# Multiscale computational study of battery materials: From Density Functional Theory to Monte Carlo simulations

## Ali Jaberi

Department of Mining and Materials Engineering

McGill University, Montreal

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#### Abstract

Lithium-ion batteries are among the most promising energy storage devices required for the rapid energy transition necessitated by the escalating climate change crisis. The performance of these batteries relies on the properties of their critical components. Of particular interest is the lithium (Li) transport characteristic in the battery materials which is crucial in high-power applications. In addition, chemical and structural information of battery materials acquired by electron microscopes is vital and yet challenging as these materials are highly suspectable to beam damage, especially knock-on damage. In this thesis, multiscale computational approaches are utilized to investigate Li transport and knock-on damage in battery materials to, respectively, give atomistic insight into the Li transport behaviour in battery materials and give an efficient strategy for reducing the beam damage in beam-sensitive battery materials.

A multiscale computational approach ranging from Density Functional Theory (DFT) to Monte Carlo (MC) simulations was employed to investigate the Li diffusivity in LiNi<sub>0.333</sub>Mn<sub>0.333</sub>Co<sub>0.333</sub>O<sub>2</sub> (NMC111) as a layered cathode material. The MC simulations revealed a perfect honeycomb-like arrangement of Li ions in the Li layer at a concentration of 0.8. This precise arrangement of Li ions resulted in a substantial drop in the thermodynamic factor, leading to a minimum value of the chemical diffusion coefficient at the stated concentration. Moreover, at Li concentrations of 0.2 and 0.3, respectively, a parallelogrammatic and triangular partial ordering of Li ions in the Li layer was observed, which raised additional fluctuations in the thermodynamic factor. By integrating the atomic configuration-dependent barrier energy model into the kinetic Monte Carlo (KMC) simulation, the chemical diffusion coefficient was determined. This diffusion coefficient exhibited considerable variation ranging from  $5.6 \times 10^{-13} cm^2/s$  to  $1.2 \times 10^{-11} cm^2/s$  across all states of the charge. The accuracy of our framework for investigating the transport characteristics of Li in the NMC111 crystal was confirmed by a perfect correlation between the outcomes of our simulations and the experimental measurements obtained in other studies.

The study of Li transport using a multiscale computational approach was extended to lithium oxide (Li<sub>2</sub>O) as one of the major components of the solid electrolyte interphase layer. The DFT calculations were employed to examine the mechanisms of Li diffusion and the recombination of Frenkel pairs, as well as their first-principle total energies. Based on our calculations, the barrier

energy for the vacancy-mediated jump in the  $\langle 100 \rangle$  direction within the antifluorite structure of Li<sub>2</sub>O was found to be the lowest when compared to alternative diffusion mechanisms. As a result of incorporating the recombination of Frenkel pairs into the KMC algorithm, the diffusion coefficient of Li converged more closely to the direct experimental measurement. The KMC simulation gave a Li diffusion coefficient of  $3.8 \times 10^{-12} \text{ cm}^2/\text{s}$  in Li<sub>2</sub>O at a temperature of 300 K, which is merely one order of magnitude greater than indirect experimental measurement. This indicates the precision of our formalization for investigating Li transport in Li<sub>2</sub>O.

The knock-on damage induced in Li-containing materials by high-energy beam electrons in electron microscopes was investigated by a multiscale computational approach. For this objective, the sudden approximation technique was employed to calculate the threshold displacement energies (TDEs) for three distinct material sets: pure elements, LiX (X=F, Cl, Br), and Li<sub>2</sub>MSiO<sub>4</sub> (M = Fe, Co, Mn). By incorporating the Climbing-Image Nudge Elastic Band (CI-NEB) method into the sudden approximation technique, the accuracy of the predicted TDEs was discovered to be enhanced. In addition, the results revealed that the knock-on damage for Li in both its elemental and compound states was greatest at moderate electron energies. Furthermore, it has been demonstrated that the TDE should be the primary factor for evaluating the susceptibility of Li to knock-on damage in identical structures. It was discovered, however, that additional variables, such as atomic number, cross-section, density, weight fraction, and atomic weight, influence the knock-on damage in general.

### Résumé

Les batteries lithium-ion (LIB) se révèlent cruciales pour la transition énergétique face à la crise climatique. Cette thèse adopte des approches computationnelles multi-échelles pour examiner le transport du lithium (Li) et les dommages par chocs dans les matériaux de batterie des LIB.

Une approche allant de la théorie de la fonctionnelle de la densité (DFT) aux simulations de Monte Carlo (MC) se penche sur la diffusivité du Li dans LiNi<sub>0.333</sub>Mn<sub>0.333</sub>Co<sub>0.333</sub>O<sub>2</sub> (NMC111), un matériau cathodique en couches. Les simulations MC mettent en lumière un arrangement parfait en nid d'abeille des ions Li à une concentration de 0,8, entraînant une notable diminution du coefficient de diffusion chimique. À des concentrations de Li de 0,2 et 0,3, on observe respectivement un ordonnancement partiel en parallélogramme et en triangle des ions Li dans la couche de Li. Le coefficient de diffusion chimique, déterminé en intégrant le modèle d'énergie de barrière dans la simulation cinétique de Monte Carlo (KMC), varie de 5.6 × 10<sup>-13</sup> cm<sup>2</sup>/s à 1.2 × 10<sup>-11</sup> cm<sup>2</sup>/s à toutes les états de charge, confirmant la précision du cadre par corrélation avec d'autres études.

L'exploration du transport du Li s'étend à l'oxyde de lithium (Li<sub>2</sub>O), l'un des composants majeurs de la couche d'interphase de l'électrolyte solide. Les calculs DFT analysent les mécanismes de diffusion du Li et de recombinaison des paires de Frenkel, ainsi que leurs énergies totales de premier principe. L'énergie de barrière pour le saut médié par la vacance dans la direction  $\langle 100 \rangle$  se révèle la plus basse. Les résultats montrent qu'en incorporant la recombinaison des paires de Frenkel dans l'algorithme KMC, le coefficient de diffusion du Li converge plus étroitement vers la mesure expérimentale directe. La simulation KMC fournit un coefficient de diffusion de  $3.8 \times 10^{-12} \text{ cm}^2/\text{s}$  dans Li<sub>2</sub>O à 300 K, soit environ un ordre de grandeur supérieur à la mesure expérimentale indirecte, soulignant la précision de notre formalisation.

Enfin, l'étude des dommages causés par des faisceaux d'électrons à haute énergie dans les matériaux contenant du Li est menée par une approche computationnelle multi-échelles. La technique d'approximation soudaine calcule les énergies de déplacement de seuil (TDE) pour divers ensembles de matériaux, incluant les éléments purs, LiX (X=F, Cl, Br), et Li<sub>2</sub>MSiO<sub>4</sub> (M = Fe, Co, Mn). En intégrant la méthode Nudge Elastic Band (NEB) dans l'approximation soudaine,

la précision des TDE prédits est améliorée. Les résultats révèlent que les dommages au Li, sous forme élémentaire ou composée, atteignent leur maximum à des énergies électroniques modérées. Bien que le TDE soit le principal facteur d'évaluation de la susceptibilité, des variables supplémentaires, telles que le numéro atomique, la section efficace, la densité, la fraction pondérale et le poids atomique, influent sur les dommages de manière générale.

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### Foreword

This thesis is based on a manuscript-based format that is offered by McGill University as an alternative to the traditional thesis format. Chapter 3 of this thesis is ready to be submitted, whereas Chapters 4 and 5 have been published in peer-reviewed journals.

#### **Authorship contributions**

- 1. Ali Jaberi, Michel L. Trudeau, Jun Song, and Raynald Gauvin, Study of Lithium transport in NMC Layered oxide cathode material using atomistic simulations. To be submitted.
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For all listed manuscripts, Ali Jaberi, Professor Jun Song, and Professor Raynald Gauvin designed the simulations after conceiving the concepts. Ali Jaberi performed all simulations, analyzed the results, and wrote the manuscripts. All the co-authors reviewed and edited the manuscripts. Mr. Nicolas Brodusch conducted simulations for the electron trajectories and offered guidance on the beam damage. Professor Michel L. Trudeau assisted on the concepts related to the cathode materials with fruitful discussion.

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## List of Abbreviations

ASAT	Atomic-Scale Analytical Tomography
BSE	Back Scattered Electrons
CI-NEB	Climbing-Image Nudge Elastic Band
СМС	Canonical Monte Carlo
CV	Cyclic Voltammetry
DFT	Density Functional Theory
ECI	Effective Cluster Interaction
EELS	Electron Energy Loss Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
EM	Electron Microscope
EVs	Electric Vehicles
FCC	Face Centered Cubic
GCMC	Grand Canonical Monte Carlo
GGA	Generalized Gradient Approximation
GITT	Galvanostatic Intermittent Titration Tests
HAADF	High-Angle Annular Dark-Field
НСР	Hexagonal Closed Packed
KECI	Kinetic Effective Cluster Interactions
KMC	Kinetic Monte Carlo
KRA	Kinetically Resolved Activation
LCO	LiCoO2
LFP	LiFePO4

LIBs	Lithium-Ion Batteries
LMO	LiMn2O4
MC	Monte Carlo
MD	Molecular Dynamics
MEP	Minimum Energy Path
NCA	LiNi0.8Co0.15Al0.05O2
NEB	Nudged Elastic Band
NMC	LiNixMnyCo(1-x-y)O2
NMC111	Linio.333Mno.333Coo.333O2
ODH	Oxygen Dumbbell Hop
PBE	Perdew-Burke-Ernzerhof
PITT	Potentiostatic Intermittent Titration Tests
SEI	Solid Electrolyte Interphase
SEM	Scanning Electron Microscope
SOC	State Of The Charge
TDE	Threshold Displacement Energy
TSH	Tetrahedral Site Hop

### 1. Chapter 1. Introduction

#### 1.1. Motivation

Climate change, population growth, and the increasing cost of fossil fuels collectively require a transition from fossil fuels to renewable energy resources and from internal combustion engines to electric vehicles (EVs) [1,2]. Achieving an effective energy transition necessitates not solely the sustainable production of energy, but also the storage of energy in a manner that is both efficient and cost-effective, while also providing superior energy and power density, stability, and longevity [1–3]. Electrochemical energy storage devices, specifically lithium-ion batteries (LIBs), demonstrated enhanced functionality in comparison to alternative forms owing to their exceptional efficiency and ability to regulate energy and power [2,4,5]. Consequently, the market for LIBs has expanded significantly over the past three decades, and this trend is anticipated to continue in the coming years due to the expanding EV market segment [6].

LIBs operate by removing lithium (Li) ions from the cathode (positive electrode) of the battery during the charging process and reintroducing them back into the cathode when the battery is discharged. Materials with rapid Li transport are necessary for this process, especially in high-power applications such as EVs and hybrid EVs [7]. This characteristic also applies to the cathode materials as slow Li diffusion in these materials has been proven as the principal reason for cathode capacity underutilization at high charge/discharge rates [8,9]. Lithium cobalt oxide (LCO) was a cathode material implemented in the initial commercial LIB cell, unveiled by Sony Corporation in 1991 [10]. Despite decades of use, the performance of this material may not be adequate to accommodate the rapid energy transition necessitated by the current climate crisis. Alternatively, lithium nickel manganese cobalt oxide (NMC), which incorporates the benefits of the three transition metals, became one of the most prominent layered oxide cathode materials. It is expected that this material share 41% of the market by 2025 in all LIBs [6]. Consequently, Li transport behaviour in NMC is a fundamental property to be assessed for the successful implantation of this promising cathode material in high-power applications.

An additional element that may impede the transport of Li ions is the development of a solid electrolyte interphase (SEI) passivation layer [11,12]. This layer is produced when the redox

potential of the electrode of a battery exceeds the electrolyte's electrochemical window [13]. While the composition of this layer can differ based on factors such as the anode, cathode, type of electrolyte, and electrochemical conditions, lithium oxide (Li<sub>2</sub>O) is widely recognized in the literature as a fundamental component of SEI [14–16]. Therefore, understanding the impact of different parameters on the diffusivity of Li ions in Li<sub>2</sub>O is critical for the advancement of LIBs intended for high-power applications.

Electrochemical techniques, including Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Potentiostatic and Galvanostatic Intermittent Titration Tests (PITT and GITT), are frequently employed to investigate Li transport within the battery cell [17–19]. Despite the widespread application of these methods to Li<sub>2</sub>O [20–22] and NMC [18,23–27], they continue to have a number of drawbacks that result in substantial estimation errors when it comes to the diffusion coefficient [28,29]. In light of the existing challenges in experimental methods, it remains imperative to formulate a multiscale atomistic simulation algorithm that can provide a comprehensive understanding of Li diffusion in these materials and complement the electrochemical methods to improve the power performance of LIBs.

In addition to the Li transport behavior, the chemical and structural properties of battery materials are crucial for the development of LIBs. Electron microscopes have been widely utilized for battery materials to obtain this information in high-resolution [30–35]. Nevertheless, the material may be damaged by various mechanisms (e.g., knock-on, radiolysis, heating, and charging) when interacting with the high-energy beam-electrons [36]. As the defects induced by these damages are not intrinsic to the materials under investigation, they may misinterpret the electron microscopy characterizations. Compared to other forms of beam damage, knock-on damage is much more severe in Li-containing materials due to the high mobility of Li atoms [37,38]. Given that beam damage dictates the spatial resolution limit [39], determining an optimized operating condition to mitigate knock-on damage is thus essential when employing electron microscopes to characterize Li-containing materials. Although numerous studies have examined the effects of electron beam damage on Li-containing materials [34,37,40–42], the issue of beam damage continues to pose a substantial barrier to precise characterization of Li-containing materials using electron microscopes. Given the atomistic characteristics of the knock-on damage,

a multiscale computational method may be regarded as a potential approach for examining this damage and offering valuable insights into possible mitigation strategies.

#### 1.2. Objectives

The overall objective of this thesis is to utilize multiscale computational methods to study Li transport in battery materials for high-power applications, and also examine knock-on damage induced in battery materials during electron microscopy characterization. This study is a material level investigation; thus, the concept of diffusivity is not extended to the transport in the cell level. To be more precise, the aims of this thesis are to:

- Develop a multiscale atomistic simulation method for investigating the factors affecting the Li diffusivity in NMC to provide an atomistic point of view of Li diffusion in NMC and develop LIBs for high-power applications.
- Develop a multiscale atomistic simulation method for studying Li diffusivity in Li<sub>2</sub>O to capture the timescale of Li diffusivity in this material at low temperatures at which the LIBs usually operate for designing these batteries in high-power applications.
- Investigate knock-on damage induced during the electron microscopy characterization of battery materials to give insight into the efficient strategy for reducing this damage by determining the influencing factors and quantifying the damage.

#### **1.3.** Thesis Organization

This thesis contains seven chapters. Chapter 1 gives a general introduction to the motivation and objectives of this thesis. Chapter 2 provides a literature review on the fundamentals of LIBs, beam damage, diffusion and simulation methods and the recent research status.

In Chapter 3, an algorithm is formulated to simulate Li transport in NMC. A new model is proposed to capture the dependency of jump barrier energies on the local atomic environment. The study of diffusivity is extended by KMC simulations at each state of the charge of NMC followed by an investigation of the factors that influence the diffusivity in this material.

In Chapter 4, a multiscale atomistic simulation method is developed to study Li diffusion in the Li<sub>2</sub>O component of the SEI layer. Different diffusion mechanisms are studied and the dependency

of jump barrier energies on the local atomic environment is formulated by local cluster expansion. The kinetic Monte Carlo (KMC) is used to study the diffusivity at a large time length scale and the effect of the Frenkel defect on the diffusivity calculations is discussed.

In Chapter 5, multiscale simulations are used to investigate the knock-on damage that may be induced during electron microscopy of battery materials. The threshold displacement energies are calculated by Density Functional Theory (DFT) and then incorporated into the Monte Carlo simulation to quantify the damage. Theoretical calculations are also accompanied by these simulations to further assess the proposed methods.

Chapter 6 provide an extended discussion to the findings, existing limitations, and potential future directions of this thesis. Finally, chapter 7 summarizes the concluding remarks, contribution to the knowledge and recommendations for future.

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## 2. Chapter 2. Literature Review

In this chapter, the fundamentals of Li-ion batteries including their performance, common commercial cathodes, and solid electrolyte interphase layer are introduced. This is followed by a review of diffusion and electron microscopy with the focus on lithium diffusion and beam damage in battery materials. The last section of this chapter focuses on the theoretical foundation of the simulations and their application in battery materials.

#### 2.1. Lithium-ion batteries

A battery is "a device for storing the chemicals that react to create a direct current flow, in other words, batteries convert chemical energies into electrical energy" [1]. The LIBs are made up of three components by which they can provide energy: anode, cathode, and electrolyte. The Electrodes (i.e., anode and cathode) which are separated by electrolyte and separator, take and give the lithium-ions and electrons to generate energy for the device connected to the battery. Electrolyte provides a conductive medium for the Li-ions to travel between the anode and cathode while it is electrically insulator [1]. The electrolyte plays an important role in the stability and surface reactions on the cathode. A suitable electrolyte should have low flammability, high thermal stability, high ionic conductivity and also it should form a stable solid electrolyte interface (SEI) on the anode [1,2]. During the initial formation process, the SEI is formed on the anode (usually) in which some lithium atoms make a permanent bond with the anode and this results in the permanent loss of active lithium-ions and consequently irreversible capacity loss [1].

LIBs consist of one or more electrochemical cells in which oxidation and reduction (redox) reactions take place to generate an electromotive force for the flow of electrons through the circuit. Oxidation occurs when an element loses one or more electrons while reduction means an element gains one or more electrons. During discharging, the Li-ions travel from anode to cathode through the electrolyte, while electrons will flow in the external circuit from anode to cathode which results in an electric current in the opposite direction as shown in Figure 2.1. Lithium as a small particle can reversibly intercalate into/from the active materials. This allows the repetition of charge/discharge, and ultimately shuttling of Li-ions between the electrodes [1].



Figure 2.1. Li-ion battery operation during discharging [1].

#### 2.1.1. Performance

The materials used for each component of LIBs have their unique performance characteristics which makes one fit better than others depending on the designated application [1]. Voltage, energy, and power are among the most critical performance characteristics and will be explained in the following sections.

#### 2.1.1.1 *Voltage*

The voltage is determined by the potential difference between the anode and the cathode. This voltage depends on the type of battery materials and varies with the state of the charge (SOC) as illustrated in Figure 2.2, known as the voltage curve [1,3]. In some cases, the voltage curves are plotted versus the capacity which is a key property of the active materials since it determines the amount of the lithium-ions that can intercalated to/from the structure [4]. The capacity can be simply calculated by multiplying the discharge current by the discharge time.



Figure 2.2. Voltage curves upon first charging [2].

The Voltage is determined by the difference of electrochemical potential between the cathode and anode. However, at equilibrium, the voltage of can be determined by the difference of chemical potentials of the cathode and anode  $(\mu_{Li}^{cat}, \mu_{Li}^{an})$  [2,3]:

$$V_{eq} = -\frac{\mu_{\rm Li}^{\rm cat} - \mu_{\rm Li}^{\rm an}}{e} \tag{2.1}$$

where e is the electron charge magnitude. However, the operating voltage of a battery cell differs from the equilibrium voltage and varies with the current, *I*, as follow [3]:

$$V_{ch} = V_{eq} + \eta(I_{ch}, q)$$
 and  $V_{dis} = V_{eq} - \eta(I_{dis}, q)$  (2.2)

This deviation from the equilibrium voltage,  $\eta$ , is called polarization on discharge or overpotential on charge which depends on the current and the internal cell resistance, R, through  $\eta = IR(q)$ where q is the state of charge [3].

#### 2.1.1.2 *Energy and capacity*

Gravimetric energy density, or the energy per unit weight (Wh/kg), is usually used to compare battery performances in the aerospace industries, while volumetric energy density, or the energy per unit volume (Wh/L), is used to assess the battery performance in automotive industries [1]. The specific energy of a battery can be determined through:

$$E = \int_0^Q V(q) dq \tag{2.3}$$

where V is voltage, q is the SOC and Q is the specific capacity [3]. So, the energy density depends on the capacity of the battery as well as the voltage.

Specific capacity, often known as capacity, refers to the quantity of charge that a cell can hold per unit weight. Specific capacity is commonly measured in milliampere-hours per gram (mAh/g). According to Faraday's first law, the value of Q may be determined using the following formula:

$$Q = \frac{nF}{M} \quad \left(\frac{A.s}{g}\right) \tag{2.4}$$

where n is the number of Li-ions, M is the molecular weight, and F is the Faraday constant.

#### 2.1.1.3 *Power*

In high-power applications, such as portable power tools, electric vehicles, and hybrid electric vehicles, not only the energy density but also the rate capability is crucial. In these applications, fast lithium diffusion is necessary to meet this high power demand [2,4–8]. So, the rate capability, i.e. the ability to quickly charge and discharge, should be evaluated through either power density (the power per liter (W/L), or the power per weight (W/Kg)) or maximum C-rate. C-rate indicates the amount of rate at which the battery is discharged [1].

#### 2.1.2. Cathode materials

The efficiency of the battery is believed to be constrained by the cathode, primarily because of its significant influence on energy density and cost [9,10]. The initial commercialized Lithium-ion battery utilized LiCoO<sub>2</sub> (LCO) as the cathode and graphite as the anode. The invention of LCO as a cathode was initially made by Goodenough et al. [11] in 1980 and then commercialized by Sony Corporation in 1991 [12]. The actual capacity of LCO is around 140 milliampere-hours per gram (compared to a theoretical capacity of 270 milliampere-hours per gram) at an intercalation voltage of around 3.9 volts (compared to the voltage of Li+/Li). Although this material has been utilized for many years, its efficiency may not be adequate to meet the demands of the rapid energy shift required in the current climate crisis. Therefore, the development of the cathode materials is still

in progress to satisfy this energy transition. The current available commercial cathode materials including LiCoO<sub>2</sub> (LCO), LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>(1-x-y)</sub>O<sub>2</sub> (NMC), LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA), LiMn<sub>2</sub>O<sub>4</sub> (LMO), and LiFePO<sub>4</sub> (LFP) are compared in Table 2.1 which is adapted from reference [13].

Cathode Material	Midpoint voltage vs. Li (C/20)	Specific Capacity (Ah/kg)	Advantages	Disadvantages
LCO	3.9	155	Excellent cycle life, and high energy	Low thermal stability
LMO	4.0	100-120	Excellent thermal stability, affordability, and power capability	low energy density
NCA	3.7	180	Excellent energy, power capability, and cycle life	Moderate thermal stability, moisture- sensitive even when discharged.
NMC	3.8	160	Outstanding balance of characteristics (energy, power, cycle life, and thermal stability)	Patent issues
LFP	3.4	160	Excellent thermal stability and cycle life, as well as good rate capability	Low energy, special preparation condition

Table 2.1. Properties of different commercial cathode materials

These cathode materials have different crystal structures including layered in LCO, NMC or NCA, spinel in LMO, and olivine in LFP as illustrated in Figure 2.3. Therefore, the intercalation process requires Li diffusion in 1D, 2D and 3D space in the olivine, layered, and spinel structures, respectively [14]. This signifies the importance of the atomistic point of view to the Li transport as the change in the atomistic configuration in the structure could completely change the Li diffusion characteristics.



Figure 2.3. Schematic of the crystal structure of commercial battery materials: a) layered, b) spinel, and c) olivine [15]. The green circles depict the Li-ions.

As illustrated in Table 2.1, NMC is the only material that possesses a well-balanced combination of properties with the least drawbacks. Additionally, NMC gained more attraction after setting the target energy density to 350 Wh/kg in the U.S. Battery Consortium 2017 [16]. By 2025, this material is anticipated to account for 41% of the market in all LIBs [17]. Therefore, to effectively tackle the present climate change crisis, it is imperative to further enhance the performance of this material.

During the high-temperature synthesis, NMC forms an O3 layered structure (R-3m symmetry) where oxygen atoms are set in a cubic close-packed framework and form ABCABC stacking of oxygen sheets. In this structure, Lithium atoms will be placed on the 3a octahedral sites while transition metals will occupy the 3b octahedral sites in the alternating layers as illustrated in Figure 2.4 [2,18].



Figure 2.4. Schematic of the layered structure of NMC [2].
Whittingham et al. [7] showed that by increasing the rate of discharge, the voltage curve of NMC drops significantly (Figure 2.5), reducing the battery performance. While particle size, electronic conductivity, structural transformation and effective capacity influence the rate capability, he argued that Li diffusion is the limiting factor for the high rate performance of this cathode material [7]. In addition, Chiang et al. [19] revealed that at high voltages the Li diffusion in the bulk is the kinetic control process in a single NMC particle. So in this study, a detailed investigation of Li diffusion in NMCs is performed to improve this material for high-power applications such as EVs.



Figure 2.5. Discharge curve of NMC 333: current densities increase from 0.1 to 0.5, then 1, 3, 5, 8 mA/cm<sup>2</sup> [7].

## 2.1.3. Solid Electrolyte Interphase (SEI)

The solid electrolyte interphase (SEI) layer is usually formed when the redox potential of the electrode exceeds the electrolyte's electrochemical window [20]. If the SEI is not adequately passivating or stable, it might lead to the ongoing production of this layer, causing the constant depletion of the electrolyte [17]. Thus the characteristics of an optimized SEI layer should be high electrolyte diffusion resistance, negligible electrical conductivity, and high selectivity and permeability for lithium ions [21]. SEI is typically composed of a dense layer of inorganic compounds adjacent to the electrolyte phase [20]. **Table 2.2** shows the main components of the SEI reported in the literature [22].

Components	Reference	Notes
(CH <sub>2</sub> OCO <sub>2</sub> Li) <sub>2</sub>	[23]	It is predominantly present in the SEI of electrolytes based on ethylene carbonate (EC).
ROCO <sub>2</sub> Li	[23]	They are present in the majority of electrolytes containing propylene carbonate (PC).
Li <sub>2</sub> CO <sub>3</sub>	[24]	Typically found in SEIs produced in electrolytes based on PC or EC.
ROLi	[23,25]	Most commonly found in ether electrolytes.
LiF	[24,26]	Predominantly present in electrolytes that consist of fluorinated
		salts, such as $LiAsF_6$ , $LiPF_6$ , and $LiBF_4$ .
Li <sub>2</sub> O	[27–29]	The major species comprising the SEI in butyrolactone + $LiAsF_6$ .
Polycarbonates	[26]	Located near the electrolyte phase in the uppermost layer of the
		SLI.
LiOH	[30]	Mostly formed by water contamination.
HCOLi	[31]	Present when methyl formate is employed as a co-solvent or
		additive.

Table 2.2. The main components of the SEI layer reported in the literature.

The SEM images and schematic of this layer are illustrated in Figure 2.6. At high current densities, the Li transport not only within the electrode but also at the solid/electrolyte interface should be fast enough to fulfill the high power demand [2,32], Therefore, studying Li transport at the SEI layer is also crucial for high power applications. Despite variations in composition and content based on the anode, cathode, electrolyte type, and electrochemical conditions, lithium oxide (Li<sub>2</sub>O) is commonly recognized in the literature as one of the key components of SEI [22,33,34]. In this study, we focus on the Li<sub>2</sub>O component of the SEI layer and investigate the diffusivity of Li in this material in order to enhance LIBs for high-power applications.



Figure 2.6. SEM image of the graphite electrode a) before, and b) after SEI formation [22]. Figure c) shows the schematic of this layer [35].

# 2.2. Diffusion

Slow diffusion results in a Li concentration gradient from the surface to the bulk of the active material particles. So, the Li concentration on the surface differs from the average concentration within the active material particles. On the other hand, it is the Li concentration at the surface of the active materials that determines the voltage, not the average concentration. So, the voltage upon discharging is always lower than the equilibrium voltage (The reverse happens during charging). In addition, charge stops when the surface concentrations become zero (not the average concentration), so, the charging process ends without a complete utilization of the material capacity when the concentration gradient exists. In a condition with both high charge/discharge rate and slow lithium diffusion, this Li concentration gradient becomes deeper, and this results in a larger polarization and capacity loss. On the other hand, this concentration gradient could also be intensified by slow Li diffusion in other battery materials. For example, one of the factors that can potentially hinder Li transport is the slow diffusion in the SEI layer components [32,36]. Therefore, fast Li diffusion within the battery material is critical to the successful implantation of LIBs in high-power applications [2].

Diffusion is often described at a continuum level by the well-known Fick's equations:

$$\boldsymbol{J} = -D\nabla C; \quad \frac{\partial C}{\partial t} = \nabla \cdot (D\nabla C) \tag{2.5}$$

where J is the diffusion flux, D is the diffusion coefficient, C is the concentration, and t is the time. While the importance of continuum description is inevitable, a microscopic point of view on diffusion is fundamental for understanding the factors affecting diffusivity to open the doors to the material level development. At the microscopic level, diffusion arises from the Brownian motion of atoms or molecules. In crystalline materials, this motion is translated as the atomic hops in the lattice and described by the random walk theory of diffusion. In these hops (jumps), the migration path of the diffusing particles is restricted by the crystal lattice which leads to the definition of different diffusion mechanisms.

### 2.2.1. Random walk theory

If the total displacement of a particle, R, breaks down into its components (X, Y, Z), it can be proven that the following partial differential equation holds for each component (for example X component) [37]:

$$\frac{\partial C}{\partial t} = -\frac{\langle X \rangle}{\tau} \frac{\partial C}{\partial x} + \frac{\langle X^2 \rangle}{2\tau} \frac{\partial^2 C}{\partial x^2}$$
(2.6)

where  $\tau$  is the diffusion time. Without any external driving force, the first term on the right-hand side of the equation becomes zero and leaves behind a simpler equation:

$$\frac{\partial C}{\partial t} = \frac{\left\langle X^2 \right\rangle}{2\tau} \frac{\partial^2 C}{\partial x^2} \tag{2.7}$$

This simpler equation now is identical to Fick's second equation, thus, the coefficient on the righthand side represents the x component of the diffusion coefficient. The same approach could be repeated for the other two components of the displacement which gives:

$$D_x = \frac{\langle X^2 \rangle}{2\tau}; \quad \frac{\langle Y^2 \rangle}{2\tau}; \quad D_z = \frac{\langle Z^2 \rangle}{2\tau}$$
 (2.8)

In isotropic materials, these three components are identical:

$$\langle X^2 \rangle = \langle Y^2 \rangle = \langle Z^2 \rangle = \frac{1}{3} \langle R^2 \rangle$$
 (2.9)

Consequently, the equation becomes simpler to the well-known Einstein-Smoluchowski relation as follows:

$$D = \frac{\left\langle R^2 \right\rangle}{6\tau} \tag{2.10}$$

This displacement is composed of many individual atomic hops,  $r_i$ , in a lattice and thus:

$$\boldsymbol{R} = \sum_{i=1}^{n} \boldsymbol{r}_{i} \tag{2.11}$$

It is worth noting that D shows the kinetic contribution to the diffusion. However, the thermodynamic contribution could also be included which is often described by the thermodynamic factor as is given by:

$$\Theta = \frac{\partial(\mu/kT)}{\partial Lnc} = \frac{\langle N \rangle}{\langle (\delta N)^2 \rangle}$$
 2.12)

where  $\mu$  is the chemical diffusion coefficient, k is the Boltzmann constant, and T is temperature. The concentration and number of diffusing species are described by c and N, respectively. On the right-hand side of the equation, the statistical mechanical approach of calculating this parameter is provided where N and its variation is determined by grand canonical Monte Carlo simulation.

# 2.2.2. Diffusion mechanism

In this section, we briefly describe some of the diffusion mechanisms that are usually governed in the battery materials. However, the reader is suggested to refer to the reference [37] for a comprehensive list of diffusion mechanisms.

# 2.2.2.1 Interstitial mechanism

In this mechanism, an atom jumps from one interstitial site to another intestinal site as illustrated in Figure 2.7. This mechanism is also called the direct interstitial mechanism as it directly deals with only the interstitial sites [37].



Figure 2.7. Schematic of direct interstitial mechanism [37].

# 2.2.2.2 Collective mechanism

This mechanism which is applicable for self or substitutional diffusion occurs when two or more atoms jump simultaneously (illustrated in Figure 2.8). Within this mechanism, two atoms could swap their position, which is called direct exchange, or three or more atoms could simultaneously rotate as a group to form a close loop. In these mechanisms the lattice could be defect-free, thus, they are accompanied by large lattice distortion and require large thermal fluctuations [37].



Figure 2.8. Schematic of direct exchange and ring mechanisms [37].

Another subcategory of collective mechanism is called the interstitialcy mechanism in which one interstitial atom pushes one of the lattice sites and moves it to another interstitial site (Figure 2.9). This mechanism is triggered when an interstitial atom is almost of the same size as the lattice atoms [37].



Figure 2.9. Schematic of interstitialcy mechanism [37].

## 2.2.2.3 Vacancy Mechanism

In the vacancy mechanism, a lattice atom jumps to the nearest neighbour's vacant site as shown in Figure 2.10. This mechanism has been identified as the predominant means by which matrix atoms and substitutional solutes diffuse in metals [37].



Figure 2.10. Schematic of vacancy mechanism [37].

# 2.2.3. Diffusion in Li-ion battery materials

In layered oxide cathode (like LCO and NMC as a material of interest in this study), Li-ions follow the direct interstitial mechanism. In layered structures, Li-ions jump from an octahedral site to its neighbour octahedral site as illustrated in Figure 2.11 [2,38]. In these structures, the hops are

classified based on the number of vacancies around the activated state site. If there is only one vacancy around the activated sites, it is called isolated vacancy hop (monovacancy or Oxygen Dumbbell Hop, ODH), unless it is called divacancy (Tetrahedral Site Hop, TSH). In the divacancy mechanism the Li-ions pass through the intermediate tetrahedral site in a curved path. It was found that divacancy is the dominant mechanism in layered structures as its activation barrier is less than the monovacancy jumps [39]. A small reduction in this activation barrier results in a remarkable enhancement in Li diffusion for high-power applications [5]. This activation barrier depends on the size of the tetrahedral site, the electrostatic interaction between the transition metal atoms and Li when it is in the tetrahedral site, and the Li/vacancy arrangement around the migrating atom [5,38]. Therefore, an appropriate model is required to capture the dependency of barrier energies on the local atomic environment.



Figure 2.11: Lithium diffusion path in layered oxide structure [38].

In Li<sub>2</sub>O, as one of the primary components of the SEI layer, both collective and vacancy mechanisms were reported in the literature [40–42]. The vacancies required for the vacancy mechanism in this material are provided by the Frenkel pair defects as this defect is believed to be the dominant defect in the Li<sub>2</sub>O [43–45]. In this material, the diffusion takes place at three dimensions (3D) as opposed to layer oxide cathodes in which 2D diffusion occurs. Therefore, a more complex model is required to capture the dependency of barrier energies on the local atomic environment.

Common techniques utilized to investigate lithium transport in battery cells include electrochemical methods such as Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Potentiostatic and Galvanostatic Intermittent Titration Tests (PITT and GITT) [46–50]. While these methods have been widely implemented, they continue to have several drawbacks [51]. Considering the present difficulties in the field, knowledge of the factors that

impede Li transport remains crucial to improve the power performance of LIBs. Hence, in order to complement electrochemical techniques and offer an atomistic perspective on Li diffusion, a multiscale computational approach is utilized in this study.

# 2.3. Electron Microscopy

The incident beam of electron microscopes can be scattered as a particle or diffracted as a wave [53]. The signals created by scattering processes can be further analyzed to characterize the material (Figure 2.12). Thus, the scattering processes are critical in understanding the fundamentals of electron microscopes. Two types of electron scattering known as elastic and inelastic and also the electron beam damage are explained in the following sections.



Figure 2.12. Generated signals during the electron scattering processes (adapted from [53]).

## 2.3.1. Elastic Scattering and inelastic scattering

In elastic scattering, the incident electrons interact with the Coulomb field of atomic nuclei and consequently deviate at a large angle with a negligible total energy loss. If these electrons escape the specimen surface, they are called Back Scattered Electrons (BSE) which are used as imaging signals. The probability of any scattering events is determined by interaction cross-section. The differential cross-section with respect to the solid angle  $\Omega$  can describe the angular distribution of scattering. For an electron scattered through angle  $\theta$  and solid angle  $\Omega$ , the differential cross section is given by [53]:

$$\frac{d\sigma}{d\Omega} = \frac{1}{2\pi\sin\theta} \frac{d\sigma}{d\theta}$$
(2.13)

The integration of differential cross section gives the total cross section between  $\theta$  and  $\pi$ :

$$\sigma_{\rm atom} = \int_{\theta}^{\pi} d\sigma = 2\pi \int_{\theta}^{\pi} \frac{d\sigma}{d\Omega} \sin \theta d\theta$$
(2.14)

The cross-section of all the atoms then becomes:

$$\sigma_{\text{total}} = N\sigma_{\text{atom}} = \frac{N_0 \sigma_{\text{atom}} \rho}{A}$$
(2.15)

Therefore, the differential cross-section is the only necessary term required for the calculation of the total cross-section. There are various types of differential cross-sections suggested by different literature, however, it is beyond the scope of this work and can be found elsewhere [54]. The inverse of  $\sigma_{total}$  is called the mean free path  $\lambda$  which is defined as the average distance between the scattering events.

Inelastic scattering is the result of electron-electron interaction and is accompanied by energy loss for the incident electrons [55]. The consequence of this energy loss is the production of various signals and events which can be used for materials characterization. These signals and events include Characteristic X-rays, Auger electrons, Bremsstrahlung X-rays, Phonons, Secondary electrons and plasmon excitation [53]. The probability of any of these scattering events is determined by interaction cross-section. Despite the useful information that these scattering events provide, they may cause damage to the material which will be explained in the next section.

### 2.3.1. Beam damage

The beam-induced damage is the main limiting factor of electron microscopes to study LIB materials. The beam damages can be examined in four different levels [56,57]: Displacement (knock-on) damage, Ionization damage (radiolysis), Electrostatic charging, and Heating.

Among these mechanisms, radiolysis and knock-on are the main sources of beam damage in LIB materials investigated by electron microscopes. These two damage mechanisms will be explained in the following sections.

#### 2.3.1.1 *Displacement (knock-on) damage*

Knock-on damage is a result of high-angle elastic scattering. As mentioned before, an interaction is called elastic if the total energy of both electron and nucleus is constant in a localized collision. However, this does not mean that the energy of the electron itself is constant. In fact, the electron should transfer energy to the nucleus during the elastic interaction based on the conservation of momentum and energy [56,57]. This amount of energy can be calculated as follows:

$$E = E_{\max} \sin^2(\theta/2) \tag{2.16}$$

where  $\theta$  is the scattering angle and  $E_{\text{max}}$  is the maximum possible energy loss and can be calculated by:

$$E_{\rm max} \approx 2E_0 (E_0 + 2m_0 c^2) / (Mc^2)$$
 (2.17)

where  $E_0$  is the incident beam electron energy,  $m_0$  is the electron mass, c is the light speed and M is the nuclear mass. The knock-on displacement occurs in the material if the transferred energy E overcomes a barrier called Threshold Displacement Energy,  $E_d$  or TDE [58]. As the equations (2.16) and (2.17) suggest, the transferred energy is a function of the incident beam energy  $E_0$ , the scattering angle  $\theta$  and the atomic mass M. Therefore, high energy beam electrons scattered at high angle in a light atom are more likely to cause knock-on damage. Taking into account the extreme case where  $\theta = 180^\circ$ , the transferred energies as a function of incident beam energy for different materials are illustrated in Figure 2.13 [58].



Figure 2.13: Transferred energy at 180° scattering angle as a function of beam energy [58].

Figure 2.13 clearly shows the vulnerability of lithium atoms to knock-on damage; the transferred energy to lithium is higher than all the other elements. Even at very high energies, the transferred energy to some elements is lower compared to Lithium in low beam energies.

The knock-on damage is only a result of momentum transfer, therefore, decreasing the temperature of a sample like using cryo-EM cannot decrease this damage. The only way to stop this event is to either work below the threshold beam energy or to use a lower amount of dose rate [57]. The threshold energy is the beam energy below which there is no knock-on damage and can be simply determined by putting  $E_{max} = E_d$  in equation (2.17), which gives:

$$E_0^{\min} = m_0 c^2 \{ [1 + (M/2m_0)(E_d/m_0 c^2)]^{1/2} - 1 \}$$

$$\approx (511 \text{keV}) [(1 + AE_d/651 \text{eV})^{1/2} - 1]$$
(2.18)

where A is the atomic weight. The only required parameter to calculate the threshold energy (equation (2.18)) is the displacement energy  $E_d$ . This parameter which depends on bond strengths, lattice parameters, and local environment [59] can be calculated by Density Functional Theory (DFT). While the threshold displacement beam energy is an appropriate quantity to determine the reduced beam damage condition for heavy elements, it cannot be practical for LIBs materials since this energy is too low to acquire enough signals for quantitative analysis of Lithium. Therefore, determining a proper operating condition is of great importance for lithium quantitative analysis with electron microscopes.

### 2.3.1.1 Ionization damage (radiolysis)

Radiolysis is the result of inelastic scattering (i.e. the electron-electron interaction). During inelastic scattering, electrons can lose any amount of energy from a few eV to hundreds of eV. This creates a hole in the atomic electron shell which makes the atom unstable. In metals, the electrons in the system can quickly fill this electron hole while in insulators this vacancy can remain in the system for a longer time. Thus, the excited atom in non-conductive specimens may have enough time to be displaced from its original site which consequently leads to bond breakage or even can cause cross-linking in polymers [56,60]. The displaced atoms can group and form a dislocation loop while the vacancies can accumulate and create a hole when they are thermally mobile. Thus, radiolysis is a temperature-dependent phenomenon and can be controlled by reducing the temperature, e.g. using a cryo-electron microscopy technique [57,61–63].

# 2.3.2. Beam damage in Li-ion battery materials

Knock-on damage is of particular importance in Battey materials due to the lightweight nature of the Li element. The existence of this damage in Li-rich layered cathode materials was confirmed by Wang et al. [64] through the utilization of high-angle annular dark-field (HAADF) images. Lu et al. [65] applied rapid atomic-scale chemical imaging to identify this degradation in a cathode material as well. As a result, in order to utilize electron microscopes to characterize lithium-containing materials, it is essential to establish an optimal operating condition that minimizes knock-on damage, since beam damage dictates the spatial resolution limit [66].

Insufficient research has been conducted on electron beam damage in materials containing lithium. Cui et al. [63] demonstrated that beam damage can be substantially reduced when examining battery materials with electron microscopes at cryogenic temperature and under specified experimental conditions. Nevertheless, achieving this experimental condition can be difficult and is not always feasible. Xin et al. [67] established that a diminished electron dose rate effectively mitigates beam damage in lithium-containing materials. Nevertheless, this does not invariably hold, as certain analyses may result in an inadequate signal-to-noise ratio when a reduced dosage is implemented. As a result, Meng et al. [59] proposed an optimized dosage of electrons to mitigate this damage. Despite the efforts made to address this concern, beam damage continues to pose a substantial barrier to the utilization of electron microscopes for the

investigation of Li-containing materials. Therefore, in this study, we employ a multiscale computational approach ranging from DFT to Monte Carlo simulations to quantify this damage in battery materials and determine the influencing factors.

# 2.4. Multiscale simulation

To understand various phenomena and properties in the materials, different computational approaches could be utilized. Each approach has its limitations in terms of time and length scale (shown in Figure 2.14), restricted by the computational costs and the underlying physics describing the properties/phenomena [68]. Therefore, the multiscale computational approach surpasses these limitations and combines the advantages of each of them.



Figure 2.14. Different computational methods in terms of time/length scale [68].

To study Li diffusivity and beam damage in battery materials, different theoretical backgrounds in the fields of quantum mechanics and statistical mechanics are required. In the next three sections, we will briefly describe the theory and the formulations behind these concepts.

#### 2.4.1. Density Functional Theory

The ground state energy of a system is achieved by solving the Schrodinger equation for the wave function  $\psi$ . Although there are several forms of the Schrodinger equation, the time-independent, non-relativistic form of this equation is considered in this study [69]:

$$\frac{-\hbar^2}{2} \sum_{i}^{N} \frac{\nabla^2 \psi_i}{m_i} + \sum_{i}^{N} V(r_i) \psi_i = E \psi$$
(2.19)

Finding the solution to the Schrodinger equation is not straightforward and requires some approximations. The first one is the Born Oppenheimer approximation, which assumes that the motion of electrons and the nucleus can be separated because the nuclei are significantly larger than the electrons [70]. Considering this approximation, the Schrodinger equation for a many-body system is then given by:

$$\left[\frac{-\hbar^2}{2m_e}\sum_{i}^{N}\nabla^2 + \sum_{i}^{N}V(r_i) + \sum_{i}^{N}\sum_{j
(2.20)$$

where N is the number of electrons,  $r_i$  and  $r_j$  are the position of the electrons and nuclei, respectively, and  $m_e$  is the mass of the electron. The term inside the bracket is an operator called Hamiltonian which considers the kinetic energy of all the electrons, the interaction between the electrons and the nuclei, and the electron-electron interactions.

This equation cannot be easily solved with Born Oppenheimer approximation alone, thus the Hohenberg-Kohn theorem is also utilized for further simplification. This theory states that the ground state energy of the system is a functional of the electron density [71]. This makes the previous equation significantly simpler since changing the wavefunction to the electron density reduces the 3N variables to only 3 coordinate variables of the electron density. Kohn and Sham [72] developed a series of one-particle equations (known as Density Functional Theory) by introducing the exchange-correlation  $V_{\rm XC}$  term which compensates for the inaccuracy of simplifications [73]. Based on these assumptions, the Kohn-Sham equation is given by:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r) + V_H(r) + V_{\rm XC}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r)$$
(2.21)

where the first term determines the kinetic energy of an electron,  $V(\mathbf{r})$  defines the interaction between an electron and the nuclei and  $V_H(\mathbf{r})$  is the Hartree Potential which is given by:

$$V_H(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3 r'$$
(2.22)

This equation considers the interaction of an electron and the all-electron density in the system. Thus, the Hartree term reintroduces an electron self-interaction energy which can be corrected in the exchange-correlation term. Therefore, the Kohn-Sham equation can be easily solved by finding the electron density which in turn gives us the wavefunction as follows:

$$n_{\rm KS}(r) = 2\sum_{i} \psi_{i}^{*}(r)\psi_{i}(r)$$
 (2.23)

So, the Kohn-Sham equations provide a practical solution to the Schrodinger equation. The main estimation in this method is the exchange-correlation potential. There are many exchange-correlation potentials each of which is suitable for a specific system [74]. The Localized Density Approximation (LDA) utilizes the local density of electrons to approximate this potential [72]. On the other hand, the Generalized Gradient Approximation (GGA) considers not only the local density but also the gradient of the density at each point. Although there are many GGA functionals, the two Perdew–Wang functional (PW91) [75] and the Perdew–Burke–Ernzerhof functional (PBE) [76] are widely used.

As mentioned before, DFT is a basic calculation for many materials properties. Amongst them is the activation barrier energy which can be found with the Climbing Image-Nudge Elastic Band (CI-NEB) method [77] which will be described briefly.

#### 2.4.2. Climbing Image-Nudge Elastic Band (CI-NEB)

In theoretical chemistry and physics, the barrier energy is a critical parameter for calculating the transition rate of chemical reactions or atomic diffusion. The goal of the CI-NEB method in conjunction with the DFT is to find the minimum energy path (MEP) between the initial and the final states and consequently, to find the saddle point.

The NEB consists of creating a set of images between the initial and the final state and placing a spring (i.e. an elastic band nature) in between. Once these images are created, the MEP is found by minimizing the force acting on the images. In this method, only the perpendicular component of the true force ( $\nabla E$ ) and the parallel component of the spring force ( $F^s_i$ ) are considered (a process called Nudging) to separate the effect of these two forces on the MEP convergence procedure. Thus, the total force acting on the images is [77,78]:

$$F_i = F_i^s \parallel -\nabla E(R_i) \mid_\perp \tag{2.24}$$

An optimization algorithm is then applied to this equation to find the sequences of the images as the MEP. The CI-NEB method modifies the highest energy image (the climbing image) to merely consider the full potential force on this image (i.e. eliminating the spring force). This modification ensures that the climbing image is converged on the saddle point and, therefore, no interpolation is required for barrier energy calculation [77].

## 2.4.3. Cluster expansion model

Density functional theory provides accurate information about the properties of materials. However, its ability is limited only to small systems since the computational cost of this method increases rapidly with the number of atoms. This limitation makes DFT an impractical method to study the properties that depend on atomic configurations and require large systems [79] (e.g. disordered systems or systems exhibiting different short-range ordering [80]). An example of such properties are ground state configuration of alloys, temperature-composition phase diagrams (phase stability) [81] and atomic displacement barrier [39,82].

The Cluster expansion method [83,84] addresses the solution to this problem by separating the configurational degrees of freedom from the structural degrees of freedom of the total energy [80] and by providing a link between the first principle calculations and the statistical mechanic [85]. This method benefits from the information of the small number of configurations to predict any other configurations. In the cluster expansion method, the lattice sites are fixed and the configurations are defined by the spin-like variables  $\sigma$  where in a binary A-B system they are +1

for A and -1 for B (or a vacancy). Then, the cluster expansion determines the total energy of a system as follows:

$$E = V_0 + \sum_{\alpha} V_{\alpha} \phi_{\alpha} \tag{2.25}$$

where:

$$\phi_{\alpha} = \prod_{i \in \alpha} \sigma_i \tag{2.26}$$

 $\phi_{\alpha}$ , called the correlation function, is the average of the product of occupation variables (of each site *i*) in the cluster  $\alpha$ . The cluster is defined as any combination of the lattice sites including empty and point clusters, pairs of sites (nearest-neighbor pairs, second nearest-neighbor pairs, etc.), triplets and so on. The *V* coefficients, describing all interatomic potentials, are called Effective Cluster Interaction (ECI) and should be determined from fitting equation (2.25) to the first-principle calculations. The advantage of the cluster expansion model is that the ECIs are the same for any configuration. Thus, once they are known, the total energy of the system *E* can be found for any configuration by evaluating the occupation variables in that configuration [79].

Equation (2.25) is exact since it considers all sizes of clusters. However, calculating the ECIs for all cluster figures is as complicated and time-consuming as applying the first principle calculation to all possible configurations. Therefore, to make this method practical, the sum over the clusters should be truncated. The first truncation is applied based on the space group symmetries that existed in the parent lattice as shown in the literature [86]. Furthermore, interactions between distant sites have less contribution to the total energy than those between near sites and also large clusters containing many lattice sites are less effective to total energy than those having fewer sites [79,87]. Thus, when the energy of a system depends mainly on the local environment, a few short-range interactions are sufficient to determine the total energy [87]. Having the first-principle calculations, the ECIs can then be calculated by either the linear programming method [87] which applies linear constraints on ECIs or the modified Connolly-Williams (CW) method [86,88] which suggests the minimization of the weighted variance, or the regularization techniques usually used in linear regression [89].

## 2.4.4. Monte Carlo simulation

Monte Carlo (MC) simulations can be used to produce/sample different atomic configurations for atomistic simulation [90] and also to simulate the electron trajectories in the samples scanned with electron microscopes [91].

A widely used method for determining the thermodynamic properties of material is Monte Carlo simulation in lattice models [92]. The main variation of different MC methods in lattice models is related to how the new configuration is generated which will be discussed below.

# 2.4.4.1 Canonical and Grand Canonical Monte Carlo

Central to the importance sampling in the Canonical Monte Carlo (CMC) process is the detailed balance condition, which for an equilibrium probability,  $P_{eq}$ , and the transition probability, W, between two consecutive states  $S_i$  and  $S_j$  is given as:

$$W_{ji}P_{\rm eq}\left(S_{j}\right) = W_{ij}P_{\rm eq}\left(S_{i}\right) \tag{2.27}$$

One of the transition probabilities that satisfies the detailed balance condition is given by the Metropolis method [93]:

$$W_{i \to j} = \exp\left(-\Delta E/k_{\rm B}T\right) \quad \Delta E > 0$$

$$= 1 \qquad \Delta E < 0 \qquad (2.28)$$

Where  $\Delta E$  is the change in energy from state  $S_i$  to state  $S_j$ , KB is the Boltzmann constant and T is the temperature. To sample the configurations, a random number between 0 and 1 is generated and the trial move is accepted if this random number is smaller than the transition probability.

The idea for Grand Canonical Monte Carlo (GCMC) is similar to the CMC, with the exception that, the trial states are accepted or rejected based on the change in the Grand Canonical energy. Additionally, as the name suggests, the number of particles in the system could also fluctuate in GCMC.

## 2.4.4.2 *Kinetic Monte Carlo (KMC)*

For diffusion studies, the n-fold way Monte Carlo method [94], also known as Kinetic Monte Carlo (KMC), is usually utilized. Unlike the standard MC method where the sites are randomly chosen and the jumps are evaluated with their probabilities, in the KMC simulation the site is selected based on jump rates and then the atom immediately jumps [95]. Assuming N atoms exist in a crystal that can jump to the c nearest-neighbour vacant sites to form a new atomic configuration. To make a new configuration, the spin-like variables defined in the cluster expansion can be either flipped or exchanged. The attempt to change the spin variable at any lattice site represents the same amount of time, therefore, the number of attempts can be utilized to measure the time [95]. Considering this approach, the mean waiting time, also called the reduced lifetime of the initial configuration, for such a system at time t is given by [96]:

$$\tau_N = \frac{1}{\Gamma_{tot}(N,t)} \tag{2.29}$$

where  $\Gamma_{tot}$  is the sum of all individual transition rates  $\Gamma_i$  which can be calculated from transition state theory [39]:

$$\Gamma_i = \nu^* \exp\left(\frac{-\Delta E_a}{kT}\right) \tag{2.30}$$

where  $\Delta E_a$  is the activation barrier and depends on the local environment of the jumping atoms and  $v^*$  has the dimension of the frequency and depends on the entropy change (usually equals  $10^{13}$  Hz).

Then, the evolution of the system at any given configuration can be found by the three following steps:

- (i) The first step consists of calculating all the transition rates  $\Gamma_i$
- (ii) Then the *k*th jump is chosen such that:

$$\frac{1}{\Gamma_{tot}} \sum_{i=1}^{k-1} \Gamma_i < \xi_1 \le \frac{1}{\Gamma_{tot}} \sum_{i=1}^k \Gamma_i$$
(2.31)

where  $\xi_1$  is a random number between (0,1).

(iii) Finally, time is updated after performing a jump in the previous step. The time increment (i.e. time interval between each attempt) is calculated by (proved in [95]):

$$\Delta t = -\frac{1}{\Gamma_{\rm tot}} \ln \xi_2 \tag{2.32}$$

where  $\xi_2$  is a random number between (0,1).

KMC consists of iteration of steps (i) to (iii) which can be used to study the vacancy migration in the materials [94].

# 2.4.4.3 Monte Carlo for electron trajectory

Exploration of solid-electron interactions in materials has frequently employed Monte Carlo simulation. Prior software that assisted microscopists in interpreting the results of Monte Carlo simulations is Win X-ray [97] and CASINO V2.42 [91], both of which are effective and user-friendly.

The basis of this Monte Carlo method is the single scattering approach which considers the elastic collisions of each electron as shown in Figure 2.15.



Figure 2.15. Geometry used in single scattering Monte Carlo [98].

To obtain the geometry shown in Figure 2.15, four random numbers (i.e.,  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$ ) sampled between 0 and 1 are used together with the equations describing the elastic and inelastic collisions. In this approach, the distance between elastic collisions  $L_j$ , is calculated by [98]:

$$L_j = -\lambda_{\rm el} \ln \left( R_1 \right) \tag{2.33}$$

where  $\lambda_{el}$  is the total elastic mean free path. The polar angle  $\theta_j$  is calculated using the partial Rutherford cross-section which is simplified to the following equation:

$$\cos \theta_j = 1 - \frac{2\delta_i R_2}{1 + \delta_i - R_2}$$
(2.34)

where  $\delta_i$  is the screening parameter for element *i* and is calculated by [99]:

$$\delta_i = \frac{3.4 \times 10^{-3} Z_i^{2/3}}{E_j} \tag{2.35}$$

where  $Z_i$  is the atomic number of the element and  $E_j$  is the electron energy at point  $P_j$ . The atom responsible for the collision at point  $P_{j+1}$  is determined using the third random number in the inequality  $P_{k-1} \leq R_3 < P_k$ , where  $P_k$  is a probability defined as:

$$P_k = \frac{\sum_{i=1}^k \frac{c_i \sigma_{\text{el}}^i}{A_i}}{\sum_{i=1}^n \frac{c_i \sigma_{\text{el}}^i}{A_i}}$$
(2.36)

where  $c_i$ ,  $\sigma_i$ , and  $A_i$  are the concentration, total elastic scattering, and atomic weight of element *i*, respectively. Finally, to determine the azimuth angle  $\phi_j$  which is uniformly distributed from 0 to  $2\pi$ , the following equation is used:

$$\phi_j = 2\pi R_4 \tag{2.37}$$

Once all the geometries for the first collision are determined, the energy for the next elastic collision at point  $P_{j+1}$  should be evaluated since the electron loses energy during the inelastic collisions. This is determined by:

$$E_{j+1} = E_j + \frac{\mathrm{d}E}{\mathrm{d}S}L_j \tag{2.38}$$

Where dE/dS is the energy loss rate for which Joy and Lou's modification to Beth's equation is used [100]:

$$\frac{\mathrm{d}E}{\mathrm{d}S} = -7.85 \times 10^4 \frac{\rho}{E_j} \sum_{i=1}^n \frac{c_i Z_i}{A_i} \ln\left(\frac{1.166E_j}{J_i^*}\right) (\mathrm{keV/cm})$$
(2.39)

Where  $\rho$  is the density and  $J_i^*$  is the modified potential of the element given by:

$$J_{i}^{*} = \frac{J_{i}}{1 + k_{i} \frac{J_{i}}{E_{j}}}$$
(2.40)

where:

$$J_i = 11.5Z_i(\text{eV}) \quad Z_i < 13$$
 (2.41)

$$J_i = 9.76 + 58.5 Z_i^{-0.19} (\text{eV}) \quad Z_i \ge 13$$
(2.42)

$$k_i = 0.734 Z_i^{0.037} \tag{2.43}$$

## 2.4.5. Simulation in Li-ion battery materials

Due to experimental difficulties mentioned in section 2.2.3. first-principles calculations and/or simulations have been utilized in an effort to determine the diffusivity of Li in battery materials. For Li<sub>2</sub>O, a limited number of studies [40,101–103] have employed DFT and the NEB approach to examine vacancy-mediated Li diffusion. Classical MD simulation was utilized by Benitez et al. [104] and Tasaki et al. [105] to investigate the diffusivity of Li in the Li<sub>2</sub>O component of SEI at a length scale exceeding that of DFT. The application of MD is limited to liquids or solids that are superionic at exceedingly high temperatures due to the discrepancy between timescales [41]. Li<sub>2</sub>O demonstrates superionic characteristics beyond the transition temperature of approximately 1200 K; consequently, the majority of molecular dynamics investigations on the diffusivity of Li in this substance have been carried out at elevated temperatures [42,106–108]. Therefore, it is necessary to devise a suitable atomistic method that can accurately capture the timescale of Li diffusivity in Li<sub>2</sub>O at low temperatures, which is the typical operating temperature of LIBs.

For the diffusivity of Li in the NMC, only limited computational investigations have been conducted [109–111]. To determine the barrier energies of Li hops in these investigations, DFT calculations combined with the NEB method were employed. Although these studies provide helpful insights into barrier energy, they cannot fully capture the relationships between jump barrier energies and local atomic configurations that Li-ions may face during intercalation, especially at the non-dilute limit. The diffusion coefficient of Li in NMC was estimated by Wei et al. [110] via ab initio MD simulations. The diffusivity at room temperature was approximated through linear fitting of diffusivity data obtained at high temperatures, due to the limited accessible timescale of MD. This methodology might not comprehensively capture the fundamental principles of physics, as some diffusion mechanisms might remain inactive at ambient temperature due to the small thermal vibration of atoms. As a result, the estimate of diffusivity at ambient temperature may be subject to significant error when employing this method. For this reason, in order to provide an atomistic perspective on Li diffusion in NMC, it is essential to develop an appropriate atomistic method for examining the factors that influence the diffusivity of Li in NMC.

In our multiscale computational approach, the investigation of Li transport in battery materials is initiated with DFT which subsequently scales up with a first-principles statistical mechanical approach based on Kinetic Monte Carlo (KMC) simulation. Since Li ions may encounter various local atomic environments during diffusion, a model is developed to characterize the dependence of barrier energies on the local atomic environment. To the best of our knowledge, this approach has not been used in previous works to study Li transport in Li<sub>2</sub>O and NMC.

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# 3. Chapter 3. Study of Lithium transport in NMC Layered oxide cathode material using atomistic simulations

As reviewed in Chapter 2, fast Li transport is crucial in high-power applications for the effective implementation of NMC as a promising cathode material of Lithium-ion batteries. To achieve the full potential of this cathode material in these applications, it is vital to initially investigate the variables that influence lithium transport. In this chapter, we develop a multiscale computational approach to acquire an atomistic point of view on the factors influencing Li transport in NMC. This will offer valuable insights into Li transport behaviour and the possibility of improving this material for high-power applications.

 This chapter was submitted as Ali Jaberi, Michel L. Trudeau, Jun Song, and Raynald Gauvin, Study of Lithium transport in NMC Layered oxide cathode material using atomistic simulations.

## 3.1. Abstract

Enhancing the rate capability of lithium-ion batteries (LIBs), as a promising energy storage device, requires a comprehensive understanding of lithium (Li) transport in their constituent parts. In this study, the Li transport in the LiNi<sub>0.333</sub>Mn<sub>0.333</sub>Co<sub>0.333</sub>O<sub>2</sub> (NMC111) cathode active material was examined by a multiscale computational approach ranging from Density Functional Theory (DFT) to Monte Carlo (MC) simulations. The approach was first applied to Lithium cobalt oxide (LCO) to compare a novel model with an existing available one for barrier energies in layered structures. The DFT calculation was first combined with the nudged elastic band (NEB) method to study the tetrahedral site hop (TSH) diffusion mechanism in LCO for different local atomic configurations. Subsequently, two barrier energy models, named the interpolated barrier model and the local cluster expansion, together with the periodic cluster expansion were integrated into the KMC algorithm. Results of KMC simulations attempting to predict the Li transport behaviour in LCO were similar using both barrier models. Thus, the approach was then applied to NMC111 using only the much simpler interpolated barrier model. Our MC simulations showed a perfect honeycomb-like ordering of Li ions in the Li layer of NMC111 at the Li concentration of 0.8. This

perfect ordering of Li ions caused a significant decrease in the thermodynamic factor which consequently reflected as a minimum in the chemical diffusion coefficient at this concentration. In addition, a parallelogrammatic and triangular partial ordering of Li ions in the Li layer was found at the concentrations of 0.2 and 0.3, respectively, creating more fluctuations in the thermodynamic factor. Consequently, a wide variation of chemical diffusion coefficient spanning between  $5.6 \times 10^{-13} \text{ cm}^2/\text{s}$  and  $1.2 \times 10^{-11} \text{ cm}^2/\text{s}$  was yielded across all concentrations of Li. A perfect correlation between the results of our simulations and the experimental measurements of other studies reflected the precision of our formalism to study the transport behaviour of Li in the NMC111 crystal.

*Keywords*: layered oxide cathode, NMC and LCO, Lithium-ion battery, solid-state diffusion, Kinetic Monte Carlo Simulation, Cluster expansion.

## 3.2. Introduction

The need to switch from environmentally harmful fossil fuels to sustainable energy resources has become more demanding due to climate change. The successful implementation of this energy transition necessitates using an energy storage device with an extended lifespan, enhanced stability, superior energy and power density, and cost-effectiveness [1–3]. Electrochemical energy storage devices, in particular lithium-ion batteries (LIBs), exhibit superior performance compared to alternative forms due to their high efficiency and energy/power adaptability [2,4,5]. The performance of LIBs is ultimately determined by the properties of their critical components, specifically the cathode active materials [2,6]. In high-power applications, such as electric vehicles (EVs) and hybrid EVs, LIBs require cathode materials that possess rapid lithium (Li) transport to meet this high-power demand [7,8]. Therefore, understanding the effect of various parameters on lithium diffusivity in cathode active materials is essential for the development of LIBs in high-power applications.

Layered oxide materials are among the most promising cathodes in the LIBs [9]. Lithium cobalt oxide (LCO) was successfully used as a layered cathode material in the first commercial LIB cell introduced by Sony Corporation in 1991 [10]. While this material has been used for decades, its performance may not be sufficient to fulfill the fast energy transition in this climate crisis. Another prominent layered oxide cathode material is the lithium nickel manganese cobalt oxide (NMC)

which combines the advantages of the three transition metals. In this cathode material, nickel (Ni) provides high specific capacity, whereas manganese (Mn) and cobalt (Co) offer enhanced stability and layered structure integrity [11–15]. To experimentally determine the Li transport in NMC, electrochemical techniques such as Potentiation and Galvanostatic Intermittent Titration Test (PITT and GITT), and Electrochemical Impendence Spectroscopy (EIS) have been extensively employed [9,12,16–19]. These electrochemical methods consider the collective behavior of the electrochemical cell, wherein several kinetic processes, such as solid-state diffusion, Li diffusion within the electrolyte, and ion transfer at the solid-electrolyte interface contribute to the overall cell response [7,12,20]. However, these techniques typically assume the solid-state diffusion as the sole kinetic control event to determine the diffusion coefficient [21]. Furthermore, electrochemical techniques require information on the shape and size of the electrode particles, and uncertainty regarding these quantities results in large estimation errors for the diffusion coefficient [22]. Besides, these techniques usually fail to reveal the underlying mechanism of diffusion. Therefore, atomistic simulations are crucial to complement the electrochemical techniques and provide an atomistic point of view for Li diffusion in NMC.

Li-ions in layered oxide cathode materials migrate from one octahedral site to the adjacent octahedral site via oxygen dumbbell hop (ODH) or tetrahedral site hop (TSH) mechanisms [23]. In the ODH mechanism, the diffusing Li-ion, which is surrounded by a single vacancy, passes through the centre of the oxygen dumbbell in a straight line. However, when a divacancy exists in the first nearest neighbour sites of the diffusing Li-ion, it follows a curved path through the intermediate tetrahedral site via the TSH mechanism. During the cathode intercalation, Li-ions pass through different local atomic configurations and concentrations. Consequently, the jump barrier energies of these diffusion mechanisms vary depending on the local atomic environment. Therefore, an appropriate model needs to be formulated to capture the dependency of Li migration on the local atomic environment.

A limited number of computational studies have examined the diffusivity of Li in the NMC [24–26]. These studies coupled the density functional theory (DFT) calculations with the nudged elastic band (NEB) method to determine the barrier energies of Li hops in NMC. Although these studies offer useful insights into barrier energies, they are insufficient to capture the complete dependencies between jump barrier energies and local atomic configurations that Li-ions may

encounter during intercalation, especially at the non-dilute limit. Wei et al. [25] employed ab initio molecular dynamics (MD) simulations to determine the diffusion coefficient of Li in NMC. Due to the limited accessible timescale of MD, they estimated the diffusivity at room temperature by linear fitting of diffusivity data at high temperatures. This fitting approach may not fully represent the underlying physics as some diffusion mechanisms could be inactive at room temperature owing to small thermal fluctuations of atoms. Consequently, large errors could be introduced in estimating the diffusivity at room temperature with this approach. To overcome the limited accessible timescale of MD simulations, the first principle statistical mechanical approach based on Kinetic Monte Carlo (KMC) can be used to separate the atomic vibration from the rare events (i.e., Li hops). Van der Ven et al. [27] utilized this KMC formalism to study Li diffusivity in LCO. To evaluate the jump probabilities in the KMC simulation, they used the local cluster expansion model to capture the dependency of barrier energies on the local atomic configuration. However, their approach is computationally intensive for NMC due to the presence of three transition metals in the structure, creating large configurational space for constructing the local cluster expansion model. Hence, an appropriate model still needs to be developed to study Li diffusivity in NMC.

In this study, a formalism was developed to investigate Li diffusivity in NMC. The approach was first applied to LCO to compare a newly proposed model for barrier energies with the existing model in layered structures. Initially, a periodic cluster expansion was formulated to establish the connection between the first-principles total energies and atomic configurations. Subsequently, the DFT calculation coupled with the climbing image-NEB (CI-NEB) method was used to study the tetrahedral site hop (TSH) diffusion mechanism in LCO for different local atomic configurations. Then, both the local cluster expansion model and a newly proposed one, named the interpolated barrier model, were employed to account for the dependence of barrier energies on local atomic configurations in LCO. Following this, Monte Carlo (MC) simulations were conducted to determine the stable atomic configuration at each state of charge. Finally, Kinetic Monte Carlo (KMC) simulations were employed to assess the Li diffusivity in stable structures of LCO at various Li concentrations. The same approach was repeated for NMC with one difference being that the assessment of the atomic configurational dependency of barrier energies only relied on the newly proposed model. We found that the local arrangement of atoms could significantly affect the Li diffusivity which was consistent with experimental results from other studies. Our

multiscale computational approach would therefore facilitate the development of LIBs for highpower applications by offering an atomistic view of the Li transport properties in battery material.

## **3.3.** Model and Method

#### 3.3.1. DFT and CI-NEB

Within the Quantum ESPRESSO package [28], the PAW pseudopotential [29], and the PBE-GGA exchange-correlation functional [30], were utilized to perform DFT calculations for LCO. The spin-polarized calculation was not considered for LCO as the effect of spin polarization was reported to be negligible for this material [31]. A shift of no more than 3 meV per  $Li_xCoO_2$  formula unit was found in previous calculations including spin polarization. This small shift in the energy is therefore negligible even for the calculation of barrier energies with the values of several hundred eV. The optimal kinetic energy cutoff of 500 eV was determined by increasing the cutoff energy until the difference in energy per atom was less than 1 meV. The total energies were determined by relaxing the atoms until the force components acting on each atom were less than 0.025 eV/Å. For the calculation of the barrier energy of Li hops in LCO, the DFT was combined with the CI-NEB method [32], in which seven images were interpolated between the initial and final positions of the diffusing particles. After minimizing the forces applied to each image, the activation barrier was determined by the energy difference between the initial and the saddle point. In these calculations, large supercells containing 108 atomic sites (27 LCO formula units) were used to maintain a minimal interaction between the periodic images.

Even though our simulations could be applied to all transition metal ratios in NMC, the Li(Ni<sub>0.333</sub>Mn<sub>0.333</sub>Co<sub>0.333</sub>)O<sub>2</sub> composition (NMC111) was chosen in this study. The reason is that the most stable ordering of the atoms in the transition metal layer in this ratio was confirmed experimentally [33,34], which facilitates the implication of our approach. For NMC111, spin-polarized DFT calculations were performed using the PBE-GGA exchange-correlation functional and PAW pseudopotentials. The Vienna Ab Initio Simulation Package (VASP) [35–37] was employed as we found this package to handle the DFT+U calculations efficiently. The U values of 6.20, 3.90, and 3.32 eV as recommended by Materials Project [38] for Ni, Mn, and Co, respectively, were used to correct the correlation between the d orbital electrons in the transition metals. The kinetic energy cutoff was set to 520 eV. Then, the first-principle total energies were

determined by relaxing the atoms until the force components became smaller than 0.025 eV/Å. In these calculations, large supercells containing 144 atomic sites (36 NMC formula units) were used to minimize the interactions in periodic boundary conditions.

#### 3.3.2. Cluster expansion

As Li-ions deintercalate from the structure, some of the Li sites become unoccupied in the structure which we refer to as vacancy throughout this paper. The first-principle total energies of the system depend on the configuration of Li-ions and vacancies in the Li layer. Therefore, an appropriate Hamiltonian should be constructed to calculate the energy of the system at each Li/vacancy configuration at a small computational cost. The Cluster expansion method [39,40] provides a computationally efficient approach for calculating the total energies by separating configurational dependence from structural dependence [41,42]. As a generalized Ising model, the configurations in the cluster expansion method were defined by the spin-like variable  $\sigma$ , which is +1 for the presence of Li and -1 for the vacancy. The cluster expansion then computed the system's total energy as follows:

$$E = \sum_{\alpha} V_{\alpha} \phi_{\alpha} \tag{3.1}$$

where,

$$\phi_{\alpha} = \prod_{i \in \alpha} \sigma_i \tag{3.2}$$

The correlation function,  $\phi_{\alpha}$ , is the mean of the product of occupation variables for each site, *i*, within the cluster. The cluster is any possible combination of the lattice sites, including empty, point clusters, pairs, triplets, etc., each of which may be nearest-neighbor, second nearest-neighbor, etc. The V coefficients, also known as effective cluster interactions (ECI), were obtained by fitting the cluster expansion into the calculated first-principles energies.

The cluster expansions of LCO and NMC111 were constructed using the CLEASE package [43]. The Li-layered sublattice was chosen for generating random Li/vacancy configurations at different Li concentrations. This led to a total of 237 and 328 random configurations for LCO and

NMC111, respectively. Also, because the contribution of clusters to the total energy reduces with the cluster size [42], the clusters were limited to only individual points, pairs, triplets, and quadruplets in the framework of the cluster expansion formalism. For LCO the maximum cluster diameter was set to 7, 7, and 6 Å, while for NMC111, it was set to 6, 6, and 5 Å for quadruplets, triplets and pairs clusters, respectively. As the cluster expansion formalism reflects the linear regression model in machine learning, ridge regression was used for fitting this formalism to the first-principles energies of the random configurations in order to obtain the ECIs.

#### 3.3.3. Jump barrier energy models

As mentioned earlier, two different diffusion mechanisms known as ODH and TSH exist in layered oxide cathode materials. In the ODH mechanism, the diffusing Li-ion follows a straight line while it jumps through a curved path in the TSH mechanism as shown schematically in Figure 3.1. Notably, the barrier energy of the ODH mechanism is roughly double that of the TSH mechanism for both LCO [23] and NMC111 [25] making the TSH the dominant diffusion mechanism, especially at the non-dilute limit. Thus, the barrier energy model was formulated only for the TSH mechanism in this study.



Figure 3.1. Li hop mechanisms in layered oxide cathodes. The black circles depict the Li-ions and the white circles are Li vacancies. The small blue rectangle in the TSH mechanism shows the position of the intermediate tetrahedral site

As the barrier energy of Li hops relies on both the local atomic environment and the jump direction, the so-called kinetically resolved activation (KRA) barrier,  $\Delta E_{KRA}$ , [27] was used for directional independent barrier energies. The  $\Delta E_{KRA}$  is simply the saddle point energy  $E_{sp}$ 

subtracted by the average energy of the system when Li is located on one of the three endpoints sites (i.e., nearest octahedral sites). Thus,  $\Delta E_{KRA}$  is given by:

$$\Delta E_{KRA} = E_{sp} - \frac{1}{n} \sum_{j=1}^{n} E_{ej}$$
(3.3)

Where  $E_{ej}$  is the energy of the system when the Li-ion is located at the endpoint *j* (which is called the endpoint energies in this study). n is the number of endpoint sites which is three in this case. This  $\Delta E_{KRA}$  barrier depends only on the local atomic environment which was evaluated by the local cluster expansion or the interpolated barrier model (discussed in the next section). Once, the  $\Delta E_{KRA}$  was determined by either of these models, the true barrier energy,  $\Delta E_t$ , was obtained using the equation (3.4) in which the endpoint energies  $E_{ej}$  were calculated with the periodic cluster expansion:

$$\Delta E_{t} = \frac{1}{n} \sum_{j=1}^{n} E_{ej} + \Delta E_{KRA} - E_{i}$$
(3.4)

In this equation,  $E_i$  is the initial energy of the system before the Li-ion hop.

#### 3.3.3.1 Local Cluster expansion

The first model used to parametrize the configurational dependency of  $\Delta E_{KRA}$  in LCO was the local cluster expansion [27]. This model has the same formalism as the periodic cluster expansion. Thus, the  $\Delta E_{KRA}$  was formulated as a linear combination of correlation functions,  $\phi_{\alpha}$ , and kinetic effective cluster interactions (KECI),  $K_{\alpha}$ , as follows:

$$\Delta E_{KRA} = \sum_{\alpha} K_{\alpha} \phi_{\alpha} \tag{3.5}$$

To implement point group symmetry in the construction of the local cluster expansion, the saddle point was approximated to the intermediate tetrahedral site (blue rectangle in Figure 3.1), as determined by our CI-NEB calculations. Since  $\Delta E_{KRA}$  is a local property, clusters close to the saddle point should be adequate for KECI convergence. Therefore, to construct the local cluster expansion of the TSH mechanism, only the first and second nearest-neighbour sites of the saddle

point were considered, excluding the three endpoints around the saddle point. This yielded a total of nine sites as illustrated in Figure 3.2 (i.e., green and red circles). The KECIs of this local cluster expansion were determined by fitting a linear regression to the  $\Delta E_{KRA}$  values obtained by the CI-NEB method for nine distinct Li/vacancy arrangements in the neighbouring sites.



Figure 3.2. The schematic of the first (red circle), and second (green circle) nearest neighbour sites of the saddle point (blue rectangle) in the TSH mechanism. The three endpoints of the TSH mechanism are shown with black spheres.

#### 3.3.3.2 *Interpolated barrier model*

In the TSH mechanism, two factors affect the barrier energies of the Li hops: 1) the size of the intermediate tetrahedral site, and 2) the charge of the transition metal below the tetrahedral site [8,25]. These two factors vary as the Li concentration changes in the system during intercalation, however, in this model, we consider mainly the effect of transition metal type and its oxidation state on the barrier energies. In LCO, the oxidation state of Co changes from 3+ to 4+ as Li concentration decreases. Also in NMC111, the Ni oxidation state increases from 2+ to 4+, and Co from 3+ to 4+ by decreasing the Li concentration, while the oxidation state of Mn remains unchanged [44]. Therefore, a relation between the local Li concentration and the barrier energy might provide a good model for capturing the local dependency of  $\Delta E_{KRA}$ . For this model, the  $\Delta E_{KRA}$  for extreme oxidation states (i.e., 2+, 3+ or 4+) was acquired for each transition metal type, followed by an interpolation for evaluating the barrier at other local Li concertation. It was found that the logarithmic interpolation better captures the dependency between the valence state and the barrier energies (see the result section). The local concertation was defined as the relative number of Li-ions in the nine nearest-neighbour sites illustrated in Figure 3.2. This model was first developed for LCO to be compared with the already existing local cluster expansion model and was then applied for NMC111.

#### 3.3.4. Monte Carlo (MC)

Monte Carlo simulation in lattice models is a widely employed technique for the computation of thermodynamic or kinetic properties of materials [45,46]. This simulation technique determined the chemical diffusion coefficient,  $D_c$ , at each equilibrated Li/vacancy arrangement using the Kubo-green equation [47]:

$$D_c = \Theta D_l \tag{3.6}$$

where  $D_I$  is the jump diffusion coefficient:

$$D_{J} = \lim_{t \to \infty} \frac{1}{2dt} \left\langle \frac{1}{N} \left( \sum_{i=1}^{N} \vec{r_{i}}(t) \right)^{2} \right\rangle$$
(3.7)

In this equation,  $\vec{r}_i(t)$  is the displacement of the *i*<sup>th</sup> particle after the time *t*, which can be determined by Kinetic Monte Carlo (KMC) simulation. *N* is the total number of diffusing Li-ions, and *d* is the dimension of diffusion.  $\Theta$  is the thermodynamic factor which was found from Semi-Grand Canonical Monte Carlo simulation by:

$$\Theta = \frac{\langle N \rangle}{\langle (\delta N)^2 \rangle} \tag{3.8}$$

where  $\langle N \rangle$  is the average number of diffusing Li-ions and  $\langle (\delta N)^2 \rangle$  is the fluctuation of diffusing Li-ions in the grand canonical ensemble. Details of these Monte Carlo simulations are provided in the following sections.

#### 3.3.4.1 Canonical and Grand Canonical Monte Carlo

The equilibrium configuration of Li/vacancy was determined at a temperature of 300 K using the Canonical Monte Carlo (CMC) technique as implemented in the CLEASE package. In supercells containing 2916 atoms (i.e. 729 Li-ions) for LCO, and 3888 atoms (i.e. 972 Li-ions) for NMC111, random configurations of Li/vacancy were generated at each Li concentration. This initial state was then equilibrated through 500 CMC steps utilizing the Metropolis algorithm [48], which produces a trial state with the following probability:

$$W = \min\left\{1, \exp\left(\frac{\Delta E}{k_B T}\right)\right\}$$
(3.9)

In this equation,  $\Delta E$  is the energy change from the current to the subsequent atomic configuration, *T* is the temperature, and  $k_B$  is the Boltzmann constant. If W was greater than a random number generated between 0 and 1, the trial state was accepted. Otherwise, it was rejected. This equilibrium structure was then used as the initial structure for the KMC simulation.

Semi-grand canonical Monte Carlo (SGCMC) was utilized by the CLEASE package to determine  $\langle N \rangle$  and  $\langle (\delta N)^2 \rangle$  for computing the thermodynamic factor. The steps for SGCMC were identical to those for CMC, with the exception that the change in grand canonical energy was used to reject or accept the trial states.

#### 3.3.4.2 *Kinetic Monte Carlo (KMC)*

The KMC simulation creates large enough stochastic jumps to determine  $\vec{r_i}(t)$  for the calculation of jump diffusion coefficient,  $D_j$ . A custom Python code was written for KMC using the n-Fold way algorithm [49,50]. The following steps comprise this algorithm: i) Using the transition state theory [51], the transition rate of all possible hops,  $\Gamma_i$ , was calculated by:

$$\Gamma_i = \nu^* \exp\left(\frac{\Delta E_{t,i}}{k_B T}\right) \tag{3.10}$$

where  $\Delta E_{t,i}$  is the true barrier energy of the *i*<sup>th</sup> hop, and  $\nu^*$ , which was set to  $10^{13}$  Hz, is the attempt frequency. ii) Then, the *k*<sup>th</sup> hop was selected so as to satisfy the following inequality:

$$\frac{1}{\Gamma_{tot}} \sum_{i=1}^{k-1} \Gamma_i < \xi_1 \le \frac{1}{\Gamma_{tot}} \sum_{i=1}^k \Gamma_i$$
(3.11)

in which  $\xi_1$  is a random number generated between 0 and 1, and  $\Gamma_{tot}$  is the total sum of all transition rates. Once the  $k^{\text{th}}$  hop was performed, iii) the time, t, was increased by an increment,  $\Delta t$ , which was computed by:

$$\Delta t = -\frac{1}{\Gamma_{tot}} \ln \xi_2 \tag{3.12}$$

where  $\xi_2$  is also a number randomly sampled between 0 and 1. This process was repeated until 500 KMC steps were completed to create large enough hops for determining the jump diffusion coefficient,  $D_j$ . This number of steps were found to be large enough to get good statistic (see Figure 3.17 in supplementary information).

# 3.4. **Results and discussion**

#### 3.4.1. LCO

#### 3.4.1.1 *Configuration-dependant total energies*

Construction of a precise cluster expansion Hamiltonian is crucial for this study, as the MC and KMC required the estimation of total energies at different Li/vacancy configurations sampled by these simulations. The formation energies per formula unit of LCO with respect to the fully lithiated and delithiated LCO were calculated with both DFT energies and cluster expansion Hamiltonian which are plotted in Figure 3.3. The ten-fold cross-validation score of 0.582 meV/atom and the RMSE of 0.492 meV/atom demonstrated the good predictability of our cluster expansion model. This small estimation error gets the formation energies predicted by cluster expansion very close to the actual energies determined by DFT, as can be seen in Figure 3.3. Also, the convex hull in this figure is quite comparable to the one reported for this material in reference [31].



Figure 3.3. Predicted and actual formation energy per formula unit of LCO. The convex hull is depicted by the dashed line.

#### 3.4.1.2 *Configuration-dependant barrier energies and barrier energy models*

As mentioned in the method section, three endpoints exist around the saddle point in the TSH mechanism. Therefore, for nine different atomic configurations around these three endpoints, the  $\Delta E_{KRA}$  was determined by equation (3.3) using the energetics from the DFT/CI-NEB calculations. The configurations and the associated  $\Delta E_{KRA}$  are shown in Figure 3.4.

0.468 eV	0.547 eV	0.669 eV	0.322 eV	0.615 eV
• • • •				) • •
0.565	5 eV 0.39	94 eV 0.42	0 eV 0.478	eV

Figure 3.4. Li/vacancy configurations and the associated  $\Delta E_{KRA}$  values. The orange circles are the three endpoints, the gray spheres are vacancies, and the green spheres are Li-ions.

In Figure 3.4, the  $\Delta E_{KRA}$  values show a wide range between 0.322 and 0.615 eV, reflecting the necessity of developing a model to capture the local configurational dependency of this parameter. In this regard, the local cluster expansion was one of the models used for LCO. This model consisted of five clusters in the first and second nearest-neighbour sites illustrated in Figure 3.2. These five clusters include two point-clusters, two pair clusters, and one triplet cluster as illustrated in Figure 3.5. Fitting the local cluster expansion formalism of these five clusters into the  $\Delta E_{KRA}$  values given in Figure 3.4, yielded the KECIs of these clusters as depicted in Figure 3.5. The KECI of the empty cluster with the value of 0.472 eV is not included in this figure for better visualisation of other KECIs.



Figure 3.5. The clusters used for the construction of the local cluster expansion model of LCO. The bar chart shows the associated KECIs of these clusters. The empty cluster with the KECI value of 0.472 eV is not illustrated in this figure for better visualization.

The  $\Delta E_{KRA}$  of the configurations in Figure 3.4 were recalculated with the local cluster expansion and are given in Figure 3.6 together with the actual values already calculated with the DFT/CI-NEB energies. The RMSE of this model is only 27 meV which brings the predicted  $\Delta E_{KRA}$  values to the close proximity of actual  $\Delta E_{KRA}$  as shown in Figure 3.6. In this figure, the  $\Delta E_{KRA}$  has a general decreasing trend since the oxidation state of Co decreases with the Li concentration, increasing the electrostatic repulsion between Co and Li in the TSH mechanism. In addition, the intermediate tetrahedral site in this mechanism expanded with Li concertation which decreases the  $\Delta E_{KRA}$  values specially at dilute limit [27].



Figure 3.6. Predicted and calculated  $\Delta E_{KRA}$  of different local atomic configurations. The local cluster expansion was used for the predicted values.

Alongside the local cluster expansion, the interpolated barrier model was also developed for capturing the dependency of  $\Delta E_{KRA}$  on the local atomic environment in LCO. Two extreme points with the local Li concertation of 0.05 and 0.9 were chosen for interpolation. It was found that the logarithmic interpolation, as described by the equation  $\Delta E_{KRA} = -0.093 \ln C_{Li} + 0.3154$ , yielded the most accurate estimate. In this equation,  $C_{Li}$  denotes the local Li concentration which as already defined is the relative number of Li-ions in the nine nearest-neighbour sites illustrated in Figure 3.2. The average  $\Delta E_{KRA}$  encountered by Li-ions during KMC simulations at each Li concentration was monitored for both barrier models (i.e., local cluster expansion of interpolated model). These averages of  $\Delta E_{KRA}$  at each Li concentration alongside the interpolated barrier model line as a function of local Li concentration are illustrated in Figure 3.7. This figure clearly shows that the interpolated barrier model gives a very similar average  $\Delta E_{KRA}$  as the local Li concentration cluster model cluster clearly shows that the interpolated barrier model gives a very similar average  $\Delta E_{KRA}$  as the local cluster cluster cluster cluster model cluster mo

expansion model that was previously suggested in the literature for LCO [27]. This highlighted the great predictability of the interpolated barrier model for  $\Delta E_{KRA}$  with less complexity and computational cost than the already existing local cluster expansion model in layered structure.



Figure 3.7. Interpolated barrier model together with the average  $\Delta E_{KRA}$  in the KMC at each Li concentration for LCO. The dashed line is the logarithmic interpolated line between the two extreme endpoints of local Li concertation.

#### 3.4.1.3 Diffusion coefficient

The thermodynamic factor and the jump diffusion coefficient are illustrated in Figure 3.8 for LCO at each Li concentration. The thermodynamic factor indicates the degree to which a diffusing species in a solid deviates from ideality with respect to the host it is diffusing in [52]. Hence, the thermodynamic factor approaches unity at the extremely diluted limit and subsequently rises with increasing Li concentration. This trend is consistent with our findings in Figure 3.8-a. The calculated thermodynamic factor in this figure is remarkably similar to that reported in the literature for LCO [27], highlighting the precision of our periodic cluster expansion.



Figure 3.8. a) Thermodynamic factor (from SGCMC simulation), and b) jump diffusion coefficient of Li in LCO at each Li concentration (from KMC simulation).

In Figure 3.8-b, the jump diffusion coefficient using both the interpolated barrier model and local cluster expansion is in good agreement with the literature suggesting the validity of our proposed interpolated barrier model for layered oxide structure. The sudden drops in the diffusivity at the Li concentrations of 0.3 and 0.5 were found to be the result of the ordered arrangement of Li/vacancies at these concentrations [27]. Similar to previous studies [31,53,54], an ordered arrangement for Li/vacancies was found in the equilibrated structure of LCO with CMC simulation at a Li concentration of 0.5 (Li<sub>0.5</sub>CoO<sub>2</sub>) as shown in Figure 3.9. This specific arrangement not only is governed by the energetic associated with this configuration of Li-ions but also should be permitted by the certain concentration of vacancies. The interpolated barrier model successfully captured the abrupt decreases of diffusivity in these concentrations, demonstrating the model's capability to accurately depict the local atomic environment of diffusing Li-ions.



Figure 3.9. Zigzag arrangement of Li/vacancy in a Li layer of LCO at the Li concentration of 0.5. The green and gray circles depict Li and vacancy, respectively.

The chemical diffusion coefficient was obtained by multiplying the jump diffusion coefficient and the thermodynamic factor (i.e., equation (3.6)) and is illustrated in Figure 3.10. At diluted Li concentration, the diffusivity decreases due to higher barrier energies at low Li concentrations. At high Li concentrations, however, the number of vacant sites available for Li hops decreases, resulting in a further decrease in diffusivity in the concentrated regime. This behaviour was predicted using both local cluster expansion and interpolated barrier model in KMC (illustrated in Figure 3.8-b and Figure 3.10), demonstrating once more the applicability of the interpolated barrier model in layered oxide cathodes.



Figure 3.10. Chemical diffusion coefficient of Li in LCO at each Li concentration.

#### 3.4.2. NMC111

# 3.4.2.1 Configuration-dependant total energies

Similar to LCO, a precise cluster expansion Hamiltonian is required for evaluating the total energies at different Li/vacancy configurations during the MC and KMC simulations. The formation energies per formula unit of NMC111 were determined using both DFT energies and cluster expansion Hamiltonian which are plotted in Figure 3.11. In this figure, the predicted formation energies are in close proximate to the actual one, resulting in an acceptable ten-fold cross-validation score of 12.55 meV/atom and the RMSE of 2.29 meV/atom. Also, the position and the depth of the convex hull in this figure are consistent with the one found by Ceder et al. [44].



Figure 3.11. Predicted and actual formation energy per formula unit of NMC111. The convex hull is depicted by the dashed line.

#### 3.4.2.2 Barrier energy models

The interpolated barrier model was developed to capture the dependency of  $\Delta E_{KRA}$  on the local atomic environment in NMC111. Three distinct models for  $\Delta E_{KRA}$  were formulated for the three transition metals in the NMC111. Therefore, to determine the transition rates in the KMC

algorithm, the type of transition metal beneath the Li-ion should first be identified when it passes through the intermediate tetrahedral site (i.e., saddle point). As reported in [44], the redox reactions Ni<sup>3+</sup>/Ni<sup>4+</sup> and Ni<sup>2+</sup>/Ni<sup>3+</sup> occur at the Li concentration ranges of  $1/3 \le C_{Li} \le 2/3$  and  $2/3 \le C_{Li} \le 2/3$ 1, respectively, while the Co<sup>3+</sup>/Co<sup>4+</sup> reaction is observed between  $0 \le C_{Li} \le 1/3$ . Consequently, two interpolated barrier models were developed for Ni and Co in these concentration ranges, whereas in the remaining concentration ranges, a constant  $\Delta E_{KRA}$  was extended to encompass the complete spectrum of Li concentrations. For Mn, a constant  $\Delta E_{KRA}$  was used across the entire Li concentration since its oxidation state remains unchanged during the Li intercalation [44]. In Figure 3.12, the interpolated models and the constant regions for  $\Delta E_{KRA}$  are illustrated with the dash and solid lines, respectively, together with the regions showing the oxidation states of each transition metals. In this figure, the extreme points used for interpolation were extracted from the reference [8]. The logarithmic interpolated model for Ni and Co (i.e., dashed lines in Figure 3.12) found to have the equations  $\Delta E_{KRA}^{Ni} = -0.2533 \ln C_{Li} + 0.208$  and  $\Delta E_{KRA}^{Co} =$ was  $-0.0515 \ln C_{Li} + 0.2529$ , respectively. In addition, the average  $\Delta E_{KRA}$  that the Li-ions experienced during KMC simulations using this model is shown in this figure at each Li concentration. The average  $\Delta E_{KRA}$  in the KMC simulations falls around the minimum  $\Delta E_{KRA}$  that is provided by all transition metal at each Li concentration. That is, at very dilute Li concentrations up to 0.25, Mn provided the  $\Delta E_{KRA}$  value, while at the medium and high Li concentrations, the  $\Delta E_{KRA}$  values are provided by Co and Ni, respectively.



Figure 3.12. Interpolated barrier model together with the average  $\Delta E_{KRA}$  in KMC at each Li concentration for NMC. The dashed lines are the logarithmic interpolated line between the extreme endpoints of local Li concertation and the solid lines are the constant  $\Delta E_{KRA}$ .

#### 3.4.2.3 Diffusion coefficient

The thermodynamic factor and the jump/chemical diffusion coefficients are illustrated in Figure 3.13 for NMC111 at each Li concentration. Similar to LCO, the thermodynamic factor tends to unity at the very diluted limit and increases with the concentration of Li. The fluctuation of this parameter between 0.2 and 0.3 Li concentrations could be due to the partial ordering of Li/vacancy at the Li layer. In this concentration range, a parallelogrammatic and triangular partial ordering of Li ions in the Li layer was observed in CMC simulations at concentrations of 0.2 and 0.3, respectively, with an intermediate transition at 0.25 as illustrated in Figure 3.14. Additionally, a perfect honeycomb-like ordering of Li ions was found at the Li concentration of around 0.8 as shown in Figure 3.14. This perfect ordering caused a significant drop in the thermodynamic factor at this concentration as illustrated in Figure 3.13-a. The intense variations of the thermodynamic factor just before 0.8 Li concentrations may be attributed to the Li ions being partially ordered in the form of a honeycomb at the Li layer. It is noteworthy that Frohlich et. al. [9] similarly reported this abrupt decrease in the thermodynamic factor at the Li concentration of 0.8 in their

experimental investigation. Like LCO, these configurations should be governed by both energetics of Li-ions and certain vacancy concentrations that permit such arrangements. To the best of our knowledge, no previous studies could reveal these ordering at these concentrations and their consequent effects on the thermodynamic factor with simulations. In the future, this ordering of Li ions may be revealed experimentally by the multi-slice electron ptychography technique suggested by Muller et. al. [55] or possibly other atomic-scale analytical tomography (ASAT) techniques [56].



Figure 3.13. a) Thermodynamic factor (from SGCMC simulation), and b) chemical/jump diffusion coefficients of Li in NMC111 at each Li concentration (from KMC simulation).



Figure 3.14. Li/vacancy ordering in the Li layer of NMC111 at different Li concentrations. The green and gray circles show the Li and vacancy, respectively.

The abrupt drop in thermodynamic factor at the Li concentration of 0.8 was transferred to the chemical diffusion coefficient (Figure 3.13-b), highlighting the significance of the thermodynamic factor in regulating the behavior of Li diffusivity in this material. Additionally, the diffusivity behaviour was affected by the kinetic factor (i.e., jump diffusion coefficient). To explain the variations in the jump diffusion coefficient, the average true barrier energy and the transition metal type below the tetrahedral sites in the TSH mechanisms were monitored in the KMC simulations. The percentage of TSH jumps for each transition metal type together with the average true barrier energy at each Li concentration are shown in Figure 3.15. This figure is consistent with the results in Figure 3.12, reflecting the fact that the majority of jumps at the diluted limit were observed through the tetrahedral sites under which Mn is located. However, at intermediate and high Li concentrations, Co and Ni, respectively, occupied the beneath site. Therefore, the average true

barrier energy (Figure 3.15) remained almost unchanged up to the concentration of 0.25. In this constant barrier energy region, the jump diffusion coefficient thus decreased due to fewer vacant sites available for Li jumps as depicted in Figure 3.13-b. After the Li concentration of 0.25, the true barrier energy followed a general decreasing trend as more jumps were passed through Co and Ni. Consequently, the jump diffusion coefficient generally increased up to 0.65 except at 0.4 and 0.6 as observed in Figure 3.13-b. After the Li concentration of 0.65, the jump diffusion coefficient decreased again due to a tiny fraction of vacant sites available for the Li jumps. It is worth noting that the abrupt increase in the true barrier energy at the 0.95 concentration is due to an increase in the number of jumps performed by the ODH mechanism. Consequently, the combined effect of both thermodynamic factor and jump diffusion coefficient created a wide variation in chemical diffusion coefficient, ranging from as low as  $5.6 \times 10^{-13} \text{ cm}^2/\text{s}$  to as high as  $1.2 \times 10^{-11} \text{ cm}^2/\text{s}$  across the whole Li concentrations.



Figure 3.15. The percentages of TSH jumps for each transition metal are shown in the bar chart (Left Yaxis). The white circles indicate the average true barrier energy (right Y-axis) in KMC

In Figure 3.16, the chemical diffusion coefficient calculated with KMC is compared to experimental measurements using PITT [19], GITT [57], and EIS [17] reported in the literature. Due to errors inherited in the experimental methods, the absolute values of experimental measurements show large variations from one another, nevertheless, these measurements show a similar trend in diffusivity. In this figure, the EIS and PITT both predicted a minimum at high concentrations of 0.9 and 0.8, respectively. Also, Shaju et. al. [18] and Frohlich et. al. [9] reported the minimum at around 0.85 and 0.8, respectively. These experimental results are in great agreement with the position of the minimum we found at the Li concentration of 0.8. As already mentioned, this minimum arises from the significant drop in the thermodynamic factor at this concentrations ranging from 0 to 0.55 were magnified and inserted into the upper left corner of Figure 3.16. The ups and downs of PITT and KMC in the inserted figure are identical, with the exception of a 0.1 shift in the final decline on the right side of the inserted figure. These consistencies between our simulations and the experimental measurements signify that our formalization effectively represents the transport characteristics of Li in the NMC111 crystal.



Figure 3.16. chemical diffusion coefficient together with the experimental results from the literature. The figure is zoomed in from the concentration range of 0 to 0.55 and is inserted in the left-hand corner.

## 3.5. Conclusion

Li transport in LIBs, specifically in the cathode active material as one of their critical components, is crucial for developing these batteries for high-power applications such as EVs. In this study, Li transport in NMC111 was investigated with a multiscale computational approach starting from Density Functional Theory (DFT) to Monte Carlo simulation. The approach was initially applied to LCO to conduct a comparative analysis between a novel model and the existing model for barrier energies in layered structures. As an alternative to the pre-existing local cluster expansion model, the interpolated barrier model, which is considerably more straightforward, captured the effect of the local atomic environment on kinetically resolved activation barrier energies ( $\Delta E_{KRA}$ ) in LCO with remarkably similar outcomes. The diffusion coefficient for Li varied by several orders of magnitude due to the intense concentration dependence of the barrier energies. Consistent with the previous study for LCO, our simulations predicted a similar trend for the diffusion coefficient. Similar to previous studies at Li concentration of 0.5, we also predicted a zigzag configuration of Li ions which could be governed by both energetic of Li-ion configurations and vacancy concentration.

The approach was then applied to NMC111 using only the interpolated barrier model. It was found that at the diluted limit, the jumps were performed mostly through the tetrahedral sites under which the Mn is occupied, while at the intermediate and high Li concentrations, the beneath site is occupied by Co and Ni, respectively. It was also found that the thermodynamic factor revealed a substantial drop at the Li concentration of 0.8 due to a perfect honeycomb-like ordering of Li ions in the Li layer. This drop in the thermodynamic factor reflected itself as a minimum in the chemical diffusion coefficient which was consistent with the experimental measurements of other studies. As a result, the chemical diffusion coefficient exhibited considerable variation, ranging from  $5.6 \times 10^{-13} \text{ cm}^2/\text{s}$  to  $1.2 \times 10^{-11} \text{ cm}^2/\text{s}$ , across all Li concentrations. Also, a parallelogrammatic and triangular partial ordering of Li ions in the Li layer was discovered by MC simulations at Li concentrations of 0.2 and 0.3, respectively, which might be responsible for variations of the thermodynamic factor at these concentrations range. These configurations should be governed by both energetic of Li-ion configurations and vacancy concentration that permits such configurations in the structure. Furthermore, the fluctuations observed in the chemical diffusion coefficient at low concentrations align with the experimental findings reported in the

literature. These correlations observed between the results of our simulations and the experimental measurements suggest that our formalization could effectively represent the transport behaviour of Li in the NMC111 crystal.

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# 3.8. Supplementary information

As shown for the  $Li_{0.5}CoO_2$  in Figure 3.17, the convergence of log(D) and the constant slope of displacement at the last simulation steps indicated a reasonable choice for the simulation steps to perform large enough stochastic jumps.



Figure 3.17. Variation of a) log(D) and b) displacement with simulation step.
# 4. Chapter 4. Study of lithium transport in Li<sub>2</sub>O component of the solid electrolyte interphase in lithium-ion batteries

In the previous chapter, Li transport was examined in NMC cathode material to gain insight into enhancing the power capability of lithium-ion batteries in high-power applications. However, Li transport may also be hindered by the formation of the solid electrolyte interphase (SEI) layer. So, investigating Li transport in Li<sub>2</sub>O as one of the key components of the SEI layer is crucial which is the focus of this chapter. A multiscale computational approach is presented in this chapter to obtain an atomistic perspective on the factors that influence Li transport in Li<sub>2</sub>O. This will provide in-depth insights into the transport behavior of lithium and potentially enhance the performance of lithium-ion batteries in high-power applications.

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#### 4.1. Abstract

A deeper understanding of Li transport in components of Lithium-ion battery (LIB), as a promising energy storage device, is crucial for improving their rate capability. In this study, the Li transport in lithium oxide (Li<sub>2</sub>O), as one of the key components of the solid electrolyte interphase (SEI) layer, was examined by a multiscale computational approach ranging from Density Functional Theory (DFT) to Monte Carlo simulations. The DFT calculations were used to investigate the recombination of Frenkel pairs, their first-principle total energies, and the Li diffusion mechanisms. The effect of atomic configurations on both first-principle total energies and diffusion barrier energies was formulated by periodic and local cluster expansions. These formalisms were then incorporated into the Monte Carlo and Kinetic Monte Carlo (KMC) simulations to calculate the diffusion coefficient of Li. Our calculations revealed that the vacancy-mediated jump along the  $\langle 100 \rangle$  direction in the antifluorite structure of Li<sub>2</sub>O possesses the lowest barrier energy compared to other diffusion mechanisms. The KMC simulations indicated that the diffusion coefficient of Li better converged with the direct experimental measurement when the

recombination of Frenkel pairs was integrated into the simulations. At a temperature of 300 K, the KMC simulation yielded a Li diffusion coefficient of  $3.8 \times 10^{-12} \ cm^2/s$  in Li<sub>2</sub>O. This is only one order of magnitude larger than indirect experimental measurement, suggesting the accuracy of our formalism for studying Li transport in Li<sub>2</sub>O.

*Keywords*: Lithium oxide, Lithium-ion battery, solid-state diffusion, diffusion mechanism, Kinetic Monte Carlo Simulation, Cluster expansion.

#### 4.2. Introduction

Climate change has motivated modern societies to adopt sustainable energy resources over polluting fossil fuels. This energy shift requires an energy storage device with a long cycle life, prolonged stability, high energy/power density, and low-cost [1–3]. Electrochemical energy storage is preferable to other forms of energy storage due to the combination of high efficiency and energy/power flexibility. The lithium-ion battery (LIB), which consists primarily of an anode, a cathode, and an electrolyte, is a promising electrochemical energy storage technology [2,4,5].

The LIBs implemented for high-power applications (e.g., electric vehicles and hybrid electric vehicles) require materials with fast lithium (Li) transport to satisfy this high-power demand [6]. Electrochemical methods such as Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Potentiostatic and Galvanostatic Intermittent Titration Tests (PITT and GITT) are among the common methods to study Li transport in the battery cell [7–9]. Although these techniques have been extensively employed, they still possess several disadvantages [10]. Firstly, these methods are not capable of unveiling the underlying diffusion mechanism. Secondly, for the determination of diffusion coefficients in these techniques, some information and assumptions are essential which are not always accessible. For instance, the size and shape of the particles are required in some of these techniques and uncertainties in these parameters lead to large errors in estimating the diffusion coefficient [11]. Also, in these techniques, the response of the entire electrochemical cell is measured where all kinetic processes play their own role which could contradict the assumption of these techniques [7]. Chiang et al. [12] proposed the use of a single-particle electrochemical test to overcome some of these challenges, however, this method is not always feasible and is experimentally challenging. Given the current challenges in the field, understanding the factors that restrict Li transport is still necessary knowledge to enhance the

power performance of LIBs. Slow Li diffusion at high charge/discharge rates is recognized as the primary reason for the underutilization of the battery capacity [13,14]. One of the factors that can potentially hinder Li transport is the formation of solid electrolyte interphase (SEI) passivation layer [15,16]. This layer forms when the redox potential of a battery's electrode is beyond the electrochemical window of the electrolyte [17]. Although the content/composition of this layer varies depending on the anode, cathode, electrolyte type, and also electrochemical conditions, it is generally accepted in the literature that lithium oxide (Li<sub>2</sub>O) is one of the SEI key components [18–20]. Thus, the study of Li diffusivity in this material is crucial for designing the LIBs in high-power applications.

Little is known about Li diffusivity in Li<sub>2</sub>O, and most studies focused on the formation process and the function of this material in the performance of the LIBs, [15,17,19,21]. Oishi et al. [22] utilized the isotope of Li to directly determine the diffusivity of Li in Li<sub>2</sub>O from the concentration profile measured by the sectioning technique. However, since the diffusivity is very low at room temperature, their method was applicable only at high temperatures where Li ions could diffuse rapidly. Guo et al. [19] and Longer et al. [23] measured the diffusivity by electrochemical methods which still suffer from the aforementioned challenges that existed in these techniques. Hence, due to these difficulties and challenges in experiments, attempts to analyze Li diffusivity in Li<sub>2</sub>O have relied mostly on first-principles calculations and/or simulations. Few studies [24–27] have investigated vacancy-mediated Li diffusion using density functional theory (DFT) and the nudged elastic band (NEB) approach. Benitez et al. [28] and Tasaki et al. [29] used classical molecular dynamics (MD) simulation to study Li diffusivity in the Li<sub>2</sub>O component of SEI at a length scale larger than DFT. The limitation of MD is the accessible timescale, which is often significantly less than the duration of typical jump events in the diffusion process. As a result, the number of diffusion events commonly seen in MD simulations is insignificant, leaving the estimation of diffusion coefficients imprecise and/or computationally expensive at this limited accessible timescale. This mismatch between timescales restricts the application of MD to liquids or solids that are superionic at extremely high temperatures [30]. In the case of  $Li_2O$ , this material exhibits superionic behavior above the transition temperature of around 1200 K; hence, most MD studies on the Li diffusivity in this material have been conducted at high temperatures [31–34]. Therefore, an appropriate atomistic method still needs to be developed to capture the timescale of Li diffusivity in Li<sub>2</sub>O at low temperatures at which the LIBs usually operate.

The atomistic description of Li diffusivity in Li<sub>2</sub>O entails a thorough grasp of this material's structures and properties. The dominant intrinsic defect in the antifluorite structure of this material is the cation Frenkel pair (i.e. Li vacancy and Li interstitial pair), as the formation energy of the Schottky defect is around double as of the Frenkel pair [35–37]. It should be emphasized that Frenkel pairs can recombine, and this process is often characterized by the recombination radius [38–40]. Consequently, the method describing the diffusion in this material should consider the cation Frenkel defect and the recombination effect.

In this work, we developed a multiscale atomistic simulation method for studying Li diffusivity in Li<sub>2</sub>O. While an exact recombination radius may not be defined in this material [41], to approximate the vacancy and interstitial recombination in this study, an estimated recombination distance was determined by DFT calculations. Considering only the cation Frenkel defect in the structure, the possible diffusion mechanisms, including vacancy-mediated and collective mechanisms, were investigated with DFT and climbing image-NEB (CI-NEB) method. To study the Li diffusivity in Li<sub>2</sub>O at a larger time/length scale, a first principle statistical mechanical approach based on Kinetic Monte Carlo (KMC) simulation was employed. Since different local atomic environments could be met by Li ions during diffusion, the local cluster expansion was formulated to account for the atomic environment dependence of jump barrier energies. In addition, as the first-principles energy of Li<sub>2</sub>O is affected by the configuration of the Frenkel defects, the periodic cluster expansion of this material, including the Frenkel defects, was constructed to parametrize the configurational dependence of the total energy. The VESTA software [42] was used to create all of the atomic visualizations in this paper.

#### 4.3. Methods

#### 4.3.1. First-principles calculations

#### 4.3.1.1 *DFT*

All DFT calculations were performed in the antifluorite structure (space group Fm3m) of  $Li_2O$  where the oxygens (O) are located on the FCC sublattice, and Li-ions sit on the tetragonal sites forming a cubic sublattice, as illustrated in Figure 4.1. In this figure, the gray spheres on the

octahedral sites between the O atoms indicate the position of interstitial sites where the Li interstitial of a Frenkel defect can be located.



Figure 4.1. The unit cell of Li<sub>2</sub>O (space group Fm3m): Red spheres depict the Oxygens, green spheres are Lithium, and small gray spheres show the interstitial sites.

The DFT calculations were carried out using Quantum ESPRESSO [43], with the PAW pseudopotential [44], and the PBE-GGA exchange-correlation functional [45]. The optimum kinetic energy cutoff of 680 eV was determined by ensuring that the difference in energy per atom is smaller than 1 meV by increasing the cutoff energy. The first-principle total energies were obtained by relaxing the atoms until the components of forces applying on each atom were less than 0.025 eV/Å.

The approximate recombination distance was determined by investigating the stability of cation Frenkel pairs in four supercells containing an intestinal and a vacancy placed at different distances. One Li-ion occupied one of the interstitial sites, and one vacancy was created at the first, second, third or fourth neighbour site on the cubic sublattice. This separated the Li interstitial and the vacancy by 2.02 Å, 3.86 Å, 5.08 Å, and 6.05 Å for the first, second, third and fourth neighbour vacancies, respectively. In Figure 4.2, the Li plane containing the vacancy and the adjutant O plane, including the Li interstitial, are illustrated for these four distances. Large supercells containing  $3 \times 3 \times 3$  unit cells were used to ensure that the interactions between the Frenkel pairs from periodic images were small. After the lattice parameters and the atomic positions were fully relaxed until the force components on each atom were less than 0.025 eV/Å, the stability of Frenkel pairs was examined.



Figure 4.2. The Li interstitial and the vacancy separated by a) 2.02 Å, b) 3.86 Å, c) 5.08 Å, and d) 6.05 Å. Image e) shows the side view of Li and O planes. The vacancy is depicted by a blue hexagon, Li by green circles, O by red and interstitial sites by gray circles.

4.3.1.2 *CI-NEB* 

To examine the diffusion mechanisms, the DFT combined with the CI-NEB method [46] was used in this study. In the NEB method, a set of five images was interpolated between the initial and the final state of the diffusing particles, and a spring was placed between the images to ensure the continuity of the diffusion path. The minimum energy path was determined by minimizing the forces applied on each image, and the activation barrier was determined by the difference between the initial energy and the saddle point energy. To locate the saddle point more precisely, the climbing image modification was added to the NEB (i.e., CI-NEB) to remove the effect of springs on the maximum energy image. In all cases, a large supercell of the size  $3 \times 3 \times 3$  was used to ensure that the interaction of the diffusing particles from the periodic images was small.

#### 4.3.2. Cluster expansion

The total energy of Li<sub>2</sub>O depends on the configuration of Frenkel defects. The Cluster expansion method [47,48] separates configurational from structural degrees of freedom of the total energy [49,50]. Therefore, with the knowledge of a limited number of configurations, this method estimated the total energy of any other Frenkel defect configurations with minimal computational cost. In the cluster expansion method, as a generalized Ising model, the configurations were defined by the spin-like variable  $\sigma$ , which is +1 for the presence of Li and -1 for the vacancy. The cluster expansion then calculated the total energy of the system as follows:

$$E = \sum_{\alpha} V_{\alpha} \phi_{\alpha} \tag{4.1}$$

where,

$$\phi_{\alpha} = \prod_{i \in \alpha} \sigma_i \tag{4.2}$$

 $\phi_{\alpha}$ , the correlation function, is the average of the product of occupation variables of each site, *i*, in the cluster  $\alpha$ . The cluster  $\alpha$  is any combination of the lattice sites, including empty, point clusters, pairs, triplets, etc., each of which could be nearest-neighbour, second nearest-neighbour, and so on. The *V* coefficients, called effective cluster interactions (ECI), were determined by fitting the cluster expansion formalism into the first-principles calculations.

The cluster expansion of Li<sub>2</sub>O was constructed with the CLEASE package [51]. The cubic and interstitial sublattices were chosen for generating random Li/vacancy configurations on each sublattice. In this process, the number of Li-ions on the interstitial sublattice was forced to be the same as the number of vacancies on the cubic sublattice to ensure that the Li interstitials and vacancies of Frenkel defects are equal in number. Furthermore, since the concentration of Frenkel defects is very small [33,52], the number of vacancies was set to be less than 5 percent of the total number of Li in the supercell. In addition, the configurations that are generated randomly by CLEASE do not account for the recombination effect. Thus, in a subsequent screening process, we eliminated configurations in which the recombination occurred by comparing the initial and relaxed structures. This leads to a total of 46 random configurations of Frenkel defects in the

dataset. Also, as the contribution of clusters to the total energy decreases with cluster size [50], only the point clusters, pairs, triplets, and quadruplets with a maximum diameter of 4.5, 5, and 7 Å, respectively, were included in the cluster expansion formalism. This formalism resembles a machine learning linear regression model. Therefore to obtain the ECIs, ridge regression was utilized to fit the cluster expansion formalism to the energy of those 46 random configurations acquired after the screening step.

#### 4.3.3. Local Cluster expansion

As the activation energy of Li hops depends on both the local atomic environment and the jump direction (i.e. forward/backward jump), the so-called kinetically resolved activation (KRA) barrier,  $\Delta E_{KRA}$ , [53] can be used to remove the directional dependency. The  $\Delta E_{KRA}$  is simply the saddle point energy  $E_{sp}$  subtracted by the average energy of the initial  $E_i$  and the final  $E_f$  states. This is shown schematically for the vacancy-mediated jump in Li<sub>2</sub>O in Figure 4.3. Thus,  $\Delta E_{KRA}$  is given by:

$$\Delta E_{KRA} = E_{sp} - \frac{E_i + E_f}{2} \tag{4.3}$$

This barrier depends only on the local atomic environment; thus, the local cluster expansion [53] was implemented to parametrize this configurational dependency. The local cluster expansion has the same formalism as the periodic cluster expansion. Thus, the  $\Delta E_{KRA}$  was expressed as a linear combination of correlation functions,  $\phi_{\alpha}$ , and kinetic effective cluster interactions (KECI),  $K_{\alpha}$ , as follows:

$$\Delta E_{KRA} = \sum_{\alpha} K_{\alpha} \phi_{\alpha} \tag{4.4}$$

Then by combining the periodic cluster expansion for initial/final points and the local cluster expansion for  $\Delta E_{KRA}$ , the true barrier energies,  $\Delta E_t$ , was determined by:

$$\Delta E_t = \frac{E_i + E_f}{2} + \Delta E_{KRA} - E_i \tag{4.5}$$



Figure 4.3. The schematic of  $\Delta E_{KRA}$  and the corresponding position of jumping Li-ion at the initial, final and saddle points. The vacancy is depicted by a blue hexagon, Li by green circles, O by red and interstitial sites by gray circles.

For Li<sub>2</sub>O, the local cluster expansion was only constructed for the Li hops to the nearest neighbour vacancy along the  $\langle 100 \rangle$  direction since this vacancy-mediated mechanism was identified as the dominant diffusion method (discussed in the results section). To apply the point group symmetry in the building of this local cluster expansion, the saddle point was approximated to the midpoint between the initial and final position, as this was derived from our CI-NEB calculations. Since  $\Delta E_{KRA}$  is a local property, clusters near the saddle point should be sufficient to converge the KECIs. Therefore, we considered only the first, second, and third nearest-neighbour sites of the saddle point, to construct the local cluster expansion of this diffusion mechanism, as illustrated in Figure 4.4. The KECIs of this expansion were determined by the linear regression fit to the  $\Delta E_{KRA}$  values found by the CI-NEB method for 28 different Li/vacancy arrangements in the neighbour sites shown in Figure 4.4.



Figure 4.4. The first (blue), second (orange) and third (pink) nearest neighbour sites of the saddle point (gray) in the vacancy-mediated diffusion mechanism. The Li jump path is shown with green spheres.

#### 4.3.4. Canonical Monte Carlo (CMC)

Monte Carlo simulation in lattice models is a popular technique for calculating the thermodynamic properties of the materials [54]. The CMC method implemented in CLEASE [51] was used to find the equilibrium arrangement of Frenkel defects at a temperature range between 300 and 1000 K: First, in a Li<sub>2</sub>O supercell containing 2000 Li ions, random configurations of Frenkel pairs were generated such that no vacancies were initially present within the Li interstitial recombination distance. This initial state was then equilibrated by 500 MC steps using the Metropolis algorithm [55], in which a trial state is produced with the following probability:

$$W = \min\left\{1, \exp\left(\frac{\Delta E}{k_B T}\right)\right\}$$
(4.6)

In this equation,  $\Delta E$  is the change in the energy between the subsequent and the current configuration,  $k_B$  is the Boltzmann constant, and T is the temperature. The trial state was then accepted if W was greater than a random number sampled between 0 and 1; otherwise, it was rejected. In addition to this conventional criterion for accepting/rejecting the trial move, each trial move was checked for the recombination effect. That is, if a vacancy was within the recombination distance, that trial state was rejected. This equilibrated structure where then used as the input structure for the KMC simulation.

#### 4.3.5. Kinetic Monte Carlo (KMC)

The KMC simulation allows the determination of the diffusion coefficient. Thus, a customwritten Python code was developed for KMC using the n-Fold way algorithm [56,57]. This algorithm consists of the following steps: first, i) the transition rate of each possible jump,  $\Gamma_i$ , was determined using the transition state theory [58] by:

$$\Gamma_i = \nu^* \exp\left(\frac{\Delta E_{t,i}}{k_B T}\right) \tag{4.7}$$

where  $\Delta E_{t,i}$  is the true activation barrier of the *i*<sup>th</sup> jump, and  $\nu^*$  is the attempt frequency which was set to 10<sup>13</sup> Hz. ii) Then, the *k*<sup>th</sup> jump was chosen such that the following inequality was held:

$$\frac{1}{\Gamma_{tot}} \sum_{i=1}^{k-1} \Gamma_i < \xi_1 \le \frac{1}{\Gamma_{tot}} \sum_{i=1}^k \Gamma_i$$
(4.8)

where  $\xi_1$  is a random number sampled between 0 and 1, and  $\Gamma_{tot}$  is the sum of all the transition rates. After the  $k^{\text{th}}$  jump was performed, iii) the time, *t*, was updated with the time increment,  $\Delta t$ , calculated by:

$$\Delta t = -\frac{1}{\Gamma_{tot}} \ln \xi_2 \tag{4.9}$$

where  $\xi_2$  is also a random number sampled between 0 and 1. These three steps were repeated until 500 KMC steps were performed. The tracer diffusion coefficient was then calculated using the Einstein equation given by [59]:

$$D^* = \lim_{t \to \infty} \frac{\langle R^2 \rangle}{2dt}$$

$$\tag{4.10}$$

where  $\langle R^2 \rangle$  is the mean square displacement of Li ions, *d* is the dimension of diffusion, and *t* is the diffusion time.

To approximate the recombination effect in the KMC algorithm, the boundary atoms located at the recombination distance away from each Li interstitial were identified prior to each jump. This approximate recombination distance was found to be 3.86 Å by DFT calculations (discussed in the

results section). After performing a jump, if a vacancy was exchanged with one of these boundary atoms, the vacancy and Li interstitial vanished rapidly by spontaneous recombination. The 2D schematic of this process is illustrated in Figure 4.5. In this figure, the approximate recombination area is highlighted by a large brown circle, the vacancy is shown by a blue hexagon, and the green, red, gray, and brown small circles depict the Li, O, interstitial site, and boundary atoms, respectively.



Figure 4.5. The 2D schematic of the recombination process implemented in the KMC algorithm: a) A vacancy is exchanged with one boundary atom, b) the vacancy is present within the recombination distance from Li interstitial, and c) vacancy and Li interstitial recombine. The vacancy is depicted by a blue hexagon, Li by green circles, O by red and interstitial sites by gray circles.

#### 4.4. **Results and discussion**

#### 4.4.1. Diffusion mechanisms

The operation of two types of diffusion mechanisms in Li<sub>2</sub>O, including the collective and vacancy mechanisms, were investigated in Li<sub>2</sub>O. In the collective mechanism, two or more Li ions were displaced simultaneously. Three types of collective mechanisms in Li<sub>2</sub>O were studied: 1) Interstitialcy mechanism in which a Li interstitial pushed a Li-ion in the cubic sublattice and moved it to another interstitial site, 2) ring mechanism, which involved the simultaneous jumps of four nearest neighbour Li ions to create a closed loop of Li rotation, and 3) direct-exchange in which two nearest neighbour Li ions were swapped in the cubic sublattice. It should be noted that the ring and direct-exchange methods are defect-free diffusion mechanisms, while in the interstitialcy

method, an existing Li intestinal disappeared and a new one was created immediately. Figure 4.6 illustrates these mechanisms from top and side perspectives along with their corresponding barrier energies. In this figure, the yellow-highlighted atoms indicate the initial position of Li-ions before the jump. In Figure 4.6-d, it is observed that among these three jumps, the interstitialcy mechanism has the lowest barrier energy of 0.47 eV, while the barrier energies of the direct-exchange and ring mechanisms are 1.92 and 2.16 eV, respectively. This can be explained by the fact that no defect is involved in the direct-exchange and ring mechanisms, thus the diffusing atom must squeeze through the neighbouring atoms, resulting in large lattice distortion and high barrier energies [59].



Figure 4.6. Collective mechanisms of Li diffusion on Li<sub>2</sub>O: a) Interstitialcy mechanism, b) ring mechanism, c) direct-exchange mechanism. Figure d) shows the energy barrier of each collective mechanism. The vacancy is depicted by a blue hexagon, Li by green circles, O by red and interstitial sites by gray circles. The atoms highlighted in yellow show the initial position of Li-ions before the jump.

Meanwhile, on the side of the vacancy-mediated mechanism, a Li-ion in the cubic sublattice jumped to a vacancy in the same sublattice. Notably, to prevent the recombination of Frenkel pairs, the vacancy-mediated jumps were performed outside of the approximate recombination distance away from the Li interstitial. Three types of migration paths were distinguished with the CI-NEB method based on Li jumps along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , or  $\langle 111 \rangle$  directions. These three vacancy-mediated jumps and their associated barrier energies are illustrated in Figure 4.7. The barrier

energy of the jump along the (100) direction was found to be 0.21 eV, while this value is 1.38 and 1.48 eV for (110) and (111) directions, respectively. This trend is also consistent with what was reported in the literature [24,25].

Comparing the barrier energies of all the discussed mechanisms reveals that the vacancymediated jump along the (100) direction has the smallest barrier energy which is comparable to that of the previous research [26–28,60]. Therefore, the remaining mechanisms could occur more often at high temperatures where the thermal fluctuations are large enough to overcome their high barrier energies. Similar results were also reported in prior investigations using MD simulations [25,30,33]. Because the focus of this study is limited to the low-temperature range at which LIBs usually function (i.e., below transition temperature), our KMC simulation considered only this dominant mechanism. Consequently, the local cluster expansion was constructed only for this mechanism to capture the local dependency of barrier energies.

In the vacancy-mediated mechanism, the barrier energy could be affected by the distance between the Li interstitial and the Li jumps. Therefore, we repeated our simulations for the dominant vacancy-mediated mechanism by placing the Li interstitial at 5.08, 6.05, 6.89, 8.32, and 10.09 Å away from the vacancy. The barrier energies for these distances are 0.228, 0.228, 0.213, 0.210, and 0.206 eV, respectively. The difference between the greatest and smallest values in these barrier energies is only 0.022 eV, indicating the negligible effect of the Li interstitial position on the barrier energies. This is because the Li interstitial was placed at a distinct location from the Li hop to avoid the recombination effect; consequently, the influence of the Li interstitial on the barrier energies is already minimal. Therefore, the local cluster expansion constructed for this dominant mechanism only included the configuration of Li/vacancy arrangements around the diffusing Li in the cubic sublattice and excluded the configurations of Li interstitial.



Figure 4.7. Vacancy-mediated diffusion mechanism in Li<sub>2</sub>O for Li jumps along: a) (100), b) (110), and
c) (111) directions. Figure d) shows the associated barrier energies for these three jumps. The vacancy is depicted by a blue hexagon, Li by green circles, O by red and interstitial sites by gray circles.

4.4.2. Configurational-dependent total and barrier energies

The total energies per atom predicted with periodic cluster expansion and calculated with DFT are illustrated in Figure 4.8 for different configurations of Frenkel pairs. The RMSE of the cluster expansion model was 0.113 meV per atom with a 3-fold cross-validation score of 0.307 meV per atom. This brings the predicted energies to a close approximation of the DFT-determined actual energies, as is clear in Figure 4.8.



Figure 4.8. The actual/predicted total energy per atom for different Frenkel pair configurations. The actual values were determined with DFT, and the predicted ones were calculated by cluster expansion.

To obtain an optimal local cluster expansion model for predicting the  $\Delta E_{KRA}$ , it is essential to choose the clusters that properly describe the local atomic environment. The combination of nine clusters depicted in Figure 4.9-a provided the highest level of predictability for local cluster expansion in Li<sub>2</sub>O. This combination consists of three point-clusters, four pair-clusters, one triplet, and one quadruplet distributed across the nearest-neighbour sites of the saddle point illustrated in Figure 4.4. The associated KECIs of these clusters (illustrated in Figure 4.9-b) were determined using the  $\Delta E_{KRA}$  of 28 different Li/vacancy arrangements in the neighbour sites. As the KECIs are merely the fitting coefficient, their values may not necessarily represent any physical interpretation, nevertheless, a general remark may be made concerning the point clusters. The cluster with the highest absolute KECI value is the second-nearest neighbor point-cluster (cluster number 2). Therefore, the presence of vacancy at this site should increase the  $\Delta E_{KRA}$  in general. If the vacancy is located on the first or third nearest-neighbour site of the saddle point, the opposite behaviour should generally be observed.



Figure 4.9. a) The clusters that provided the highest predictability for the local cluster expansion. b) The KECIs of the cluster. In figure a), the first, second, and third nearest neighbour sites of the saddle point (gray) are depicted with blue, orange, and pink circles, respectively. The migrating Li is shown with green circles. The clusters are highlighted in black.

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The actual and predicted  $\Delta E_{KRA}$  are shown in Figure 4.10-a) as a function of the number of vacancies in the neighbouring sites. This figure clearly shows that the vacancy configurations on these sites can reduce the  $\Delta E_{KRA}$  to as low as 0.06 eV and as high as 0.44 eV. This signifies the necessity of implementing local cluster expansion to capture this local environmental dependency. The RMSE of the local cluster expansion model was 23 meV with a maximum error of 17%, resulting in the actual and predicted  $\Delta E_{KRA}$  lying along the x=y line as shown in Figure 4.10-b).



Figure 4.10. The actual and predicted KRA barrier,  $\Delta E_{KRA}$ , a) as a function of the number of vacancies in the neighboring sites, and b) their scattering with respect to the x=y line

4.4.3. Recombination of Frenkel pairs

As already mentioned, an approximate distance for the recombination of Frenkel pairs is required to implement this effect in the KMC simulation. The analysis of structures shown in Figure 4.2 before and after relaxation could give insight into the recombination effect in Li<sub>2</sub>O. It was discovered that Li vacancy and Li interstitial disappeared through recombination when separated by 2.02 Å and 3.86 Å. However, when they were separated by 5.08 Å and 6.05 Å only local atomic relaxation was observed without complete recombination. In these cases, the neighboring Li-ions around the vacancy were locally relaxed toward the vacancy, whereas the neighboring Li-ions around the Li interstitial were relaxed slightly away from the Li interstitial, as depicted in Figure 4.11 for the distance of 5.08 Å. As the recombination of Li vacancy and Li

interstitial was observed for the separation distance of 3.86 Å and less, the recombination distance was approximated to 3.86 Å. This distance is merely an approximation to the recombination effect, as an exact radius may not be defined in  $Li_2O$  [41]. Therefore, a dynamic model would need to precisely capture the recombination, whereas our static DFT calculations may underpredict this event. Nevertheless, this approximate recombination distance could be sufficient to be implemented in the KMC simulation, as we will demonstrate in the next section.



Figure 4.11. 2D schematic of local relaxation around Li vacancy and Li interstitial when separated by 5.08 Å. The vacancy is depicted by a blue hexagon, Li by green circles, O by red and interstitial sites by gray circles.

### 4.4.4. Diffusion coefficient

The diffusion coefficient of Li in Li<sub>2</sub>O determined by KMC simulations is illustrated in Figure 4.12 with the green circles. Although the focus of this study is limited to the ambient temperature at which LIBs usually function (i.e., 300 K), the diffusivity was also determined up to 1000 K to compare the result with the Li diffusivity directly measured from the diffusion couple experiment by Oishi [22]. It should be noted that the KMC simulations were not performed at temperatures larger than 1000 K as at this temperature a transition to disorder structure was reported [61]. Also, additional simulations were performed with no recombination effect, and the corresponding results were added to Figure 4.12 with red circles. Clearly, when the recombination effect was incorporated into the KMC algorithm, the results converged more closely with the tail of experimental values, demonstrating the significance of incorporating the recombination effect into the KMC algorithm. This also emphasizes that the approximate recombination distance could be sufficient for capturing this effect for the KMC simulation without the need to fully capture the dynamics of this process. In addition, results from MD simulations reported in the literature

[28,29,31,34] were included in Figure 4.12. It is evident from this figure that between 800 and 1000 K, the KMC simulation results are closer to the experimental values than the MD simulations. However, at temperatures above 1000 K, the MD simulations become closer to the experiments as the Li diffusivity approaches the accessible timescale of MD.

At 300 K, the KMC simulations determined the Li diffusion coefficient in Li<sub>2</sub>O to be  $3.8 \times 10^{-12} \ cm^2/s$ . To the best of our knowledge, no direct experimental measurement of Li diffusivity in Li<sub>2</sub>O has been reported in the literature at this temperature; nevertheless, the MD simulation from Benitez [28] and Tasaki [29] at 300 K demonstrates excellent agreement with the KMC result of this study (illustrated Figure 4.12). This signifies the accuracy of our KMC algorithm to capture the recombination effect and the configuration-dependent activation barriers without the complications regarding the limited accessible timescale of MD, causing the high computational cost of MD at low temperatures. Also, indirect measurement of Li diffusivity in the bulk Li<sub>2</sub>O by Lorger [23] yielded a value of  $2 \times 10^{-13} \ cm^2/s$  which is only one order of magnitude different from the result of the present study. However, indirect measurements in the thin film of Li<sub>2</sub>O by Guo [19], gave the value of  $2 \times 10^{-9} \ cm^2/s$  for Li diffusivity which is approximately three orders of magnitude greater than the diffusivity in bulk. This high Li diffusivity in Li<sub>2</sub>O might be explained by the larger contribution of high diffusivity paths like grain boundaries when it is formed as a thin film. The contribution of grain boundaries to the transport of Li in a thin film of Li<sub>2</sub>O could be the subject of interesting future work.



Figure 4.12: Diffusion coefficient of Li in Li<sub>2</sub>O plotted as Log(D) vs 1/T. Previously reported results from molecular dynamics (triangles) and experimental studies (crosses) are displayed for comparison.

### 4.5. Conclusion

Improving the rate capability of LIBs as a promising energy storage device requires in-depth knowledge of Li transport in their components. Li transport in Li<sub>2</sub>O, as one of the key components of the SEI layer, was investigated using a multiscale computational approach ranging from Density Functional Theory (DFT) to Monte Carlo simulations in this study. Two diffusion mechanisms including the collective and vacancy-mediated jumps were investigated using DFT and the CI-NEB method. These calculations revealed that the vacancy-mediated jump along the  $\langle 100 \rangle$  direction has the lowest barrier energy compared to the collective diffusion mechanisms and the

vacancy-mediated jump along the  $\langle 110 \rangle$  and  $\langle 111 \rangle$  directions. Therefore, the other mechanisms may occur more frequently at high temperatures where thermal fluctuations are sufficient to overcome their large barrier energies. Cluster expansion models were also developed to capture the dependence of total energy and kinetically resolved activation barriers ( $\Delta E_{KRA}$ ) on atomic configurations, both of which were required for evaluating the jump processes in the KMC simulations. When the recombination of Frenkel pairs was incorporated into the KMC algorithm using an approximation of the recombination distance, the diffusivity values were found to be better aligned with MD simulations and experimental measurements from the other studies in the literature. The KMC simulation incorporating the recombination effect calculated the Li diffusivity at 300 K to be  $3.8 \times 10^{-12} \text{ cm}^2/\text{s}$ , which is only one order of magnitude larger than the indirect experimental measurement. This demonstrates the precision of our KMC algorithm, which incorporates underlying physical concepts such as configurationally dependent barrier and firstprinciples energies, as well as the recombination of Frenkel pairs.

## 4.6. Acknowledgements

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#### 4.7. References

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# 4.8. Supplementary information

To construct the dataset for the cluster expansion, a total of 46 random configurations of Frenkel defects were created. These random configurations after being fully relaxed are illustrated in Figure 4.13 to Figure 4.18. Note that in these figures the boundary atoms are not illustrated.



Figure 4.13. Random configurations of Frenkel pairs that were added to the dataset for constructing the cluster expansion formalism.



Figure 4.14. Random configurations of Frenkel pairs that were added to the dataset for constructing the cluster expansion formalism.



Figure 4.15. Random configurations of Frenkel pairs that were added to the dataset for constructing the cluster expansion formalism.



Figure 4.16. Random configurations of Frenkel pairs that were added to the dataset for constructing the cluster expansion formalism.



Figure 4.17. Random configurations of Frenkel pairs that were added to the dataset for constructing the cluster expansion formalism.



Figure 4.18. Random configurations of Frenkel pairs that were added to the dataset for constructing the cluster expansion formalism.

# 5. Chapter 5. Prediction of primary knock-on damage during electron microscopy characterization of lithium-containing materials

In the previous two chapters, lithium transport characteristics in two battery materials (NMC and Li<sub>2</sub>O) were examined. In addition to the kinetic behavior, chemical and structural information of battery materials are vital for the development of lithium-ion batteries. While electron microscopes have been widely utilized to obtain this information in battery materials, they may damage the battery materials by various mechanisms. Lithium-containing materials are particularly susceptible to knock-on damage which is the focus of this chapter. A multiscale computational approach combined with theoretical calculations is presented in this chapter to quantify knock-on damage and investigate the parameters affecting this damage. This gives insight into the efficient strategy for reducing knock-on damage in lithium-containing materials, thereby facilitating the development of lithium-ion batteries through more reliable electron microscopy characterization.

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#### 5.1. Abstract

To fulfill power and energy demands, lithium-ion battery (LIB) is being considered as a promising energy storage device. For the development of LIBs, high-resolution electron microscopy characterization of battery materials is crucial. During this characterization, the interaction of beam-electrons with Li-containing materials causes damage through several processes, especially knock-on damage. In this study, we investigated this damage by determining the probability of knock-on damage and performing Monte Carlo simulation. For this objective, the threshold displacement energies (TDEs) were computed using sudden approximation
technique for three sets of materials, including pure elements, LiX (X=F, Cl, Br), and Li<sub>2</sub>MSiO<sub>4</sub> (M = Fe, Co, Mn). By including the Climbing-Image Nudge Elastic Band (CI-NEB) method into the sudden approximation approach, it was found that the accuracy of the predicted TDEs could be improved. Results also indicated that at moderate electron energies, the knock-on damage for Li in both its elemental and compound forms maximized. In addition, it was shown that the TDE should be the principal parameter for assessing the Li sensitivity to knock-on damage across similar structures. Nonetheless, other parameters, including cross-section, density, weight fraction, atomic weight, and atomic number, were found to impact the knock-on damage.

*Keywords*: Lithium-ion battery, Electron-beam damage, knock-on damage, Threshold displacement energy, Monte Carlo Simulation, Density Functional Theory

## 5.2. Introduction

Climate change, the increase in population, and the rising cost of fossil fuels necessitate a shift from fossil fuels to renewable energy resources and, consequently, from internal combustion engines to electric vehicles [1,2]. A successful energy transition requires not only the generation of energy in a sustainable manner, but also efficient storage of energy. In this regard, lithium-ion batteries (LIBs) are being considered as a promising energy storage device to meet the power and energy demands [1-3]. The performance of LIB relies on the chemical and structural properties of its components [4-6], which consist of lithium-containing materials either in cathode/anode or within the solid electrolyte interface (SEI) [2]. To develop LIBs, studying lithium-containing materials at high spatial resolution is of great importance. While electron microscopes are powerful tools for obtaining chemical and structural information of battery materials at high resolution, the interaction of beam-electrons with the specimen can damage the material through different mechanisms (e.g., knock-on damage, radiolysis, heating, and charging) [7]. These damages consist of two main steps: initially, the beam damages produce defects in an athermal primary step, then, the defects evolve on a long-timescale through thermally activated processes and cascade events, causing subsequent changes in the structure and properties of the material [8,9]. In previous studies, these defects were observed under the electron microscope at the atomic scale [10,11] and micro-scale [12]. These damages may misinterpret the electron microscopy characterizations as they are not inherent to the materials being examined.

Knock-on damage is more critical in Lithium-containing materials due to the high mobility of lithium atoms [5,13]. This damage occurs when a beam-electron scatters elastically and transfers an energy larger than the threshold displacement energy (TDE) to the atom, ejecting the atom from the original lattice sites, which creates a Frenkel pair defect within the material or sputters the atom out of the sample if the interaction takes place close to the irradiated surface [14]. Wang et al. [15] established the presence of this damage in Li-rich layered cathode materials using high-angle annular dark-field (HAADF) images. Using fast atomic-scale chemical imaging, Lu et al. [16] also discovered this damage in a cathode material. Therefore, to characterize lithium-containing materials with electron microscopes, it is crucial to determine an optimized operating condition to minimize the knock-on damage as the beam damage controls the limit of the spatial resolution [17].

Few studies have investigated electron beam damage in Li-containing materials. Cui et al. [4] showed that examining battery materials with electron microscopes at cryogenic temperature and under specific experimental conditions can significantly reduce beam damage. However, this experimental condition is not always accessible and is challenging to perform. Xin et al. [13] demonstrated that small electron dose rate reduces the beam damage in lithium-containing materials; however, this is not always feasible since, in some analyses, a reduced dosage may lead to a poor signal-to-noise ratio. Meng et al. [18], therefore, suggested an optimized electron dosage to reduce this damage. Despite these valuable works to overcome this issue, beam damage still remains a significant obstacle in the investigation of Li-containing materials using electron microscopes.

This work focuses on the primary step of knock-on damage and does not account for the longer timescale evolution of this damage, as the impact of the consequent events can be diminished if the primary step of this damage is controlled. Determining the relationship between knock-on damage and its contributing factors to quantifying this damage could be the most effective strategy for reducing this damage. Therefore, a formula for the probability of primary knock-on damage,  $P_{KOD}$ , was derived, which considers the influence of electron energy, elastic cross-section, scattering angle, and sample thickness on the probability that a knock-on event occurs. To compare the  $P_{KOD}$  with the simulation, a Monte Carlo algorithm was developed to simulate the knock-on damage in materials. In addition, knowledge of TDE is necessary for both the simulation and

derived formula; however, unlike pure elements, this parameter for lithium-containing materials is not well known in the literature. Therefore, the TDE of these materials was determined using Density Functional Theory (DFT). The remaining sections of this document are as follows: the derivation of the  $P_{KOD}$  is presented in the *Theory/Calculations* section, the Monte Carlo algorithm and DFT calculations of TDE are then described in the *Methods*, followed by the *Results and discussion*, and finally the *Conclusion*.

# 5.3. Theory/Calculation

In this section the theoretical calculations for finding the  $P_{KOD}$  will be explained. An interaction between an incident electron and an atom is considered elastic if the electron collides with the nucleus of the atom with a negligible energy loss. This does not, however, imply that the electron's energy remains constant. Indeed, based on momentum and energy conservation, the electron should transfer energy to the nucleus during the elastic collision [7,19]. The following formula computes the transferred energy from the incident electron to the nucleus [7]:

$$E = E_{max} \sin^2\left(\frac{\theta}{2}\right) \tag{5.1}$$

where  $\theta$  is the scattering angle,  $E_{\text{max}}$  is the maximum transfer energy which is calculated by:

$$E_{max} \approx \frac{2E_0(E_0 + 2m_0c^2)}{Mc^2}$$
 (5.2)

where  $E_0$  is the kinetic energy of the incident electron,  $m_0$  and M are electron and nucleus mass, respectively, and c is the speed of light.

Knock-on damage happens when the transfer energy is larger than TDE, which is a material property and depends on the structure, bond strength, displacement direction, and position of the displaced atom [7,8,20] (A detailed explanation on the calculation of this parameter using DFT is provided in the Method section). Therefore, putting E = TDE gives the following equation for the minimum scattering angle,  $\theta_{min}$ , leading to knock-on damage:

$$\sin^{2}\left(\frac{\theta_{min}}{2}\right) = \frac{TDE \ (Mc^{2})}{2E_{0}(E_{0} + 2m_{0}c^{2})}$$
(5.3)

The probability of having a scattering angle greater than  $\theta_{\min}$  can be proved to have the following relationship with  $\theta_{\min}$ : (see Appendix for the derivation):

$$P(\theta \ge \theta_{min}) = \frac{1}{1 + \left(\frac{\theta_{min}}{\theta_0}\right)^2}$$
(5.4)

In this equation  $\theta_0$  is the relativistic screening parameter which depends on atomic number, Z, and the kinetic energy of the incident electron,  $E_0$  (in keV), by:

$$\theta_0 = \frac{Z^{1/3}}{\sqrt{84.94E_0 + 0.083E_0^2}} \tag{5.5}$$

Furthermore, the probability of elastic scattering is given by [21]:

$$P_{El} = 1 - e^{-t/\lambda} \tag{5.6}$$

where *t* is the sample thickness and  $\lambda$  is the total elastic mean free path which is calculated using the total elastic cross sections as described in [22]. Multiplication of these two probabilities (i.e., equations (5.4) and (5.6)) gives the probability of scattering events that cause knock-on damage,  $P_{KOD}$ :

$$P_{KOD} = \frac{1 - e^{-t/\lambda}}{1 + \left(\frac{\theta_{min}}{\theta_0}\right)^2}$$
(5.7)

### 5.4. Methods

### 5.4.1. Monte Carlo Simulation

Monte Carlo simulation has been widely used to examine solid-electron interactions in materials. Win X-ray [22] and CASINO V2.42 [23] are two efficient and user-friendly software developed previously to aid microscopists in interpreting their results by Monte Carlo simulation.

In this work, to increase the applicability of this modelling tool, the prediction of primary knockon damage was incorporated into the Monte Carlo algorithm.

The Monte Carlo code developed in this work simulated the electron trajectories within the solid using the single scattering approach similar to that of CASINO and Win X-Ray. The formulations and details of the single scattering approach can be found in reference [22], however, a brief overview is provided here. In this approach, the trajectory of each electron was changed at each collision as it scattered through polar and azimuth angles and then travelled for a distance before another elastic collision occurred. To determine this distance between the elastic collisions, knowledge of the elastic mean free path is necessary [24] for which the ELSEPA [25] was used in this study. At each elastic collision, the polar angle, azimuth angle, and travel distance were determined by uniformly distributed random numbers between 0 and 1 to sample these parameters from many possible stochastic events. The amount of energy the electron lost between elastic collisions was computed by the continuous slowing-down approximation [26]. To incorporate the knock-on damage, the energy of incident electrons at each elastic collision was stored in a file. Then, the energy transferred to the atom at each collision was calculated using equations (5.1) and (5.2). If this energy exceeded the TDE, a knock-on event was identified and recorded in the database. The range of the incident beam energy for these simulations was between 30 and 300 keV, with a 30 keV energy interval. The number of incident electrons was set to 5000000, which was determined to be sufficient for reducing the statistical errors inherent to Monte Carlo as a stochastic simulation. Different sample thicknesses were investigated for each incident energy, beginning with 50 nm, then 100 to 500 nm with an interval of 100 nm. In order to replicate the simulation in a bulk material that encompasses the entire pear-shaped interaction volume, an additional simulation was performed for a thickness greater than the electron range.

## 5.4.2. Calculation of TDE

The most direct method for TDE calculation is ab-initio molecular dynamics [27,28]; however, the high computational cost of this method prevents it from modelling large supercells and reduces its efficiency [8,29]. Therefore, in this work, the static DFT calculation was applied within the sudden approximation approach [30] for calculating TDE. In this method, all the atoms except the knock-on atom are kept fixed at their initial position, while the knock-on atom is displaced towards

different directions. The potential energy barrier along the displacement trajectory then gives an approximate of TDE. It is worth noting that atomic displacement towards different directions leads to large variations in TDE. However, since our focus is to study the primary knock-on event and the onset of this radiation damage, the displacement direction with the lowest TDE value was considered.

All DFT calculations were performed with Quantum ESPRESSO code [31] using the PAW pseudopotential [32] and PBE-GGA exchange-correlation functional [33]. In all calculations, a large supercell was used to minimize the interaction of knock-on atoms between the periodic boundary images. For optimum kinetic energy cutoff, convergence tests were performed to ensure that the change of increasing cutoff energy is less than 1meV per atom. From convergence test, this optimal kinetic energy cutoff, was set between 380 and 630 eV, depending on the material type. For all materials, the lattice parameter and the atomic positions were fully relaxed until each component of forces acting on atoms was less than 0.025 eV/Å. In addition, the lattice was first relaxed to examine the stability of the Frenkel pair produced by the knock-on damage. When the knock-on atom did not recombine with its original position, this defect was regarded as stable, and then TDE for this stable Frenkel defect was calculated with sudden approximation. All the atomic visualizations in this paper were carried out using VESTA package [34].

The TDE of three sets of materials was investigated: 1) Pure elements including Li, Al, Cu, Pd, Mg, 2)  $Li_2MSiO_4$  (M = Co, Fe, Mn), and 3) LiX (X = F, Cl, Br). Details of each set of materials are further explained. Compared to pure elements, TDE of Li-containing materials is not widely available in the literature. Hence, the pure elements were additionally studied to compare with the available TDE in the literature and investigate the reliability of our TDE calculation method.

The pure elements investigated in this study have three distinct structures: 1) face centered cubic (FCC) for Al, Pd, and Cu, 2) body centered cubic (BCC) for Li, and 3) hexagonal closed packed (HCP) for Mg. These three structures are presented in Figure 5.1 with the octahedral positions depicted by the small red circles. The knock-on atom in these structures was displaced from its initial position, marked by the letter A in Figure 5.1, to the octahedral site that forms a stable Frenkel pair and is indicated by the letter B.



Figure 5.1. Schematic of knock-on displacement in a) FCC, b) BCC, and c) HCP structures. Small red circles represent the octahedral sites, and the large circles are the original atoms in the structure.

For Li<sub>2</sub>MSiO<sub>4</sub> materials with the Pmn2<sub>1</sub> space group symmetry, the knock-on lithium was displaced from its original site (indicated with a star symbol in Figure 5.2-a) to the octahedron formed by oxygen atoms (shown in gray in Figure 5.2-a) to create a stable Frenkel pair. In LiX materials with rocksalt structure, a stable Frenkel pair was generated by moving the knock-on lithium from its original site to the tetrahedral site coordinated by halide ions (Figure 5.2-b).

It should be noted that other than the final sites indicated in Figure 5.1 and Figure 5.2, there exist other interstitial sites that can produce a stable Frenkel defect by knock-on damage. However, the displacements to the final sites illustrated in these two figures belong to knock-on damages with the smallest TDE value, as our objective is to study the primary knock-on damage that leads to the onset of this damage. In addition, the TDE, especially in compounds, is not necessarily related to the straight line connecting the initial and the final position of the knock-on atom; rather, it can be deflected by its closest neighbouring atoms [35,36]. Therefore, the Climbing-Image

Nudge Elastic Band (CI-NEB) method [37] was implemented while fixing all the atoms except the knock-on atom to find an approximate to this deflected path of the knock-on atom.



Figure 5.2. Schematic of knock-on displacement in a)  $Li_2MSiO_4$  (M = Co, Fe, Mn), and b) LiX (X = F, Cl, Br). The knock-on atom is depicted with a star symbol, and the center of the tetrahedron and octahedron is indicated by a white circle.

# 5.5. Results and discussion

Knock-on displacements in different directions lead to different TDEs. In the case of pure Al, for instance, when the atom located at position A (illustrated in Figure 5.1-a) was displaced to position C, the displacement energy was 28.32 eV, whereas this value reduced to 22.17 eV when it was moved to position B. We selected the smallest TDEs for computing the  $P_{KOD}$  and for Monte Carlo simulation, as our research focuses on the primary knock-on event and the onset of this radiation damage. All the displacements explained in the Method section are related to the direction with the smallest TDEs, and their values for three sets of materials of interest are summarized in Table 5.1 and Table 5.2 and are shown with a bar chart in Figure 5.3.

Materials group	Symbol	Space group	TDE (eV)	
			This study	Reference
	Li	<i>I</i> 3 <i>m</i> 3 (BCC)	$4.33\pm0.30$	9 ± 7 [38], 5-10 [39]
	Al	Fm3m (FCC)	$22.17\pm0.30$	$16 \pm 3$ [38], $24 \pm 2$ [40]
Pure Element	Cu	Fm3m (FCC)	$32.43\pm0.30$	$20 \pm 4$ [38], 33 [41], 28-30 [42]
	Pd	Fm3m (FCC)	$45.24\pm0.30$	34 ± 7 [38], 41 [41]
	Mg	<i>P</i> 6 <sub>3</sub> / <i>mmc</i> (HCP)	$13.3\pm0.30$	10 ± 2 [38], 9.9-13.2 [43]

Table 5.1. TDEs of Pure elements found with the sudden approximation approach and from references

Table 5.2. TDEs of Li in Li-containing compounds found with the sudden approximation approach

Materials group	Formula	Space group	TDE of Li (eV)
	LiF		$7.90\pm0.30$
LiX	LiCl	$Fm\overline{3}m$ (rocksalt)	$4.76\pm0.30$
	LiBr		$4.19\pm0.30$
	Li <sub>2</sub> CoSiO <sub>4</sub>		$4.69\pm0.30$
Li <sub>2</sub> MSiO <sub>4</sub>	Li <sub>2</sub> FeSiO <sub>4</sub>	$Pmn2_1$	$4.97\pm0.30$
	Li <sub>2</sub> MnSiO <sub>4</sub>		$5.84\pm0.30$



Figure 5.3. TDEs of three sets of materials of interest. The TDE of Cu and Pd are not shown here to enhance the readability of the bar chart.

Since the accuracy of DFT-PBE method in predicting the energy-dependent material properties is around 0.3 eV [44], an error margin of 0.3 eV should be considered for the TDE values in Table 5.1 and Table 5.2. The TDEs of pure elements calculated with sudden approximation are close to the TDE range found for these elements in the literature (Table 5.1), demonstrating the validity of the sudden approximation approach in determining the TDEs. Also, previous studies [10,35,45] have demonstrated that the sudden approximation provides a good estimate to model the dynamic

events. This validity can be explained by the time scale at which the knock-on damage happens: The time required for the lattice relaxation is substantially longer than the time needed for knockon atom displacement, thus, the TDE found in a frozen lattice (i.e. sudden approximation approach) gives a reasonable estimate of this parameter [46,47]. In reality, however, neighbouring atoms react slightly to the motion of the knock-on atom, hence, lowering the threshold energy [8,46]. Therefore, the sudden approximation usually provides the upper limit of TDEs, which is also evident in Table 5.1 from comparing our computed TDEs with those from the literature.

In addition, the presence of defects like vacancies and boundaries could alter the value of TDEs as it depends on the local atomic environment. To investigate this effect for Al, one or two vacancies were created in the vicinity of the knock-on displacement as illustrated in Figure 5.4.a. In this figure, the two brown circles show the position of the vacancies. In the first simulation, only one of these brown circles was unoccupied, and in the second one, both were unoccupied to simulate the knock-on damage in the presence of one and two vacancies. As illustrated in Figure 5.4.b, the TDEs were reduced from 22.17 to 14.53 and 7.52 eV when one and two vacancies were created around the displacement path, respectively. This could be due to a more open structure after introducing the vacancy in the system. Similarly, the reduction of TDEs for knock-on displacement around the boundaries and surfaces (i.e., sputtering) is inevitable as less bond breakage and more open structures are available for knock-on damage [19]. Nevertheless, since the concentration of these defects is usually small relative to the number of atoms at the bulk, the TDEs calculated in the perfect structure were used in this study.



Figure 5.4. a) Schematic of knock-on displacement for Al in the presence of vacancies, and b) the energy profile of knock-on displacement with no vanacy, one vanacy, and two vanacies in the structure. The blue and brown circles depict the Al atoms and vacancy, respectively, and the small red circles show the position of interstitial sites.

For determining the TDE in Li-compounds, the CI-NEB method deflected the displacement of the knock-on atom to a curved path, and the TDE was found along this path in the frozen lattice. This deflection of knock-on displacement to a curved path was also reported in references for alloys [48] and LiAlO<sub>2</sub>[36]. Figure 5.5 depicts this curved path for the LiF along with its associated energy profile. We found that this remarkably improves the accuracy of the sudden approximation method. For example, in the case of LiX, when the Li knock-on ion was displaced in a straight line connecting the initial and final position, the displacement energies of 22.9, 21.22, and 21.01 eV were achieved for X= F, Cl and Br, respectively. These values are around five times larger than the range of 2-6 eV reported for TDE of alkali halides in reference [49]. On the other hand, when TDE was obtained along the curved path found by CI-NEB in the frozen lattice, the calculated TDEs were reduced to only 7.9, 4.76 and 4.19 eV for X= F, Cl and Br, respectively. That is, implementing the CI-NEB method in the sudden approximation approach brought the calculated TDEs of alkali halides into the reasonable range reported in [49]. This can be explained by the large potential field around the halide atoms that bulges the potential energy surface close to these atoms. Consequently, the knock-on Li atom deviates from the straight line to maximize its distance from the halide site, leading to a smaller barrier in the potential energy surface. In addition, it is worth noting that the trend of calculated TDEs in LiX materials confirms the expected relationship

between the TDE and the parameters affecting its magnitude: As all other parameters affecting the TDEs (i.e., structure, bond strength, displacement direction, and position of the displaced atom [7,8,20]) were the same in our DTF calculations for the three halides with the exception of bond strength, we expect this parameter to be the only contributor to the difference of TDEs in LiX materials. The bond strength is inversely proportional to the lattice parameter, which was calculated to be 4,00, 5,07, and 5,42 Å for LiF, LiCl, and LiBr, respectively, using DFT. This implies that the bond strength of the three alkali halides has the sequence of LiF > LiCl > LiBr. Since stronger bond strength leads to larger TDEs [50], the TDEs of these three materials should follow the same sequence, which is consistent with the trend we achieved (Table 5.2 and Figure 5.3) with the sudden approximation approach.



Figure 5.5. The energy profile and the curved path of knock-on displacement in LiF found with CI-NEB for the sudden approximation approach. The large green circles are Li and the small blue ones are F.

It is worth noting that all DFT calculations were conducted with a complete electronic configuration. However, the radiolysis process creates holes in the valence or inner atomic shells which may influence the calculated TDE. Therefore, the same simulation was repeated for LiCl with a hole created in the core-shell of the knock-on Li atom, causing the TDE to increase to 6.79 eV. On the other hand, when a core-hole was created in each Cl atom, the calculated TDE was reduced to 3.39 eV. This may be due to the modification of the columbic forces between the knock-on atom and its neighbours along the knock-on displacement path when the core-shell hole is created. However, the effect of radiolysis damage is primarily related to the persistence of the hole in the valence band rather than the core-shell. Particularly in non-conductive materials, the

electron-hole lifetime can be extended to microseconds or longer due to low electron concentration within the conduction band. In the meantime, some of the excited atom's energy can be converted to potential energy. This can alter the interatomic bonding and cause either bond rupture or atomic displacement [7,51], which is challenging to be incorporated into the knock-on damage simulation. This displacement may also create vacancy in the vicinity of the knock-on atoms which, as previously stated, can alter the value of TDEs. Therefore, further investigation is required to truly capture the radiolysis effect, and consequently, all the TDEs used in this work were determined in the absence of radiolysis damage. Nevertheless, the effect of radiolysis should be a greater concern at low electron energies as the radiolysis damage decreases by electron energies [52].

For the case of Li<sub>2</sub>MSiO<sub>4</sub>, the CI-NEB method again predicted that the knock-on Li atom should be deflected from the straight line connecting the initial and final position of the knock-on atom, however to the best of our knowledge, there are no TDEs available for these materials in the literature to make a similar analysis as the case of pure elements and LiX.

The  $P_{KOD}$  of three sets of materials was calculated by putting the elastic cross-section and the TDEs of Table 5.1 and Table 5.2 into equation (5.7). These damage probabilities as a function of energy for pure elements are presented in Figure 5.6 for the thickness of 50 nm. In this figure, the Pd and Cu plots do not appear as the threshold energy that leads to knock-on damage in these two materials is much higher than the energy range in which electron microscopes usually operate (i.e., 0 to 300 keV, which is used as the range of Figure 5.6).



Figure 5.6. The probability of knock-on damage,  $P_{KOD}$ , for pure elements with the thickness of 50 nm.

Our results show that the  $P_{KOD}$  initially increases with increasing electron energy, reaches a maximum and then decreases. In Figure 5.6, this behaviour is not observed for Al as the maximum is outside the energy range of this figure. As illustrated in Figure 5.6, a sharp maximum is observed at moderate energy for Li, whereas the maximum for the other two elements is reduced in magnitude and located at higher energies. This highlights the vulnerability of Li to knock-on damage due to its light nature. For pure Li, the maximum appears around 18 keV in the plot, indicating that at moderate electron energies at which scanning electron microscopes (SEM) usually operate, the knock-on damage is greatest in this element. To explain this distinct behaviour of Li, two competitive parameters should be investigated: the probability of elastic scattering,  $P_{El}$ , and the probability of minimum scattering angle leading to knock-on damage,  $P(\theta \ge \theta_{min})$ .  $P_{El}$ for thicknesses of 50 nm along with  $P(\theta \ge \theta_{min})$  are illustrated in Figure 5.7 for pure elements. Multiplying these two parameters yields the  $P_{KOD}$  given in Figure 5.6. In Figure 5.7,  $P_{El}$  of Li falls drastically with energy; hence, even though  $P(\theta \ge \theta_{min})$  increases monotonically, their multiplication produces a peak at low energies in Figure 5.6. This abrupt fall in  $P_{El}$  of Li results from a sharp decrease in the total elastic cross-section of Li with increasing energy. For Mg and Al, however, the decrease in the  $P_{El}$  is not as severe as Li, and therefore the product of these two parameters follows more the trend of  $P(\theta \ge \theta_{min})$ , so the peak appears at higher energies for these two materials.



Figure 5.7.  $P_{El}$  and  $P(\theta \ge \theta_{min})$  for the thickness of 50 nm.

This distinct behaviour of pure Li was also reported in [5] where the cross-section for knockon damage was calculated. In this article, Zhu et. al. found that a peak appears in the knock-on damage cross-section at around 18 keV which is in good agreement to what we reported here. This demonstrates the effectiveness of our straightforward theoretical model for predicting knock-on damage. In contrast, the existing equations for the damage cross-section are complex and do not account for some parameters that influence knock-on damage, including density, weight fraction, and thickness, which are particularly important for knock-on damage in compounds.

The behaviour of the Li compounds selected in this study was similar to the pure elemental Li. That is, a peak appears in the  $P_{KOD}$  of Li in LiX and Li<sub>2</sub>MSiO<sub>4</sub>, as shown in Figure 5.8.



Figure 5.8. The probability of Li knock-on damage,  $P_{KOD}$ , for a) LiX (X = F, Cl, Br) and b) Li<sub>2</sub>MSiO<sub>4</sub> (M = Co, Fe, Mn).

The curves in Figure 5.8 demonstrate that when the structures are identical, the TDE is the dominant parameter to compare the susceptibility to knock-on damage: The smaller the TDE, the greater the  $P_{KOD}$ . For example, in LiX materials, the TDE sequence is LiF > LiCl > LiBr, and the inverse trend is also persistent in the  $P_{KOD}$  shown in Figure 5.8-a. Comparing Figure 5.8-a and Figure 5.8-b, however, indicates that this approach could not be applied to materials with different structures. For instance, while Li<sub>2</sub>FeSiO<sub>4</sub> has a larger TDE than LiCl, it has a larger  $P_{KOD}$ . In addition, being the dominant parameter does not imply that the TDE is the only parameter to assess knock-on damage: examining the peak positions reveals that it could follow a different pattern than the TDE in materials. For example, the peaks in LiX materials appear at 35, 27, and 34 keV

for X = F, Cl and Br, respectively, which differs from the trend of TDEs in these materials as shown in Table 5.3. Therefore, other parameters affecting equation (5.7), including the elastic cross-section, the density of the material, the weight fraction, atomic weight and atomic number, should also play a part in the knock-on damage.

Materials group	Formula	Peak position (keV)	TDE of Li (eV)
Pure Element	Li	18	4.33
	LiF	35	7.90
LiX	LiCl	25	4.76
	LiBr	34	4.19
Li <sub>2</sub> MSiO <sub>4</sub>	Li <sub>2</sub> CoSiO <sub>4</sub>	31	4.69
	Li <sub>2</sub> FeSiO <sub>4</sub>	32	4.97
	Li <sub>2</sub> MnSiO <sub>4</sub>	35	5.84

**Table 5.3.** Peak position of  $P_{KOD}$  in Li and Li compounds

In addition to the TDE of Li, the TDE of other elements in each compound must be computed for the Monte Carlo simulation of Li compounds, as beam-electrons may collide with other elements in the materials and knock them out from their original position. Consequently, we calculated the TDE of other elements in the compounds by employing the same procedure explained for Li and tabulated the results in Table 5.4.

Materials group	Formula	Element	TDE (eV)
	LiF	F	$19.90\pm0.30$
LiX	LiCl	Cl	$9.50\pm0.30$
	LiBr	Br	$12.46\pm0.30$
	Li <sub>2</sub> CoSiO <sub>4</sub>	Со	$10.4\pm0.30$
		Si	$18.20\pm0.30$
		0	$10.7\pm0.30$
·	Li <sub>2</sub> FeSiO <sub>4</sub>	Fe	$9.5\pm0.30$
Li <sub>2</sub> MSiO <sub>4</sub>		Si	$17.80\pm0.30$
		0	$11.1\pm0.30$
	Li2MnSiO4	Mn	$14.6\pm0.30$
		Si	$19.2\pm0.30$
		0	$13\pm0.30$

Table 5.4. TDE of elements other than Li in the LiX and Li<sub>2</sub>MSiO<sub>4</sub>

The Monte Carlo simulation of knock-on damage in pure Li with the incident electron energy of 90 keV is shown in 3D together with the three principal 2D planes in Figure 5.9. In this figure,

the beam-electrons are depicted with blue lines, the backscattered electrons are shown in red lines, and the place where the knock-on event occurs is illustrated with little dots. In all Monte Carlo figures present in this work, the number of displayed electrons is far smaller than that of simulated electrons for improved visibility of knock-on events. Also, in the rest of this work, the results of the Monte Carlo simulation are illustrated only in 2D for better visualization purposes.



Figure 5.9. Monte Carlo simulation of knock-on damage in pure Li with the incident energy of 90 keV.

The threshold energy for knock-on damage in Al and Mg is large, and the Monte Carlo simulation of Al and Mg shows no knock-on events at 30 keV. Consequently, the results of the Monte Carlo simulations for the pure bulk materials (i.e., Li, Al, and Mg) were obtained utilizing a high energy of 270 keV, as shown in Figure 5.10. However, for Monte Carlo simulations of bulk LiX and Li<sub>2</sub>MSiO<sub>4</sub>, the plots, illustrated in Figure 5.11 and Figure 5.12, were obtained with a low energy of 30 keV.

The results of the Monte Carlo simulation of knock-on damage in pure elements (Figure 5.10) reveal that at this energy, Li has the highest number of knock-on damage and is thus the most vulnerable element. Mg becomes the second element susceptible to knock-on damage, whereas Al suffers the least amount of knock-on damage. This result is also consistent with our theoretical calculations, which demonstrate a similar trend in the sensitivity of these elements to knock-on damage, as illustrated in Figure 5.6.

In the Monte Carlo simulations of LiX and Li<sub>2</sub>MSiO<sub>4</sub> materials, as depicted in Figure 5.11 and Figure 5.12, respectively, only the green dots associated with Li knock-on damage are evident, indicating that other elements did not experience knock-on damage at 30 keV. To explain this, two parameters should be considered: the TDE and the mass of the elements. The lightweight and smaller TDE of Li compared to other elements in the compounds give a very low threshold collision energy required for the incident electron to cause knock-on damage, making Li the only element contributing to knock-on damage at this low energy. Nevertheless, Monte Carlo simulations at energies higher than the threshold collision energies demonstrate the presence of knock-on damage in elements other than Li. We discovered that, among the halides present in LiX materials, Cl is the most vulnerable due to its light weight and low TDE. Moreover, simulations of Li<sub>2</sub>MSiO<sub>4</sub> materials revealed that oxygen suffers the second-greatest amount of knock-on damage, behind Li, due to its low TDE and light weight. Figure 5.13 illustrates this by displaying the Monte Carlo simulation of Li<sub>2</sub>FeSiO<sub>4</sub> at 210 keV, as an example.

The consistency between Monte Carlo simulation and theoretical calculation also exists in LiX and Li<sub>2</sub>MSiO<sub>4</sub>. As is evident in Figure 5.11 for LiX materials, the number of knock-on damages for Li increases from LiF to LiCl to LiBr in ascending order. This was also predicted by our theoretical calculation shown in Figure 5.8-a. Likewise, as illustrated in Figure 5.12 for Li<sub>2</sub>MSiO<sub>4</sub> materials, the number of knock-on damages for Li follows the same sequence as our theoretical calculations given in Figure 5.8-b: Li<sub>2</sub>CoSiO<sub>4</sub> > Li<sub>2</sub>FeSiO<sub>4</sub> > Li<sub>2</sub>MnSiO<sub>4</sub>. Interestingly, the TDEs of these materials exhibit the same patterns. This leads to the same conclusion as the theoretical calculation, which is that the TDE should be used as the primary metric to compare the Li susceptibility to knock-on damage between identical structures.



Figure 5.10. Monte Carlo simulation of knock-on damage at 270 keV in a) Al, b) Mg, and c) Li.



Figure 5.11. Monte Carlo simulation of knock-on damage at 30 keV in a) LiF, b) LiCl, and c) LiBr.



Figure 5.12. Monte Carlo simulation of knock-on damage at 30 keV in a)  $Li_2CoSiO_4$ , b)  $Li_2FeSiO_4$ , and c)  $Li_2MnSiO_4$ .



Figure 5.13. Monte Carlo simulation of knock-on damage at 210 keV in Li<sub>2</sub>FeSiO<sub>4</sub>

Quantitative comparisons were performed to examine further the difference between the Monte Carlo simulation and the theoretical calculation. For this purpose, we computed the number of knock-on damages by multiplying the  $P_{KOD}$  by the total number of collisions at each energy and thickness and then compared this to the number of knock-on damages directly found from the Monte Carlo simulation. This result is shown in Figure 5.14 for the Li-containing materials at the energy of 300 keV.



Figure 5.14. Number of knock-on damages for Li found by Monte Carlo simulation and theoretical calculation at 300 keV as a function of thickness in Li-containing materials.

The number of knock-on damages calculated by simulation and theoretical calculation diverges as thickness grows. This implies that our theoretical method offers better predictability for thinner thicknesses than for thicker ones. Notably, the same comparison at energies other than 300 keV also produced the same result. This can be explained by the fact that as the beam-electrons penetrate into the materials, they lose energy during scattering events and thus, the energy of beam-electrons does not preserve in the entire interaction volume. For instance, we determined the average energy of electrons at each depth for LiF at the incident energy of 30 keV by Monte Carlo simulation using CASINO v2.5. As demonstrated in Figure 5.15-a and b, the energy of the beam-electrons in the interaction volume is comparable to the incident energy at shallow depths. Therefore, integrating the incident energy into the theoretical calculation yields close approximations of the simulation results for thin layers. However, as the thickness increases, the energy of the beam-electrons deviates further from the initial energy within the interaction volume, causing simulation and theoretical calculation results to diverge (Figure 5.14).



Figure 5.15. Results of Monte Carlo simulation for LiF using the incident energy of 30 keV: a) Energy distribution of beam-electrons and b) the average energy of beam-electrons at each depth. The legend in the upper figure shows the percentages of the initial energy at each boundary.

Figure 5.15 also gives valuable information regarding the beam-electron energy: the mean energy over the penetration depth (i.e., 17 keV) is approximately half of the incident energy, and similar analysis for different incident energies and materials led to the same conclusion. Considering this, for all the Li compounds, the number of knock-on damages found by the Monte Carlo simulation was therefore divided by the electron range, and they were then plotted as a function of the mean energy in Figure 5.16. This figure also includes the  $P_{KOD}$  determined by our theoretical calculation at the thickness of 50 nm, which is the most accurate one based on Figure 5.14. As seen in Figure 5.16, according to Monte Carlo simulations, the highest knock-on damage of Li in these compounds occurs at intermediate energies between 30 and 45 keV, and the

theoretical calculations predict the same within the energy range between 27 and 35 keV. In other words, the Monte Carlo simulation supports our theoretical prediction of the maximum beam damage at moderate energies.



Figure 5.16. Number of knock-on damages per electron range (simulation) as a function of the mean energy of beam-electrons, together with the probability of knock-on damage,  $P_{KOD}$  (theory).

## 5.6. Conclusion

In this study, the primary knock-on damage and its contributing parameters were investigated. For this purpose, the TDEs of three sets of materials, including pure elements, LiX (X=F, Cl, Br), and LiMSiO4 (M = Fe, Co, Mn), were determined by sudden approximation approach within the DFT calculation. It was found that the accuracy of estimated TDEs could be enhanced by including the CI-NEB method into the sudden approximation method. The probability of knock-on damage,  $P_{KOD}$ , was determined with theoretical calculations. These calculations indicated that at moderate electron energies, the  $P_{KOD}$  for Li in both its elemental and compound forms reach to its maximum value at moderate energies. It was speculated that this peculiar behavior of Li was due to the rapid decrease in the elastic cross-section of this element with increasing energy. A Monte Carlo code was developed to further analyse the knock-on damage. It was found that at low energies, Li is the only element in the compounds that contributes to the knock-on damage due to its low weight and small TDE. Both simulation and theoretical calculations suggested that TDE should be the primary

metric for comparing the Li sensitivity to knock-on damage amongst identical structures. This could not, however, be generalized to materials with different structures, indicating that other parameters, including cross-section, density, weight fraction, atomic weight, and atomic number, also affect knock-on damage. Simulation and theoretical calculations showed the proximity of the number of knock-on damages for Li compounds in thin thicknesses. The divergence between simulation and theory increased by increasing the thickness which could be attributed to the energy loss of beam-electrons during scattering events. Considering this energy loss, it was demonstrated that the Monte Carlo simulation similarly validates the maximization of knock-on damage at moderate energies by calculating the total number of knock-on damages per electron range.

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## 5.8. Appendix

A relation was derived for the probability of having a scattering angle larger than a minimum angle that causes the knock-on damage. For the probability of an electron scatters at an angle between 0 and  $\theta_{\min}$ ,  $P(0 < \theta < \theta_{\min})$ , a simpler notation,  $R^*$ , was used to shorten the formulas. This probability is given by [24]:

$$R^* = \frac{\int_0^{\theta_{\min}} \frac{d\sigma}{d\Omega} \sin\theta \, d\theta}{\int_0^{\pi} \frac{d\sigma}{d\Omega} \sin\theta \, d\theta}$$
(A.1)

Putting partial Rutherford cross section into the above equation gives the following equation for the evaluation of  $\theta_{\min}$ :

$$\cos\theta_{min} = 1 - \frac{2\delta R^*}{1 + \delta - R^*} \tag{A.2}$$

where  $\delta = \frac{1}{4}\theta_0^2$ . Using the Taylor series of cosine simplifies the above equation into [21]:

$$\theta_{min} = \sqrt{\frac{R^*}{1 - R^*}} \tag{A.3}$$

, which can be rearrange for the  $R^*$  as:

$$R^* = \frac{\left(\frac{\theta_{min}}{\theta_0}\right)^2}{1 + \left(\frac{\theta_{min}}{\theta_0}\right)^2} \tag{A.4}$$

Therefore, the probability of having scattering angle larger than  $\theta_{\min}$  which leads to knock-on damage is given by this relation:

$$P(\theta \ge \theta_{min}) = 1 - R^* = \frac{1}{1 + \left(\frac{\theta_{min}}{\theta_0}\right)^2}$$
(A.5)

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# 6. Chapter 6. General Discussion

The growing concern over climate change has led to increased attention to LIBs for the energy transition from fossil fuels to sustainable energy resources. As the properties of critical LIB components determine the efficiency of these batteries, advancement in the field is linked to the study of component properties [1-3]. The Li transport property exhibited by battery materials is of significant importance, especially in high-power applications [4–6]. Furthermore, the acquisition of chemical and structural properties of battery materials using electron microscopes is both crucial and difficult [7–12], given the susceptibility of these materials to beam damage, particularly knock-on damage [13,14]. In chapter 3. the Li diffusivity in NMC as one of the promising cathode materials was investigated. In addition, chapter 4. explored the behaviour of Li diffusion in Li<sub>2</sub>O as one of the key components of LIBs. These two chapters offered an atomiclevel perspective on Li diffusion in these materials for the development of these batteries for highpower applications. In chapter 5., the knock-on damage induced during the electron microscopy characterization of battery material was examined to identify the influencing factors and quantify the damage. This provides insight into the most effective strategy for mitigating this damage. The following sections provide an extended discussion to the findings, existing limitations, and potential future directions of this thesis.

# 6.1. Effect of correlation factor in diffusivity

The concentration dependence of the diffusion coefficient is not solely influenced by jump barrier energies and the availability of vacancy clusters. Additionally, the diffusivity is significantly impacted by the efficacy at which vacancy migration re-distributes Li ions across the crystal. In the vacancy-mediated mechanism, for instance, the vacancy is temporarily available adjacent to the diffusing atom immediately following the exchange, thereby increasing the probability that the atom will undergo a reverse jump. The correlation factor, f, which quantifies the deviation of the tracer diffusion coefficient,  $D^*$ , from what it would be if all subsequent Lihops were uncorrelated (i.e., random walk), is a practical metric for assessing the efficacy of diffusion. The correlation factor equals one in the absence of correlation in diffusion and decreases as the correlation between the jumps increases [15,16]. Thus, the ratio of correlated and uncorrelated motion of atoms gives the correlation factor [17]:

$$f = \lim_{n \to \infty} \frac{\langle R^2 \rangle}{\langle R_{Random}^2 \rangle}$$
(6.1)

where R is the total displacement of atoms after a large number of jumps. The correlation factor for interstitial diffusers (in extremely diluted interstitial alloys) is one, while it is less than one for defect-mediated diffusion. The correlation factor becomes a critical parameter in alloys having components with significantly different jump frequencies. However, it still offers valuable insight into diffusion mechanisms and the concentration dependence of diffusion coefficients.

We studied this effect in LCO and NMC111 using KMC simulation and plotted f as a function of Li concentration in Figure 6.1. In the case of intercalation compounds, the correlation between successive hops of the sparsely distributed Li ions approaches unity, indicating that the hops are essentially uncorrelated. In contrast, as Li concentration approaches one and the number of vacancies significantly diminishes, correlations between consecutive Li hops become substantial. In addition, at diluted Li concentration (i.e., less than 0.5), the correlation factor in NMC111 is much smaller than LCO indicating a higher correlation in this material. This may be the result of the presence of three transition metals in the structure, which hinders Li redistribution by rendering the barrier energy a highly site-dependent parameter. In both cases, the correlation factor decreases significantly with the addition of Li, indicating that vacancy clusters are ineffective in distributing Li ions within the crystal. Previous studies also revealed a similar behaviour of correlation effect in the intercalation compound [15,16]. This signifies the importance of having an atomistic point of view on diffusion to reveal the underlying physics affecting the diffusivity in the battery materials.


Figure 6.1. Correlation factor determined using KMC simulation at each Li concentration in a) LCO and b) NMC111 (scaled).

## 6.2. Effect of defects in diffusivity

The influence of defects on the material properties is inevitable and this is not excepted from the transport properties. For NMC111, a perfect crystal was considered in chapter 3., however, defects may already exist or may be introduced in the structure during battery cycling. In chapter 4. , we studied the influence of the Frenkel pair defect in the diffusivity behaviour of Li in  $Li_2O$ . Even though this is the dominant defect in the structure, the other types of defects may still have an impact on the diffusivity. Both cases will be discussed in the following.

In NMC, an abrupt increase in the dissolution of transition metals was reported after the potential of 4.5 V. The dissolution rate for Mn was found to be higher than Ni and Co above this potential [18]. In addition, Concerning cation mixing (i.e., antisite defect), the presence of Ni ions in the Li layer of NCM cathodes may obstruct the Li diffusion pathway, thereby potentially affecting the power performance [19–22]. These structural changes due to defect formation may even extend to a larger scale. Lin et al. [23] indicated that electrolyte exposure causes surface reconstruction of NCM material which further progresses with battery cycling. The surface of this material is composed of a layer  $R\bar{3}m$  structure and cubic rock-salt  $Fm\bar{3}m$  after being exposed to the electrolyte. Therefore, our KMC simulations of NMC should be interpreted with caution, especially when the battery operates for a large number of cycles and/or is charged to high potential.

In NMC111, four models are usually suggested for the ordering of transition metals including random,  $\left[\sqrt{3} \times \sqrt{3}\right] 30^\circ$  - type superlattice, parallel, and zigzag [24], as shown in Figure 6.2. The nuclear magnetic resonance (NMR) results from Cahill et. al. [25] suggested a non-random distribution of transition metals and proposed a local ordering that fits the  $\left[\sqrt{3} \times \sqrt{3}\right] 30^\circ$  - type superlattice. DFT calculations also predicted that this configuration would have the least energy [26,27]. For the study of Li diffusivity in chapter 3. , we also utilized this arrangement in all simulations. However, this ordering is significantly affected by the material synthesis under realistic conditions and by antisite defect production during battery cycling [27]. Zeng et. al. showed that the arrangement of the transition metals fits two models. The Neutron diffraction and pair distribution function (PDF) analysis revealed an arrangement close to  $\left[\sqrt{3} \times \sqrt{3}\right] 30^\circ$  - type superlattice, however, the number of Ni-Co, Co-Co, and Mn-Co pairs resembles a random structure. Nonetheless, they indicated a non-random distribution of transition metals across the whole transition metal layer and suggested local ordering of these metals. Therefore, our approach should be implemented with caution considering this variation in the structure.



Figure 6.2. Schematic of transition metal layer ordered in a)  $\left[\sqrt{3} \times \sqrt{3}\right] 30^\circ$  - type superlattice b) parallel, and c) zigzag arrangements [24].

In Li<sub>2</sub>O, the second dominant defect in the structure after the Frenkel pair is the Schottky as its formation energy is double that of the Frenkel defect [28]. In chapter 4., we only considered the Frenkel pair defect. While the contribution of Schottky to the ionic conductivity could be negligible due to its low concentration, it may affect the approximate recombination distance that was used to assess the recombination of Frenkel pairs. Therefore, future investigation may incorporate the effect of the Schottky defect in the study of Li diffusivity in Li<sub>2</sub>O to further enhance the calculation. It is worth noting that heteroatom doping was proposed for enhancing the diffusivity [29], consequently, the incorporation of doping into our algorithm will give it an exceptionally effective tool for designing an SEI layer with superionic behaviour.

Finally, we should emphasize that Li transport ultimately passes the continuum level. Therefore, larger-scale defects including grain boundaries, interfaces, cracks and also diffusivity within the cracks and porous medium in between the secondary particles should be investigated. For instance, Ma et al [30] showed that the LiF/Li<sub>2</sub>O interface provides a high diffusivity path in the SEI layer and enhances the Li transport. Thus, these larger-scale defects should be the concern of future work for improving the power capability of LIBs.

## 6.3. Knock-on damage of elements other than Li

The focus of chapter 5. was to investigate the knock-on damage of Li in battery materials. However, knock-on damage in other elements is also crucial for accurate electron microscopy characterization as displacement of other elements could ultimately lead to the reconstruction of the whole crystal structure and in severe cases may create holes in the sample. However, the damage associated with elements other than Li is usually more of a concern at TEM where high electron beam energies are usually used. The Monte Carlo simulations of knock-on damage at the high incident beam energy of 210 keV for LiX are illustrated in Figure 6.4. The same simulations were repeated for Li<sub>2</sub>MSiO<sub>4</sub> using the incident beam energy of 240 keV (illustrated in Figure 6.4).

In the LiX materials (Figure 6.3), the number of knock-on damages for Cl was larger than F while no knock-on damage occurred for Br. The TDE of these elements in Table 5.4 of Chapter 5. showed the trend of F > Br > Cl. Interestingly, the Br element showing no knock-on damage has a smaller TDE than the F. If TDE was supposed to be the sole parameter affecting the knock-on damage, then we would expect Br to have larger knock-on damage than F, however, the opposite is revealed in our simulation. This could be due to the greater atomic weight of Br than F, leading to smaller transferred energy to the nucleus. On the other hand, Cl which has a smaller TDE but larger weight than F, showed the largest amount of knock-on damage. Therefore, competition exists between different parameters affecting the knock-on damage to ultimately determine which material is more sensitive to the knock-on damage.

In the Li<sub>2</sub>MSiO<sub>4</sub> materials (Figure 6.4), the number of knock-on damages for Fe is larger than Co, whereas Mn did not experience any knock-on damage. Due to the extremely similar atomic weights of Fe, Co, and Mn, TDE should be the primary variable affecting the number of knock-on damages. Referring to Table 5.4 of Chapter 5. , the TDE of these elements has the sequence of Mn > Co > Fe, which resembles the reverse trend of the number of knock-on damages observed in Figure 6.4. For Si and O that exist in all three Li<sub>2</sub>MSiO<sub>4</sub> compounds, the TDE was found to effectively change the number of knock-on damages. This damage for Si and O was found to be smaller in Li<sub>2</sub>MnSiO<sub>4</sub> than the other two compounds due to the larger TDE of O and Si. Therefore, even in the identical structure, not only the TDE but also the atomic weight of elements impacts knock-on damage.



Figure 6.3. Monte Carlo simulation of knock-on damage at 210 keV in a) LiF, b) LiCl, and c) LiBr. The small circles show the position of knock-on damage for each element.



Figure 6.4. Monte Carlo simulation of knock-on damage at 240 keV in a) Li2CoSiO4, b) Li2FeSiO4, and c) Li2MnSiO4. The small circles show the position of knock-on damage for each element.

## 6.4. Effective strategies for reducing the beam damage

Chapter 5. investigated the knock-on damage in Li-containing materials. While these materials are highly susceptible to this damage, other types of damage may also be induced during the electron microscopy characterization. Therefore, the other beam damages should be incorporated into strategies for reducing beam damage in battery material.

Radiolysis damage from the inelastic scattering could also significantly contribute to the structural changes and prevent accurate electron microscopy characterization. In particular, the defect accumulation through thermally activated processes after the bond breakage further misinterprets the results. Therefore, the most effective strategy to prevent this damage is through the temperature drop to slow down the kinetics [11,31,32].

Sputtering, which is a special kind of knock-on damage when the atom is sputtered out the surfaces, could be reduced through the coating of the surface using a suitable material. The coating should be very thin to reduce extra scattering leading to decreased contrast. In addition, it should be a material with high atomic weight to have a larger threshold energy and become permanent. Finally, it should be amorphous to prevent artifacts in the electron microscopy characterization [33]. Previous studies found that the tungsten and carbonaceous coating could be effective in reducing this damage [34,35].

The most effective strategy to avoid knock-on damage is to operate the microscope below the threshold beam energy that causes this damage. Since this threshold is very low in battery materials, this might not be practical as operating the microscope at this beam energy reduces the quality of characterization by introducing large noises. The other strategy that we discovered in this thesis, is to avoid the moderate voltage that maximizes the knock-on damage in battery materials (between 20 to 35 keV depending on the type of Li-containing materials). In addition, since the sample thickness changes the average beam electron energies inside the specimen and also changes the specimen-electron interaction volume size, an optimized thickness may be used to reduce this damage. The Monte Carlo simulations using the incident beam energy of 30 keV in LiF at different thicknesses are shown in Figure 6.5.



Figure 6.5. Monte Carlo simulation of knock-on damage at the beam energy of 30 keV in LiF with thicknesses of 100, 8000, 30000, and 5000 nm. The red circles depict the position of knock-on damage. The dark blue lines are transmitted electrons, the red lines are the backscattered electrons and the light blue lines are the scattered electrons in the sample.

Figure 6.5 clearly shows that by increasing the thickness, the number of knock-on damage increases. This can be explained by the change in the size of the interaction volume. As the thickness increases, the number of collisions also increases which increases the chance of having knock-on damage. In addition, at very large thicknesses, the change in the average beam energy could also significantly get further away from the energy that maximizes the knock-on damage, reducing the beam damage. Therefore, there is an optimized thickness and voltage that might be used to reduce knock-on damage.

The other two types of beam damage including heating and charging should be discussed. While these two damages may not be a concern for electrodes, they could be significant in high dose rates or in sensitive materials like electrolytes or other polymer-based battery materials [36]. While there are convenient strategies for reducing these damages like conductive coating, variable pressure mode operation of microscope, dose control, and cryo-technique [37], an in-depth understanding of these damages could be the concept of future works towards facilitating a damage-free electron microscopy characterization.

Finally, an effective approach to reduce beam damage involves the implementation of a characterized dose  $D_c$  [38]. Electron dose is generally defined as the charge density (C/m<sup>2</sup>) or the energy deposited per unit mass of the material. However, the characterized dose  $D_c$  is defined as an electron dose at which a measured material property (e.g. core loss or fine structure peaks in electron energy loss spectroscopy (EELS), mass loss or diffraction pattern fading) drops to 1/e = 37% of its initial value. The number of signals collected from the unit area of the specimen is proportional to the electron dose. Hence, if one finds a working condition of an electron microscope in which  $D_c$  is higher, the material characterization process becomes more accurate under less beam-induced damage.

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# 7. Chapter 7. Synopsis

This final chapter presents the conclusions derived from the investigations, which are then followed by contributions to the knowledge and recommendations for future research.

## 7.1. Conclusion

In this thesis, Li transport and beam damage in battery materials were comprehensively studied by multiscale computational approaches to reveal the factors affecting them and provide an atomistic point of view to these phenomena. The principal findings are summarized below:

- During Li diffusion in NMC111, KMC simulations revealed that in the TSH mechanism (i.e., the dominant diffusion mechanism determined by DFT), the Li hops were performed mostly through the tetrahedral sites under which the Mn is occupied. However, at the intermediate and high Li concentrations, the site beneath the tetrahedral site is occupied by Co and Ni, respectively.
- 2. GCMC simulation in NMC111 showed that the thermodynamic factor was substantially decreased at the Li concentration of 0.8 due to a perfect honeycomb-like ordering of Li ions in the Li layer. This decrease in the thermodynamic factor was reflected in the chemical diffusion coefficient reaching its minimum at the Li concentration of 0.8. Consequently, across all Li concentrations, the chemical diffusion coefficient determined by KMC simulations varied significantly, spanning from  $5.6 \times 10^{-13} \text{ cm}^2/\text{s}$  to  $1.2 \times 10^{-11} \text{ cm}^2/\text{s}$ .
- 3. CMC simulations at Li concentrations of 0.2 and 0.3 in NMC111, respectively, identified a parallelogrammatic and triangular partial ordering of Li ions in the Li layer of NMC111. These partial orderings potentially account for fluctuations in the thermodynamic factor within this concentration range which consequently leads to fluctuation in diffusion coefficient.
- 4. DFT calculations showed that a change of vacancy configurations on the local atomic environment of the diffusing Li ion could change the  $\Delta E_{KRA}$  drastically from 0.06 eV to

0.44 eV. The local cluster expansion model could accurately capture this local environmental dependency of barrier energies.

- 5. DFT calculations in Li<sub>2</sub>O indicated that the barrier energy associated with the vacancymediated hop in the (100) direction is the lowest when compared to the barrier energy associated with the collective diffusion mechanisms and the vacancy-mediated jumps in the (110) and (111) directions. Therefore, the other mechanisms may occur more frequently at high temperatures, where thermal fluctuations are sufficient to surmount their high barrier energies.
- 6. By integrating the recombination of Frenkel pairs into the KMC algorithm using an approximation of the recombination distance, it was observed that the diffusivity values of Li in Li<sub>2</sub>O were more closely correlated with experimental measurements and MD simulations reported in other studies. By integrating the recombination effect into the KMC simulation, the diffusivity of lithium at 300 K was determined to be  $3.8 \times 10^{-12} \text{ cm}^2/\text{s}$ .
- 7. In the study of beam damage, it was found that the accuracy of estimated TDEs could be enhanced remarkably by including the CI-NEB method in the sudden approximation method. The TDE value for elemental Li was determined to be 4.33 eV, whereas it varied between 4.19 and 7.9 eV for the compounds. The calculations also revealed the dependency of TDE calculations on the electronic and atomic configuration around the knock-on atom.
- 8. Both theoretical calculations and MC simulations indicated that the knock-on damage reaches its maximum value at moderate electron energies for Li in both its elemental and compound forms. It was suggested that the rapid reduction in the elastic cross-section of Li as its energy increased was the cause of this peculiar behavior.
- 9. Based on the results of both theoretical calculations and MC simulations, it was found that the primary metric used to compare the susceptibility of identical structures to knock-on damage should be TDE. However, it is important to note that this finding does not apply to materials with distinct structures, rather the knock-on damage was

influenced by other parameters such as cross-section, density, weight fraction, atomic weight, and atomic number.

# 7.2. Contribution to the knowledge

- 1. For the first time, the specific ordering of Li ions in the Li layer of NMC111 was revealed at different Li concentrations.
- The reason for the sudden drop of Li diffusivity at the Li concentration of 0.8 in NMC111 was explained for the first time.
- The local cluster expansion was constructed using a 3D framework to capture the dependency of barrier energies on the local atomic environment in Li<sub>2</sub>O for the first time.
- 4. The recombination of Frenkel pairs was integrated for the first time into the KMC simulation of Li<sub>2</sub>O to investigate the Li transport behaviour of Li in this material.
- 5. The CI-NEB method was coupled with the sudden approximation method for the first time to calculate the TDE.
- 6. For the first time, the MC simulation using a single scattering approach was used to quantify knock-on damage in battery materials and investigate the influencing factors in this damage.
- 7. The multiscale computational approach paved a new path to enhance the properties of battery materials for the development of energy storage devices.

# 7.3. Future work

For further research, the subsequent recommendations are proposed:

 Incorporating the effect of transition metal ordering or antisite defect in the study of Li transport in NMC could be a subject of future work as these parameters may better capture the underlying physics and enhance the results.

- 2. The effect of other point defects in the Li<sub>2</sub>O on the Li transport behaviour may be the subject of future work. Also, it is necessary to investigate the contribution of interfaces between the components of the SEI layer as these high diffusivity paths may alter the ionic conductivity at a larger length scale perspective.
- 3. The effect of radiolysis damage in battery materials is a necessary future work as this damage could also misinterpret the results of electron microscopy characterization, especially at low electron beam energies and in materials with small electric conductivity.