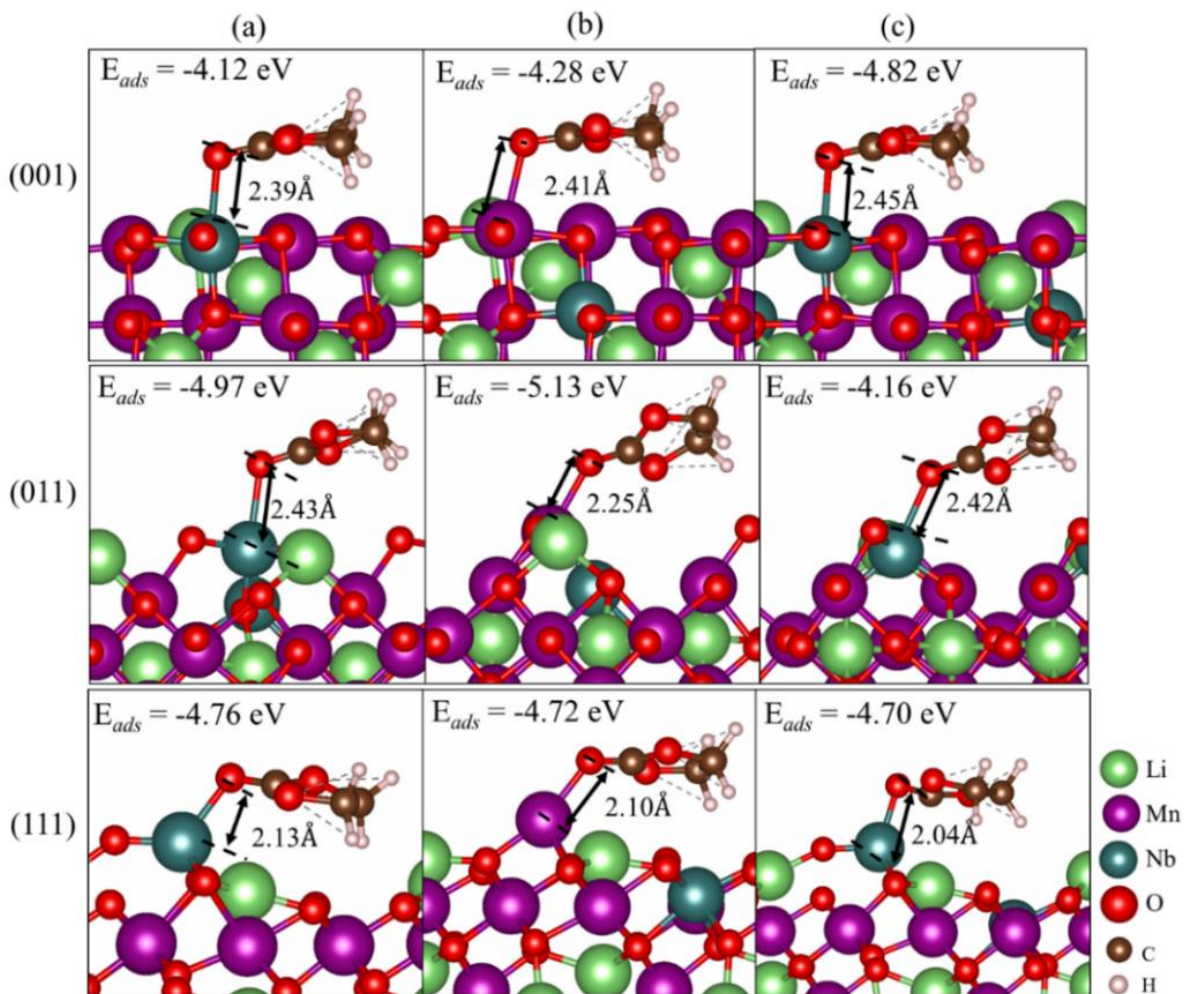


Figure 7.4: Adsorption energies and geometries calculated for ethylene carbonate (EC) molecule interacting with the Nb-doped spinel surfaces on the (a) first (Nb_{first}), (b) second (Nb_{second}), and (c) both (Nb_{both}) 1st and 2nd atomic layers.

7.3.2.2. Hydrogen fluoride adsorption

The interactions between the un-doped and Nb-doped $LiMn_2O_4$ surfaces and the acidic component of the electrolyte, hydrogen fluoride (HF), are shown in [Figure 7.5](#). The HF molecule was permitted to migrate and change shape during adsorption. As shown in [Figure 7.5](#), the HF molecule relaxes and normally dissociates spontaneously to create Mn/Nb-F and O-H species, the latter of which also interacts with nearby surface oxygen via hydrogen bonds (O-HO). However, the HF molecule only interacts with the surfaces on the (001) surface, both

undoped and after Nb_{second} doping, via a rather weak hydrogen bond, whereas it detaches from the Nb_{second} doped (111) surface. In general, the Nb_{both} site of the (001) surface had the greatest binding energy, with $E_{ads} = -5.66$ eV. With $E_{ads} = -4.26$ eV for pure un-doped surfaces, the HF molecule best interacted with the (111) surface. However, HF adsorption on doped surfaces (*i.e.*, Nb_{first}, Nb_{second}, and Nb_{both} sites) produced larger binding energies than interactions with stoichiometric surfaces.

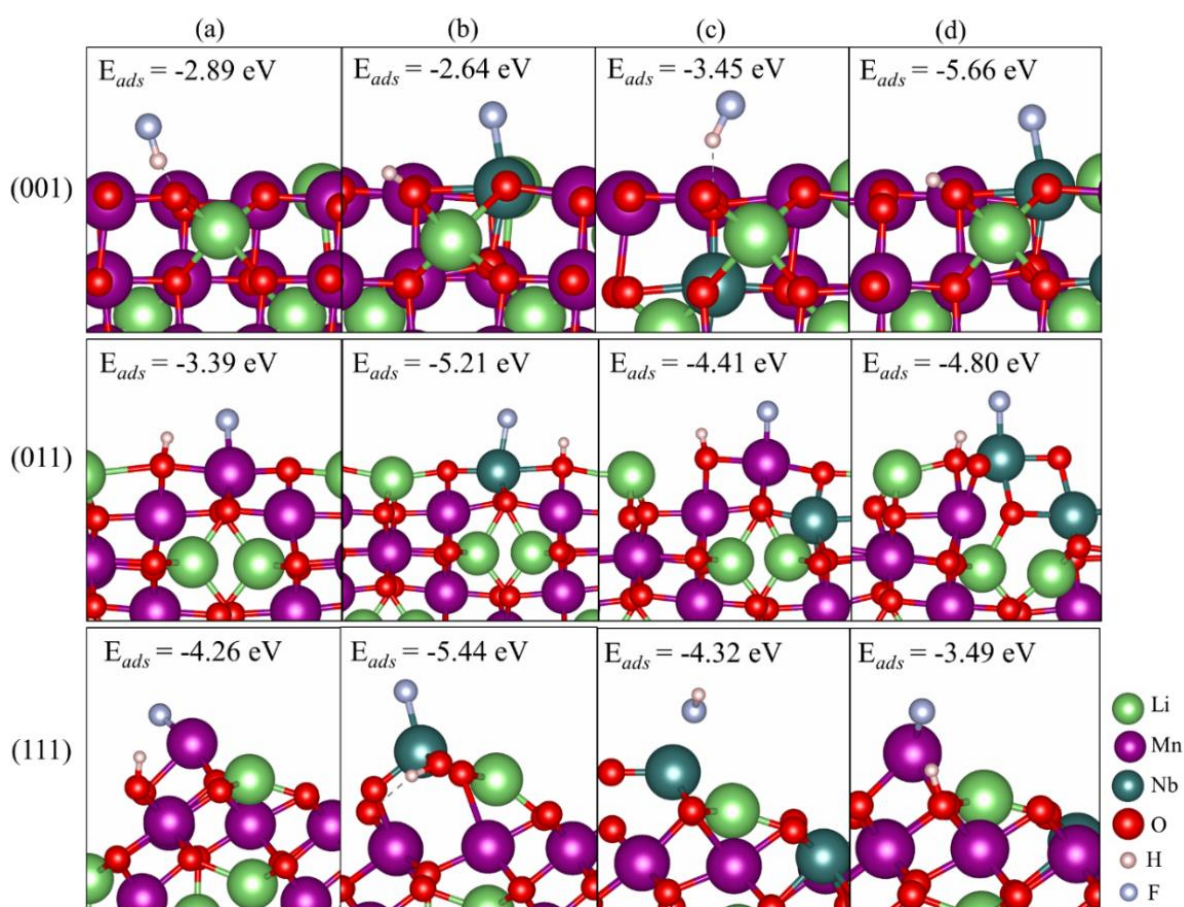


Figure 7.5: Adsorption energies and geometries calculated for hydrogen fluoride (HF) molecule interacting with the Nb-doped spinel surface on the (a) pristine (b) first (Nb_{first}), (c) second (Nb_{second}), and (d) both (Nb_{both}) 1st and 2nd atomic layers.

7.3.3. Morphologies

The effect of Nb doping and electrolyte adsorption on nanoparticle morphologies was then examined in comparison to the morphologies developed for the un-doped material. First, we discuss the effect of Nb doping on surface morphologies, as shown in [Figure 7.6a](#), where we generally see an enhancement of the (001) surface after doping the Nb_{first} position, and an increase in the expression of the (111) surface plane after doping the Nb_{second} and Nb_{both} positions, when compared to the un-doped surfaces. Nb doping in the second layers (Nb_{second}) stabilizes and improves the (111) plane, which is important because this surface supports the creation of a stable solid electrolyte interface, which minimizes Mn dissolution [388].

Second, we investigated the influence of ethylene carbonate adsorption on stable Nb-doped surfaces on the morphologies, as shown in [Figure 7.6b](#). The (001) plane dominates the spinel nanoparticles following adsorption of the EC molecule at the surfaces doped in the first (Nb_{first}) and both layers (Nb_{both}) sites, according to the built morphologies. Adsorption at the surface doped at the Nb_{second} site, on the other hand, results in dominance of the (111) plane once more. Because of its larger surface free energy than the (001) and (111) planes, the (011) surface does not present in the Wulff morphology when doped alone. However, the (011) surface returns marginally after EC adsorption, but only for Nb_{both} doped surfaces.

Finally, we looked at how HF adsorption affects the stability of pure and doped surfaces (see [Figure 7.6c](#)). The built morphologies for the undoped material show that the (111) surface is dominant during HF adsorption. However, after adsorption on surfaces doped on the Nb_{second} site, the (111) plane became more stable, dominating the morphology, whereas the (001) plane became more prominent when the surfaces were doped on both the Nb_{first} and Nb_{both} sites.

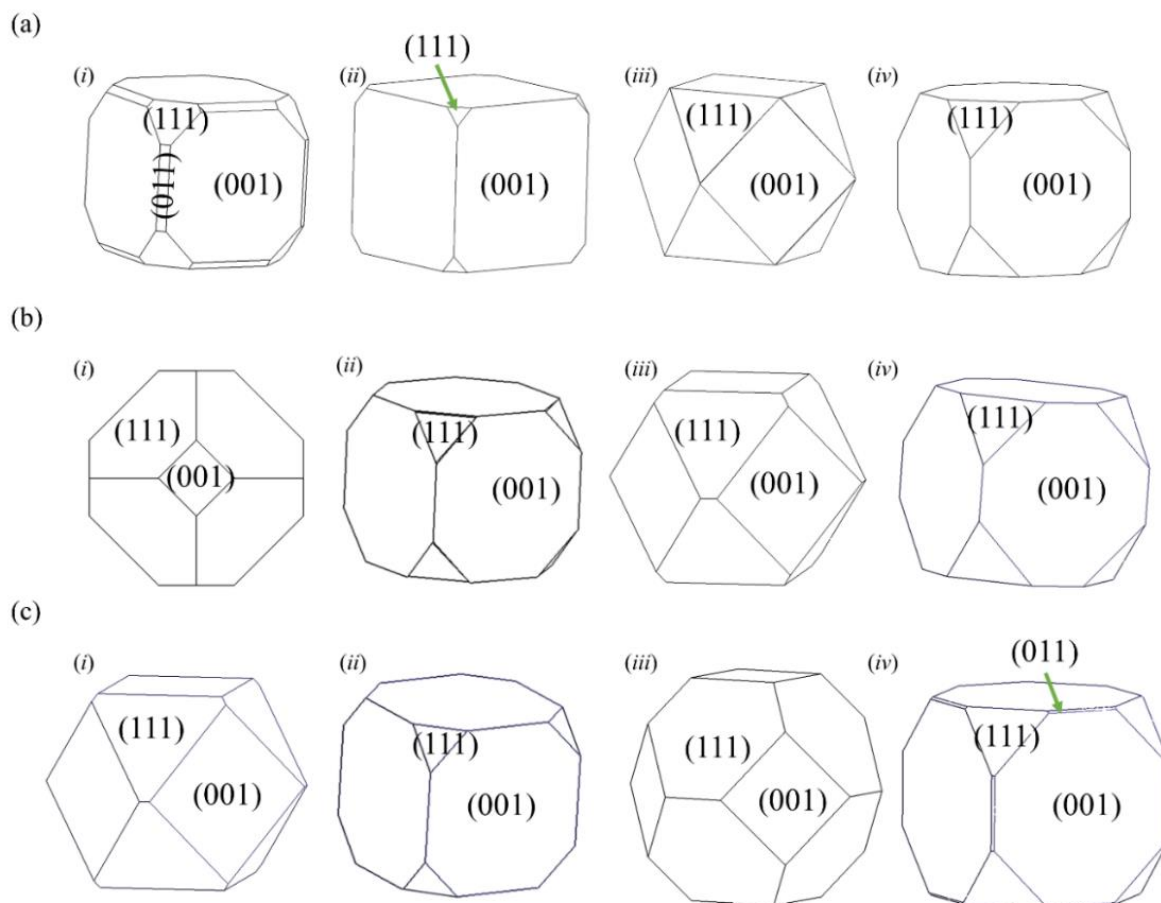


Figure 7.6: Constructed morphologies of the (i) undoped facets, and with Nb substituted on different Mn positions, *i.e.* (ii) Nb_{first}, (iii) Nb_{second} and (iv) Nb_{both}, for the (a) clean surfaces and with adsorbed (b) ethylene carbonate and (c) hydrogen fluoride.

7.3.4. Bader Charge Analysis

[Table 7.1](#) summarizes the electronic charge transfer (q) analysis and work functions (ϕ) following EC/HF adsorption on undoped and Nb-doped surfaces. In general, there was little charge transfer between the adsorbed molecule (HF/EC) and the pure/Nb-doped surfaces. Negligible charge transfers were computed on the undoped surface, with the greatest values of $-0.022 e^-$ seen for EC adsorbed on the (001) surface and $-0.117 e^-$ observed for HF adsorbed on the (111) surface. The largest charge transfers of $-0.428 e^-$ for EC adsorbed on Nb-doped

surfaces were found for the (111) surface doped on the Nb_{both} sites, with charge buildup of 0.889 e^- on the surface. Charge buildup of 0.295 e^- was observed on the Nb_{first} doped (001) surface for HF adsorption, with charge depletion of 0.298 e^- and rise of -0.003 e^- on interacting F and H atoms, respectively. The charge difference between the interacting atom(s), namely carbonyl oxygen (O_c) in EC and H/F atoms, was also computed and compared to the isolated adsorbate molecules ($\Delta q_{O_c/F}$ and Δq_H). The partial oxidation and reduction of the C and O atoms in the EC molecule were induced by intramolecular electron transfer from the C=O π -bond to an O-Mn/Nb σ -bond. We observed H-F bond dissociation, which led in the creation of new O-H and Nb/Mn-F bonds. Except for the Nb_{both} doped (001) surface, charge buildup was seen on the H atom. We now compare the computed work functions (ϕ) for the undoped and Nb-doped surfaces following EC and HF adsorption. The estimated ϕ for EC/HF surface interactions on Nb-doped slabs typically increases when compared to pure pristine facets. This implies that after Nb-doping, the EC/HF reactivity towards the surfaces decreases when compared to pure undoped facets.

[Figure 7.7](#) summarizes the charge density differences for the HF/EC adsorption combinations with the greatest interface charge transfer on the undoped and Nb-doped surfaces. Despite the minimal charge transfer seen during EC adsorptions, electron flow charts demonstrate that the undoped surfaces had the most charge rearrangement [361]. Charge loss on the surface Nb atom and charge gain on the interacting adsorbate atom are seen for Nb-doped surfaces. Because of the newly established interfacial Nb-O σ -bond, we also see large charge rearrangements within the EC molecule. We discovered charge depletion and buildup on the H and F atoms during HF adsorption due to the formation of Mn/Nb-F and O-H σ -bonds between the surface and the adsorbates. Because of charge compensation effects with the Mn atom, we also observed partial charge buildup and depletion on neighbouring surface O atoms. We also detected charge transfer within the O atoms of the subsurface layer after Nb doping.

Table 7.1: The Bader charge between the EC and HF molecules and the surface (Δq), as well as the charge accumulation/depletion inside the interacting atoms and their work function (ϕ). Negative charge transfer values imply charge buildup on the adsorbate, whereas positive values show charge transfer to the surface.

	Scenarios	Surface	Adsorption sites	$\Delta q_{EC/HF}$ (e^-)	$\Delta q_{O_c/F}$ (e^-)	Δq_H (e^-)	ϕ (eV)
Ethylene carbonate (EC)	Undoped [361]	(001)		-0.022	0.810		3.453
		(011)		-0.004	0.800		4.446
		(111)		-0.005	0.784		3.545
	Nb_{first}	(001)	<i>Nb-Bridge</i>	0.008	0.799		4.214
		(011)	<i>Nb-Top</i>	-0.001	0.806		5.297
		(111)	<i>Nb-Top</i>	0.048	0.797		4.033
	Nb_{second}	(001)	<i>Mn-Hollow</i>	-0.016	0.802		4.073
		(011)	<i>Mn-Top</i>	0.009	0.804		5.056
		(111)	<i>Mn-Top</i>	0.001	0.773		3.669
	Nb_{both}	(001)	<i>Nb-Hollow</i>	-0.014	0.800		4.243
		(011)	<i>Top</i>	0.012	0.790		5.424
		(111)	<i>Top</i>	-0.428	0.889		3.869
Hydrogen fluoride (HF)	Undoped	(001)		-0.055	-0.044	-0.011	3.960
		(011)		-0.073	0.082	-0.155	4.903
		(111)		-0.117	-0.018	-0.099	4.354
	Nb_{first}	(001)	<i>Nb-Bridge</i>	0.295	0.298	-0.003	11.336
		(011)	<i>Nb-Top</i>	-0.079	0.073	-0.152	4.488
		(111)	<i>Nb-Top</i>	-0.011	0.110	-0.121	3.848
	Nb_{second}	(001)	<i>Mn-Hollow</i>	-0.056	-0.028	-0.028	3.838
		(011)	<i>Mn-Top</i>	-0.064	0.077	-0.141	5.017
		(111)	<i>Mn-Top</i>	-0.138	-0.008	-0.130	4.398
	Nb_{both}	(001)	<i>Nb-Hollow</i>	-0.086	-0.113	0.027	8.153
		(011)	<i>Top</i>	-0.069	0.088	-0.157	4.584
		(111)	<i>Top</i>	-0.165	-0.026	-0.140	3.425

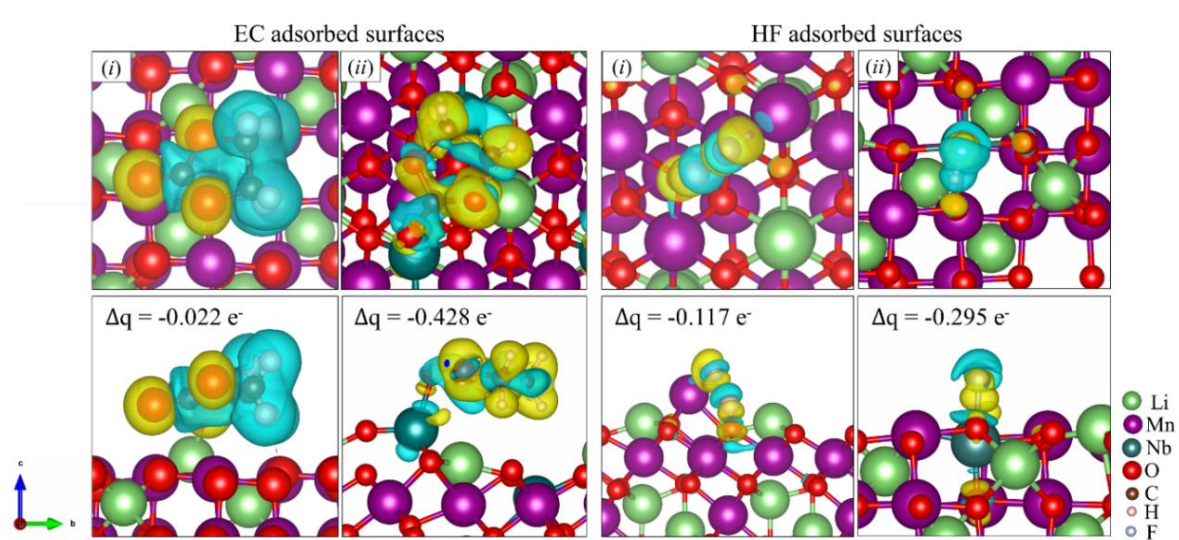


Figure 7.7: Top and side view of the charge density flow ($\Delta\rho$) for the adsorption configuration on the (i) pure and (ii) Nb-doped with the largest interface charge transfer. The density accumulation and depletion regions are indicated in yellow and blue, respectively. Iso-surfaces display a value of ± 0.012 , ± 0.010 , ± 0.008 and ± 0.003 $\text{e}/\text{\AA}^3$ for EC-pure, EC-Nb doped, HF-pure and HF-Nb doped LiMn_2O_4 , respectively.

Summary

The influence of Nb-doping on the main LiMn_2O_4 (001), (011), and (111) surfaces and their interactions with the electrolyte components, ethylene carbonate (EC) and hydrogen fluoride (HF), was studied using spin-polarized density functional theory simulations. The computed surface free energy of Nb-doped facets rise when compared to undoped facets, demonstrating that this procedure necessitates high temperatures. The Nb replacement in the second and both (*i.e.*, $\text{Nb}_{\text{second}}$ and Nb_{both}) layers considerably increased the dominance of the (111) surface plane in the Wulff morphology, although doping the first (Nb_{first}) layer preserved the same stability trend. Interestingly, because exposing the (111) surface plane enhances the creation of stable solid electrolyte interfaces (SEI), which limit Mn dissolution, we believe that Nb sub-surface doping might be an effective method for increasing (111) expression in the morphology.

Furthermore, the EC/HF electrolyte molecules favoured attaching to the surfaces via Nb atoms rather than Mn atoms, with the greatest adsorption energy computed for EC on the Nb_{second}-doped (011) surface and HF on the Nb_{both}-doped (111). When the adsorbates contact with the Nb_{second}-doped surfaces, they improve the expression of the (111) surface plane in the morphology. The differential electron density reveals that charge rearrangements inside the molecule and partial accumulations/depletions on the interacting O atom because of the creation of interfacial Nb-O σ -bonds dominate EC adsorption on the surfaces. Charge loss and gain were also detected on the H and F atoms when they interacted with the Mn/Nb and O atoms. Furthermore, the computed work function for EC/HF surface contacts on Nb-doped slabs increases when compared to pure pristine facets, implying that niobium doping decreases the reactivity of electrolyte components to surfaces.

CHAPTER 8

8. Conclusion and Recommendations

This chapter provides an overall summary of studies based on electrolyte interactions with the coating layer α -Al₂O₃ and pristine/Nb-doped LiMn₂O₄ surfaces and the heteroepitaxial formation of the α -Al₂O₃ coated LiMn₂O₄ surfaces. Some recommendations and future work are included, which may aid in further clarifications and expanding the understanding of electrolyte interactions and effect of surface modification.

8.1. Conclusion

In this thesis, we have presented a comprehensive computational work of the bulk and surfaces of spinel lithium manganese oxide (LiMn₂O₄) cathode material and aluminium oxide (α -Al₂O₃) coating material, adsorption mechanisms of the electrolyte component (ethylene carbonate - EC and hydrogen fluoride - HF) on the α -Al₂O₃, pristine/Nb-doped LiMn₂O₄, and modelled the α -Al₂O₃//LiMn₂O₄ heterostructures. All calculations in this work were based on the density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP).

In the first part of the results (Chapter 4), we discussed the convergence, structural and electronic property calculations and compared the results with existing experimental/theoretical data. The cubic LiMn₂O₄ with lattice $a = b = c = 8.249$ Å, and average Mn³⁺/ Mn⁴⁺-O bond distance of 1.989 Å matched the reference values. Negative heat of formation was observed, suggesting thermodynamic stability of the LiMn₂O₄. At the Fermi level, the electronic DOS exhibited half-metallic behaviour with Mn³⁺ e_g and O²⁻ $2p$

hybridization. For Li, Mn, and O, the average Bader charges calculated were 0.88, 1.78, and -1.10 e^- /atom, respectively. Similarly, the hexagonal α -Al₂O₃ with lattice $a = b = 4.776$ Å and $c = 13.026$ Å, and average Al³⁺-O bond distances of 1.965 Å were compatible with previously published experimental findings. The electronic DOS had a large band gap of 5.909 eV, which was comparable with previously published values of ~5.970 eV. The calculated average atomic charges amount to 0.88, 1.78 and -1.10 e^- /atom for Al and O, respectively. This chapter's results clearly identify the correctness of the parameters employed in reference to prior research of both the LiMn₂O₄ and α -Al₂O₃ bulk structures.

In the second part (chapter 5), we investigated the adsorption of a range of ethylene carbonate coverages onto the major α -Al₂O₃ (0001) surface. We began by proving the stability of the (0001) surface, considering both the Al- and O-terminated surfaces, in which Al-terminated surface showed the lowest surface energy and agreeing with the published findings. A minor charge transfer was seen with single EC adsorption, indicating physical interactions, with the parallel EC structure being the favoured binding option. When compared to single EC adsorption, increasing the EC coverage destabilizes the surface by increasing average adsorption. Bader charge accumulation was observed on the interacting EC oxygen atoms, with high steric hindrance at high coverages which led to the detachment of EC molecules. The blue shift of the symmetric and asymmetric $\nu(\text{CH}_2)$ vibrational modes also indicated steric hindrance. The STM for the clean corundum α -Al₂O₃ (0001) surface compares well with the image for the same facet of the isostructural hexagonal haematite α -Fe₂O₃ structure, which can be used for comparison with future experiments.

To shed light on the interfacial interactions between the coating layers α -Al₂O₃ and LiMn₂O₄, we simulated the α -Al₂O₃//LiMn₂O₄ interfaces while also considering varying coating thicknesses (Chapter 6). We found that the α -Al₂O₃ (11 $\bar{2}$ 0) and (0001) surfaces adeptly match

the LiMn_2O_4 (001) and (111) facets exhibiting $\{1132\}$ and $\{3121\}$ configurations, respectively, with corresponding misfits of 2.40% and 2.75%. The highest adhesion energies were computed for the $\alpha\text{-Al}_2\text{O}_3$ monolayer on the (001) and (111) surfaces, which dropped as the thickness increased. The relaxation of the $\alpha\text{-Al}_2\text{O}_3$ overlayer resulted in disorder at the boundaries for n_1 , and n_2 , but showed limited surface-surface changes at the boundaries for n_3 . We observed a minor electronic charge gain on the substrate, with a negligible charge depletion on the overlayer $\alpha\text{-Al}_2\text{O}_3$ for both heterostructures at different coating thicknesses. Notably, the largest charge transfer of $\Delta q = -0.90 e^-$ was calculated for $\{3121\} n_1$, which was attributed to electronic density gain on the interacting O and Li atoms, forming Al-O and Li-O, and partial depletion on the Mn atoms. For both interfaces, we observed the largest work function and smallest reactivity for $n = 2$. Furthermore, we investigated the effect of Li vacancy formation to simulate the charged surfaces/interfaces. Our findings aligned with the theoretical understanding of Li-ion battery operation, as we observed an increase in vacancy formation energies corresponding to the number of Li atoms removed from both pristine LiMn_2O_4 (001) and (111) surfaces. This trend was consistent for the heterostructures as well. Furthermore, our analysis of work functions suggested that the incorporation of an overlayer and partial delithiation led to a decrease in reactivity in most cases, except for $\{3121\} n_1$. These findings collectively contribute to our understanding of how $\alpha\text{-Al}_2\text{O}_3$ coatings impact the properties and behaviour of LiMn_2O_4 surfaces in the context of lithium-ion batteries.

Finally (Chapter 8), the effect of surface Nb-doping on the principal LiMn_2O_4 (001), (011), and (111) surfaces was examined. It was discovered that by substituting niobium on manganese ions positions in the second surface layers ($\text{Nb}_{\text{second}}$), the (111) surface stability increased, resulting in a better (111) plane on the morphology. However, replacing the first (Nb_{first}) and both top and bottom (Nb_{both}) layers of Mn atoms in the slabs retains the same stability trend as in the pure pristine surfaces. Furthermore, both adsorbates favored binding to the surfaces via

Nb atoms rather than Mn atoms, with the greatest adsorption energy computed for EC on the LiMn_2O_4 (011) surface doped on the $\text{Nb}_{\text{second}}$ site and for HF on the LiMn_2O_4 (111) surface doped on the Nb_{both} site. Furthermore, the EC/HF adsorptions improve the surface plane stability of the $\text{Nb}_{\text{second}}$ (111). However, for both HF and EC interacting with pure and Nb-doped surfaces, negligible charge transfer was computed. Our findings are intriguing because exposing the (111) surface enhances the establishment of a stable solid electrolyte interface (SEI), minimizing Mn dissolving and increasing EC and HF adsorption.

8.2. Recommendations

Results outlined within this work are rigorous and explain structural, surface, and electronic properties. Aside from looking for future experimental validation, several theoretical methods such as molecular dynamics that can advance and improve and provide new insights. To further understand the effect of the electrolyte interaction towards the Nb-doped surface and interface models, ci-NEB technique can be implemented to explain the reactivity and decomposition mechanism. Mostly, the reactivity of ethylene carbonate on the Nb-doped in comparison to the pristine surfaces.

To have a better knowledge of the heterojunction interactions between the surface LiMn_2O_4 and overlayer $\alpha\text{-Al}_2\text{O}_3$, molecular dynamics can be employed also exploring the effect of temperature. Also, further understanding and perfecting the heterostructures, we can use the python-based program Pymatgen to generate the interfaces and explore their interfacial stability. Considering also the orthogonalization method employed by Carter et al [367, 368, 369, 370] to model and understand the coating/HF interactions together with Li-transport.

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List of Publications

1. **Ramogayana, B.**, Santos-Carballal, D., Maenetja, K.P., Ngoepe, P.E. and de Leeuw, N.H., (2024) “Structures, electronic properties, and delithiation thermodynamics of the heteroepitaxial α -Al₂O₃/LiMn₂O₄ (001) and (111) interfaces”, *Surfaces and Interfaces*, **48**,104316. DOI: <https://doi.org/10.1016/j.surfin.2024.104316>
2. **Ramogayana, B.**, Maenetja, K.P. and Ngoepe, P.E., (2023) “Stability of NaO₂ and LiO₂ discharge products in metal-air batteries: density functional theory study”, *In MATEC Web of Conferences* (388, 07019). EDP Sciences.
DOI: <https://doi.org/10.1051/mateconf/202338807019>
3. **Ramogayana, B.**, Santos-Carballal, D., Maenetja, K.P., Malatji, K.T., de Leeuw, N.H. and Ngoepe, P.E., (2022) “A DFT+ U-D3 study of the adsorption of hydrogen fluoride and ethylene carbonate on the niobium-doped (001), (011), and (111) surfaces of lithium manganese oxide”. *Journal of The Electrochemical Society*, **169** (9), 090507. DOI: <https://iopscience.iop.org/article/10.1149/1945-7111/ac8e35>
4. Hiine, M.J., **Ramogayana, B.**, Ngoepe, P.E. and Maenetja, K.P., (2022), “Computational study of bulk and surface properties on ruthenium oxide (RuO₂)”, *In MATEC Web of Conferences* (**370**, 02003). EDP Sciences.
DOI: <https://doi.org/10.1051/mateconf/202237002003>
5. **Ramogayana, B.**, Santos-Carballal, D., Maenetja, K.P., De Leeuw, N.H. and Ngoepe, P.E., (2021) “Density functional theory study of ethylene carbonate adsorption on the (0001) surface of aluminum oxide α -Al₂O₃”. *ACS omega*, **6**(44), 29577-29587. DOI: <https://doi.org/10.1021/acsomega.1c03771>
6. Somo, T.R., Mabokela, T.E., Teffu, D.M., Sekgobela, T.K., **Ramogayana, B.**, Hato, M.J. and Modibane, K.D., (2021). “A comparative review of metal oxide surface coatings on three families of cathode materials for lithium-ion batteries”. *Coatings*, **11**(7), 744. DOI: <https://doi.org/10.3390/coatings11070744>
7. **Ramogayana, B.**, Maenetja, K.P. and Ngoepe, P.E., (2021). “The effect of niobium doping on lithium manganese oxide surfaces, LiMn_{2-x}Nb_xO₄: DFT study”, *Suid-Afrikaanse Tydskrif vir Natuurwetenskap en Tegnologie*, **40**(1), 22-26. DOI: https://hdl.handle.net/10520/ejc-aknat_v40_n1_a21

List of Oral and Poster Presentations

Oral Presentations

- “*Heteroepitaxial α - $\text{Al}_2\text{O}_3/\text{LiMn}_2\text{O}_4$ interfaces: structures, electronic and delithiation thermodynamics properties.*”, Chem4Energy Annual Conference 2023 on Materials and Processes for a Sustainable Energy Future. Johannesburg at the 26° South Hotel in Muldersdrift, South Africa. 20 - 24 March 2024.
- “*Stability of NaO_2 and LiO_2 discharge products in metal-air batteries: Density functional theory study*”, 2023 RAPDASA-RobMech-PRASA-AMI Conference, CSIR International Convention Centre in Pretoria, South Africa. 30 October – 02 November 2023.
- “*Exploring the effect of α - Al_2O_3 coated LiMn_2O_4 (001) and (111) surfaces*”, Faculty of Science and Agriculture (FSA) conference, Bolivia Lodge, Polokwane, P.O. Box 11309, Bendorpark, Polokwane, 0713, Limpopo Province, South Africa. 20-22 September 2023.
- “*Exploring the heteroepitaxial interface boundaries of α - Al_2O_3 coated LiMn_2O_4 (001) and (111) surfaces: DFT+U method*”, Symposium celebrating Nora de Leeuw's 60th birthday - From Minerals to Materials: Experimental and Computational Chemistry Approaches, Ramsey room, Chemistry Department, University College London, United Kingdom. 26 – 27 June 2023.
- “*Exploring the heteroepitaxial interfaces of alumina on the lithium manganese oxide major surfaces: DFT+U-D3 study*”, School of Chemistry, Postgraduate conference, Braggs building University of Leeds, 13 – 14 June 2023.
- “*Exploring the effect of Nb doping and ethylene carbonate adsorptions on the LiMn_2O_4 major surfaces: DFT+U study*”, Research Computing Leeds Conference 2022, University of Leeds, United Kingdom, 26 – 27 July 2022.
- “*Ab-initio study of hydrogen fluoride and ethylene carbonate adsorption on the Nb-doped on the LiMn_2O_4 surfaces*”, online Oral Presentation, South African Institute of Physics (SAIP) Conference, 04 – 08 July 2022.

Poster Presentations

- “*The ab-initio study of bulk and surface stability of layered lithium manganite Li_2MnO_3* ” CHPC National Conference 2023, Skukuza Rest Camp, Kruger National Park, Mpumalanga, South Africa. 04 – 07 December 2023.

- “*Heteroepitaxial interface boundaries of α -Al₂O₃ coated LiMn₂O₄ surfaces: DFT+U-D3 study*”, Prof Phuti Ngoepe’s 70th Birthday, Council for Geoscience, 280 Pretoria St, Silverton, Pretoria South Africa. 03 – 04 August 2023.
- “Exploring the heteroepitaxial α -Al₂O₃/LiMn₂O₄ interfaces”, Chem4Energy, Materials and Processes for a Sustainable Energy Future, NWU Sports Village, Potchefstroom, South Africa. 29 March - 02 April 2023.
- “*Lithium manganese oxide surface Nb⁵⁺ doping and its interactions with the electrolyte components*”, MCC Conference 2022, Daresbury Laboratory, Warrington, Cheshire, United Kingdom, 06 – 08 July 2022.
- “*Effect of niobium doping on the major spinel LiMn₂O₄ surfaces: DFT study*”, 15th CHPC National Conference, Virtual conference, 01 – 03 December 2021.

Awards

2022 July

Best Poster presentation, MCC 4th Conference

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Laboratory, Keckwick Lane
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2023 June

**Best PhD presentation, School of Chemistry Postgraduate
Conference**

School of Chemistry, University of Leeds,
Leeds LS2 9JT, United Kingdom

April 2022 – 2023 July

PhD visiting Student – University of Leeds

Provided funds for a year to cover research expenditures, travel,
sustenance, and equipment.

School of Chemistry, University of Leeds,
Leeds LS2 9JT, United Kingdom

Appendix A

Density Functional Theory Study of Ethylene Carbonate Adsorption on the (0001) Surface of Aluminum Oxide α -Al₂O₃

Brian Ramogayana, David Santos-Carballal,* Khomotso P. Maenetja, Nora H. de Leeuw, and Phuti E. Ngoepe*



Cite This: *ACS Omega* 2021, 6, 29577–29587



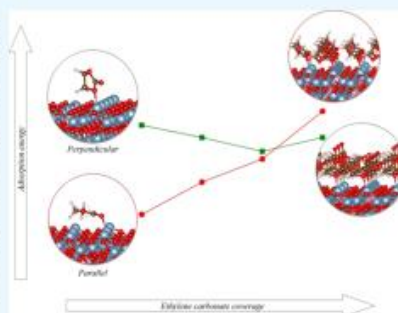
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ABSTRACT: Surface coating is one of the techniques used to improve the electrochemical performance and enhance the resistance against decomposition of cathode materials in lithium-ion batteries. Despite several experimental studies addressing the surface coating of secondary Li-ion batteries using α -Al₂O₃, the reactivity of the material toward the electrolyte components is not yet fully understood. Here, we have employed calculations based on the density functional theory to investigate the adsorption of the organic solvent ethylene carbonate (EC) on the major α -Al₂O₃(0001) surface. During adsorption of a single EC molecule, it was found that it prefers to bind parallel to the surface through its carboxyl oxygen. As the surface coverage (θ) was increased up to a monolayer, we observed larger adsorption energies per EC molecule ($E_{\text{ads}}/N_{\text{EC}}$) for parallel interactions and a reduction for perpendicular interactions. We also noted that increasing the surface coverage with both parallel and perpendicularly interacting EC molecules led to a decrease of the surface free energies and hence increased stability of the α -Al₂O₃(0001) surface. Despite the larger $E_{\text{ads}}/N_{\text{EC}}$ observed when the molecule was placed parallel to the surface, minimal charge transfer was calculated for single EC interactions and at higher surface coverages. The simulated scanning tunneling microscopy images are also presented for a clean corundum α -Al₂O₃ surface and after adsorption with different coverages of parallel and perpendicularly placed EC molecules.



<https://doi.org/10.1021/acsomega.1c03771>

Appendix B

Review

A Comparative Review of Metal Oxide Surface Coatings on Three Families of Cathode Materials for Lithium Ion Batteries

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Citation: Somo, T.R.; Mabokela, T.E.; Teffu, D.M.; Sekgobela, T.K.; Ramogayana, B.; Hato, M.J.; Modibane, K.D. A Comparative Review of Metal Oxide Surface Coatings on Three Families of Cathode Materials for Lithium Ion Batteries. *Coatings* **2021**, *11*, 744. <https://doi.org/10.3390/coatings11070744>

Academic Editor: Yifan Dong

Abstract In the recent years, lithium-ion batteries have prevailed and dominated as the primary power sources for mobile electronic applications. Equally, their use in electric resources of transportation and other high-level applications is hindered to some certain extent. As a result, innovative fabrication of lithium-ion batteries based on best performing cathode materials should be developed as electrochemical performances of batteries depends largely on the electrode materials. Elemental doping and coating of cathode materials as a way of upgrading Li-ion batteries have gained interest and have modified most of the commonly used cathode materials. This has resulted in enhanced penetration of Li-ions, ionic mobility, electric conductivity and cyclability, with lesser capacity fading compared to traditional parent materials. The current paper reviews the role and effect of metal oxides as coatings for improvement of cathode materials in Li-ion batteries. For layered cathode materials, a clear evaluation of how metal oxide coatings sweep of metal ion dissolution, phase transitions and hydrofluoric acid attacks is detailed. Whereas the effective ways in which metal oxides suppress metal ion dissolution and capacity fading related to spinel cathode materials are explained. Lastly, challenges faced by olivine-type cathode materials, namely; low electronic conductivity and diffusion coefficient of Li⁺ ion, are discussed and recent findings on how metal oxide coatings could curb such limitations are outlined.

Keywords: lithium-ion batteries; electrochemical performance; metal dissolution; metal oxide coating

<https://doi.org/10.3390/coatings11070744>

Appendix C

The effect of niobium doping on lithium manganese oxide surfaces, $\text{LiMn}_{2-x}\text{Nb}_x\text{O}_4$: DFT study

B Ramogayana ¹, KP Maenetja ¹ and PE Ngoepe ¹

Affiliations 

Published Online: 23 Feb 2022 • https://hdl.handle.net/10520/ejc-aknat_v40_n1_a21

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Abstract

Lithium manganese oxide (LiMn_2O_4) is one of the promising cathode material for lithium-ion batteries (LIBs), however, it suffers from capacity fading mainly due to surface manganese (Mn^{2+}) ion dissolution during Charge/discharge processes. Although many studies focused on reducing Mn-dissolution, surface modification has proven to be an ideal method of reducing Mn^{2+} ion dissolution in secondary Li-ion batteries. In this study, the density functional theory calculations were carried out to study the bulk properties and investigate the effect of Nb surface doping on major LiMn_2O_4 spinel surfaces. Upon surface Nb doping, we observed a decrease in surface free energy as compared to the surface energies of pure surfaces, indicating that the surface stabilizes upon doping. However, the (001) surface remained the most stable facet, with a similar trend of increasing energies and decreasing stability, *i.e.* (001) < (011) < (111). Due to the stronger binding energy of Nb-O as compared to Mn-O, doping with Nb can suppress the Mn dissolution during intercalation and hence improve the electrochemical performance.

https://hdl.handle.net/10520/ejc-aknat_v40_n1_a21

Appendix D



Journal of The Electrochemical Society, 2022 169 090507
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A DFT + U-D3 Study of the Adsorption of Hydrogen Fluoride and Ethylene Carbonate on the Niobium-Doped (001), (011), and (111) Surfaces of Lithium Manganese Oxide

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Cationic doping has been recommended as one of the most effective methods of reducing the number of trivalent manganese (Mn^{3+}) ions that undergo a disproportionation reaction in lithium manganese oxide-based (LiMn_2O_4) lithium-ion batteries. However, the effect of surface doping on the major LiMn_2O_4 surfaces and their interactions with the electrolyte components is not yet fully understood. In this work, spin-polarised density functional theory-based calculations [DFT + U-D3 (BJ)] were employed to study the adsorption of the electrolyte components ethylene carbonate (EC) and hydrogen fluoride (HF) onto the Nb-doped major LiMn_2O_4 (001), (011), and (111) surfaces. During the substitution of niobium for manganese ions in the second surface layers ($\text{Nb}_{\text{second}}$), it was found that the (111) surface stability improves, resulting in an enhanced (111) plane on the morphology. However, replacing the first (Nb_{first}) as well as both top and sub-surface (Nb_{both}) layers of Mn atoms in the slabs maintains the same stability trend as in the pure pristine surfaces. Moreover, both adsorbates greatly preferred binding to the surfaces through the Nb instead of Mn atoms, and the largest adsorption energy was calculated for EC on the LiMn_2O_4 (011) surface doped on the $\text{Nb}_{\text{second}}$ site and for HF on the LiMn_2O_4 (111) surface doped on the Nb_{both} site. Furthermore, the EC/HF adsorptions further enhance the stability of the $\text{Nb}_{\text{second}}$ (111) surface plane. However, minimal charge transfer was calculated for both HF and EC interacting with the pure and Nb-doped surfaces. Our findings are interesting, since exposing the (111) surface promotes the formation of a stable solid electrolyte interface (SEI), significantly reducing Mn dissolution and enhancing the adsorption of EC and HF.

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<https://iopscience.iop.org/article/10.1149/1945-7111/ac8e35/meta>

Appendix E

MATEC Web of Conferences 370, 02003 (2022)

Computational study of bulk and surface properties on ruthenium oxide (RuO₂)

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Abstract

Metal oxides are widely used in lithium-air batteries to improve the formation of stable discharge products and improve lifespan and electrochemical performance. Despite the intense studies on metal oxides catalysts, ruthenium oxide attracted the most attention since it doesn't only catalyse the redox processes but reduces the over-potential and stabilizes the Li cyclability. Hence, in this work we discuss the bulk and low Miller index surfaces of RuO₂ using the first principle density functional theory calculations. It was found that the lattice parameters are in good agreement with the reported results, with less than 1.4% difference. Furthermore, RuO₂ was also found to be mechanically stable with all positive independent elastic constants (C_{ij}) obeying the mechanical stability criteria and a positive tetragonal shear modulus ($C' > 0$). The bulk to shear ratio indicates that the structure is ductile. The density of states shows a slight pseudo gap for RuO₂ at the Fermi energy, which suggests that the structure is stable. Finally, low Miller index surfaces (*i.e.* (110), (010), (001), (111), and (101)) were modelled using METADISE code, and the most stable facet was in agreement with the reported literature.

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<https://doi.org/10.1051/matecconf/202237002003>

Appendix F

Stability of NaO₂ and LiO₂ discharge products in metal-air batteries: density functional theory study

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Abstract. Rechargeable metal-air batteries are considered the next generation energy storage devices with the highest energy density of ~200 Wh/kg (which is much higher than the Li-ion batteries with ~150 Wh/kg). However, their practical applications are widely affected by the formation of unstable discharge products (like Na/LiO₂, Na/Li₂O, and Na/LiO) which react with electrolyte or the porous electrode material leading to either fire or explosion. Here, we explore the stability of the bulk pyrite and marcasite lithium/sodium superoxide (Li/NaO₂) discharge products produced in Li and Na-air batteries using density functional theory calculations. The calculated lattice and heats of formations are consistent with available reported data. The electronic properties of show the *Pnmm* LiO₂ as the most stable structure with the least density of states at the Fermi. The vibrational properties also show no imaginary vibrations in all directions for *Pnmm* LiO₂. This finding can help direct and give an insight into the stability of major discharge products and give research direction towards controlling the formation of desired M-O discharge products in the batteries.

<https://doi.org/10.1051/mateconf/202338807019>

Appendix G

Surfaces and Interfaces 48 (2024) 104316



Contents lists available at ScienceDirect

Surfaces and Interfaces

journal homepage: www.sciencedirect.com/journal/surfaces-and-interfaces



Structures, electronic properties, and delithiation thermodynamics of the heteroepitaxial α -Al₂O₃/LiMn₂O₄ (001) and (111) interfaces

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ARTICLE INFO

Keywords:

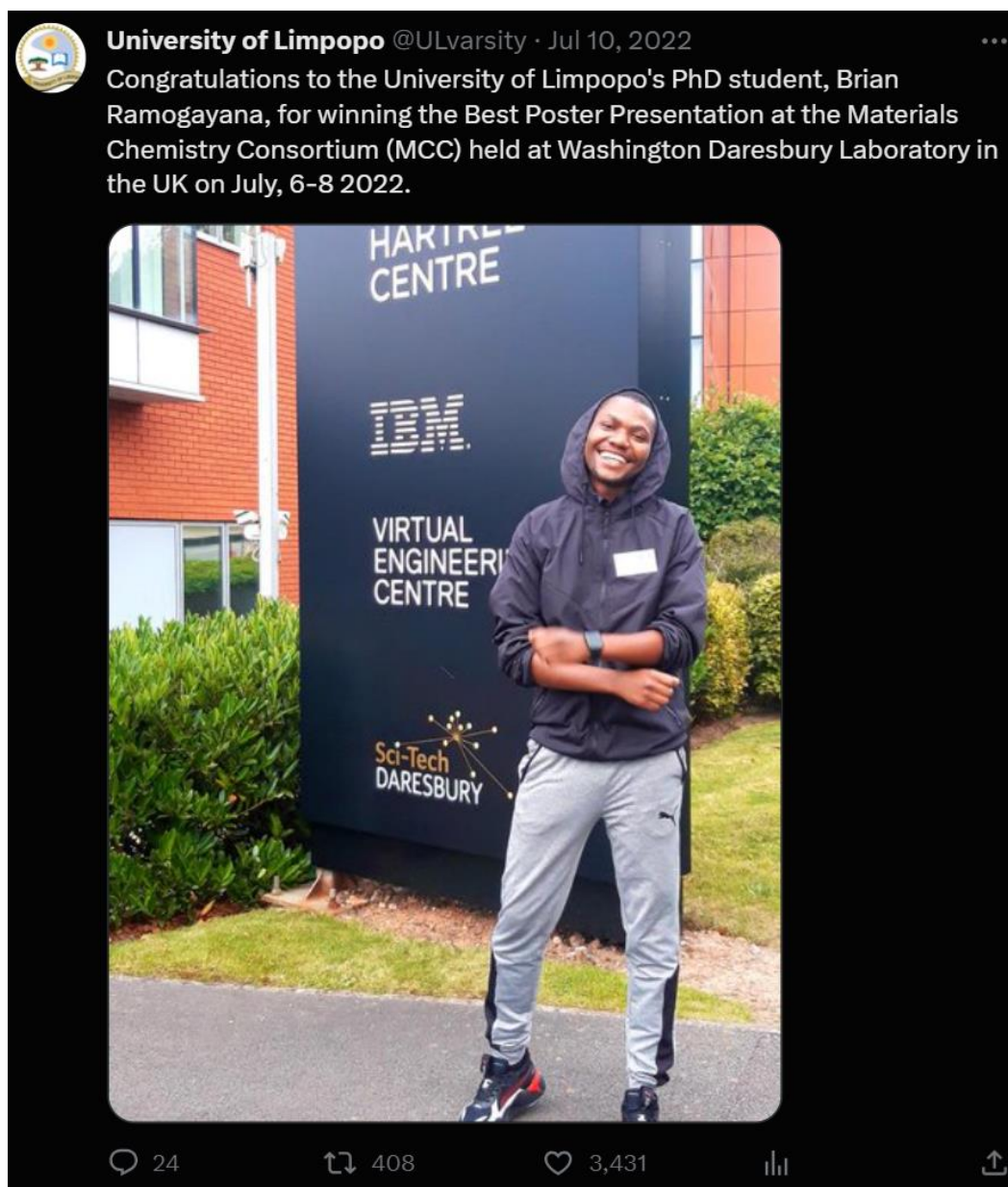
Heteroepitaxial interfaces
Aluminium oxide coating
Spinel surfaces
Li-ion batteries
DFT

ABSTRACT

Surface coatings play a pivotal role in enhancing the performance of secondary lithium-ion batteries by mitigating undesirable electrolyte activity towards the cathode materials. Metal oxide candidates have been investigated extensively, with α -Al₂O₃ emerging as a particularly promising coating material owing to its exceptional mechanical and thermal stability alongside low electrical conductivity. Despite the extensive exploration of this application of α -Al₂O₃, insight into the interplay between the coating layer and the cathode substrate remains incomplete. To address this lack of knowledge, this study employs density functional theory calculations with a Hubbard Hamiltonian and long-range dispersion corrections (DFT+U-D3) to comprehensively investigate the interfacial geometries, stabilities, and electronic properties of α -Al₂O₃-coated LiMn₂O₄ (001) and (111) interfaces of varying thicknesses. The individual surfaces were modelled first before constructing the interfaces. We found that the α -Al₂O₃ (11 $\bar{2}$ 0) and (0001) surfaces match the LiMn₂O₄ (001) and (111) facets well, exhibiting {1132} and {3121} configurations, respectively, with corresponding misfits of 2.40 and 2.75 %. We calculated the largest adhesion energies of 0.16 and 0.10 eV/Å² for monolayers with the {1132} and {3121} configurations, respectively, with the stability decreasing as the thickness of the α -Al₂O₃ layer increases. Further analysis reveals a minor charge accumulation on the substrate, attributed to charge accumulation on the oxygen atoms that participate in the Al-O bond. In contrast, we observed a depletion of charge on the manganese atoms that form the MnO₆ units. The vacancy formation energies increase following partial delithiation, prompting minor charge depletion on neighbouring Mn atoms in the form of charge redistribution. The calculated work function increases with respect to the pristine surfaces, indicating that the coated interfaces are less reactive.

<https://doi.org/10.1016/j.surfin.2024.104316>

Appendix G



Appendix H



SCHOOL OF CHEMISTRY NEWS /// TUESDAY 20 JUNE 2023

2023 School of Chemistry Postgraduate Conference

SHARE



The 2023 School of Chemistry Postgraduate Conference took place between 12 and 14 June.

It began with a postgraduate careers event, featuring presentations and networking by our sponsors. This was followed by oral presentations from the third year PhD students, and a poster session featuring second year students.

The presentations highlighted the wide scope and high quality of research in the School. They included: microscale and nanoscale carbon materials for applications in medicine and waste water treatment; the chemistry of the atmosphere on Earth, and on other planets; computer methods for designing and optimising new chemical processes for industry; and, new ways to study the structures of proteins, and design drug candidate molecules to interact with them.

The conference concluded with a plenary lecture by Professor Julie McPherson from the University of Warwick, about her conducting diamond materials for electrochemical sensing and catalysis applications. We were fortunate to host Julie so soon after her award of this year's Royal Society of Chemistry Tilden prize.

Prizes for the best talks and poster presentations were voted for by the students and staff. The prize winners from left to right are: Darcey Ridgeway-Brown, Jacob Webb, Rachel Bocking, Thomas Moore, Tom Dixon, Brian Ramogayana, Niamh Robertson and Raphael Stone (inset).

The conference was organised by Rachel Bocking and her colleagues on the Postgraduate Student Committee, and the Director of Postgraduate Studies Malcolm Halcrow. We are very grateful to Avantor, C-Capture, Keracol, Lhasa, Merck, William Blythe and the Society of Chemical Industry for sponsoring the event.

<https://eps.leeds.ac.uk/chemistry-masters/news/article/5951/2023-school-of-chemistry-postgraduate-conference>

Appendix I



UNIVERSITY OF LEEDS

POSTGRADUATE CONFERENCE 2022/23 POSTER PRESENTATION – 1ST PRIZE

SCHOOL OF CHEMISTRY
UNIVERSITY OF LEEDS

This is to certify that
Brian Ramogavana

*has been awarded the 1st prize for the best poster presentation at the
School of Chemistry Postgraduate Conference*

You will receive £100 which will be paid into your bank account

June 2023

A handwritten signature in black ink, appearing to read 'M. Alexander'.

Director of Postgraduate Studies

*****The END*****