# GENERALIZED HOMOGENIZATION THEORY AND ITS APPLICATION TO POROUS RECHARGEABLE LITHIUM-ION BATTERIES

A Dissertation

Submitted to the Faculty

of

Purdue University

by

Juan Alfonso Campos

In Partial Fulfillment of the

Requirements for the Degree

of

Doctor of Philosophy

August 2020

Purdue University

West Lafayette, Indiana

# THE PURDUE UNIVERSITY GRADUATE SCHOOL STATEMENT OF DISSERTATION APPROVAL

Dr. R. Edwin García, Chair

School of Materials Engineering

Dr. Ilenia Battiato

Energy Resources Engineering Department, Stanford University

Dr. Eric Kvam

School of Materials Engineering

Dr. Bedrich Benes

Computer Graphics Technology Department

## Approved by:

Dr. David Bahr

Head of the School Graduate Program

In loving memory to Juan Campos Carrillo

## ACKNOWLEDGMENTS

First, my recognition to CONACYT (Consejo Nacional de Ciencia y Tecnología) for the financial support provided to pursue my PhD degree.

Foremost, I would like to thank my advisor, Prof. R. Edwin García for his support, insightful discussions, and for making my PhD journey a successful experience.

I would like to express my gratitude to my committee members, Prof. Ilenia Battiato, Prof. Eric Kvam, and Prof. Bedrich Benes, for very helpful discussions and great suggestions to improve my dissertation.

I would also like to thank Dr. J. Asunción Zárate and Dr. Alex Elías for their endorsement and uninterested help and motivation, and to my group members, Dr. Aniruddha Jana, Dr. Vikrant Karras, Dr. Alfredo Sanjuan, Luke, Jarrod, and Surya for their friendship and collaboration.

Finally, I would like to express my deepest and greatest thanks to my parents Juan Campos and Ma.Cruz Gómez, my siblings Diana, Saúl, Karen, Claudia, and Karol, for their love and encouragement, and to my wife Priscilla Reynaud and my son Juan Gerardo for being supportive through the difficult times.

## TABLE OF CONTENTS

Page
LIST OF TABLES
LIST OF FIGURES
SYMBOLS
ABBREVIATIONS
ABSTRACT
CHAPTER 1. INTRODUCTION       1         1.1       Energy Storage Technology Applications       1         1.2       Rechargeable Battery Fundamentals       1         1.3       Transport Properties in Porous Electrodes       3         1.4       Overview of the Thesis       5
CHAPTER 2. MICROSTRUCTURAL LIMITS AND EXTENSIONS OF POROUSELECTRODE THEORY72.1 Introduction72.2 Theoretical Framework122.3 Implementation for Example Chemistries and Porous Microstructures202.4 Results and Discussion212.5 Summary and Conclusions30
CHAPTER 3. COARSE-GRAINED ELECTROCHEMOMECHANICAL EF- FECTS IN POROUS RECHARGEABLE LITHIUM-ION BATTERIES 31 3.1 Introduction
CHAPTER 4. FUTURE WORK
APPENDIX A. HOMOGENIZATION METHODOLOGY
APPENDIX C. ELECTROCHEMICAL DATA 72
APPENDIX D. CHARACTERISTIC TIME SCALES

## Page

APPENDIX E. NMC CHEMICAL STRAIN	75
APPENDIX F. ELECTRICAL AND MECHANICAL PROPERTIES	76
REFERENCES	77
VITA	84

## LIST OF TABLES

Tab	le	Page
1.1	Typical materials for rechargeable battery components, [10]	. 3
2.1	Summary of relations between spatially-resolved, volume-averaged and upscaled-homogenized terms. Relations used to develop different coarse- grained representations are also highlighted, noting that the upscaling process requires specific relations in addition to the averaging technique.	. 11
2.2	Macroscale parameters, solid particle size and electrode size; as reported in the literature for the different Li-ion chemistries [28–30, 39, 75–80]. These values are used to calculate the transport numbers as listed in the Table I	3.1.21
3.1	Physical parameters used in the coarsed-grained model [27–29, 68, 94–97]. The free energy definitions as well as equilibrium potentials for NMC, Graphite and EC:DMC electrolyte, can be found in the Appendix C.	. 40
B.1	Estimated values of transport numbers at the electrolyte phase and at the solid electrode particle for different chemistries. The first section (columns 2 to 8) presents the microstructural dependent transport numbers. Transport numbers dependent only on the chemistry are given in the second section (columns 9 to 15).	. 72

## LIST OF FIGURES

Figu	Page
1.1	Schematic of charged ions trajectories during cell discharge. The opposite flow occur while charging. The scheme also shows the basic elements of the dual insertion cell. Taken from Ref. [12]
1.2	Break-down of the multiple phases conforming the composite porous elec- trode. Volume fraction of the electrolyte in commercially available cathode materials is the range of 30 - 40%. Taken from Ref. [13]
2.1	Effect of the microstructure on the model validity for Li-ion transport in the electrolyte phase as a function of Péclet and Damköhler num- bers. Open symbols represent microstructure free chemistries: $\triangleright$ LiC <sub>6</sub> , $\triangle$ LiFePO <sub>4</sub> , $\bigcirc$ LiMn <sub>2</sub> O <sub>4</sub> , $\Box$ Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> , $\diamondsuit$ LiNi <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub> , $\rightleftharpoons$ LiNi <sub>0.8</sub> Co <sub>0.2-x</sub> Al <sub>x</sub> O <sub>2</sub> , $\nabla$ LiCoO <sub>2</sub> . Filled symbols describe the effect of microstructure: $\blacktriangleright$ LiC <sub>6</sub> , $\triangle$ LiFePO <sub>4</sub> , $\bigoplus$ LiMn <sub>2</sub> O <sub>4</sub> , $\blacksquare$ Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> , $\bigstar$ LiNi <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub> , $\bigstar$ LiNi <sub>0.8</sub> Co <sub>0.2-x</sub> Al <sub>x</sub> O <sub>2</sub> , $\nabla$ LiCoO <sub>2</sub> . The shaded-region above the diagonal line corresponds to the regime where Newman-type models are valid. Model predicts that New- man approaches will only be valid when diffusion dominates over reaction and the electromigration processes
2.2	Regions of validity as a function of porosity in the electrolyte and sec- ondary particle aspect ratio for LiMn <sub>2</sub> O <sub>4</sub> -based battery electrodes correspond to constant values of electrode porosity as particle aspect ratio change values, $0.1 \le c/a \le 10$ correspond to constant values of particle aspect ratio for electrode porosity moving in the range $0.1 \le \epsilon \le 1$ . ( $\blacktriangleright$ , $\blacktriangle$ , $\bigcirc$ , $\blacksquare$ , $\bigstar$ , $\bigstar$ , $\checkmark$ ) correspond to different tailored microstructures of LiMn <sub>2</sub> O <sub>4</sub> -based battery electrodes. The shaded-region corresponds to the validity regime. Inset (a) demonstrates that intercalation reaction is slower than electromigration for electrodes with $\epsilon_e \ge 0.3$ and $c/a \ge 1$ . Inset (b) reveals that the intercalation reaction is slower than diffusion except for $\epsilon_e < 0.3$ and $c/a \le 0.3$ . Aspect ratio isocontours asymptoti- cally collapse into a vertical green line I as the porosity, $\epsilon$ , approximates 1. Aspect ratios, $c/a > 1$ generate overlapping curves

#### Figure

- Regions of validity for Newman-type model of  $LiMn_2O_4$ . corresponds to 2.4maximal random packing of ellipsoids as reported by Torquato et al. [84]. Validity of the homogenized Newman-type model corresponds to the region above the blue line  $\_$ . For inset (i), the blue line represent  $Da_{\mu} = Pe_{\mu}$ , while for inset (ii) represents  $Da_{\mu}Fo = Fo_{\mu}$ . Four regimes of behavior are observed: Regime (a), where the Newman-type model simulation would be inaccurate, even for physically accessible particle packing configurations and porosities; Regime (b), where the Newman-type model is valid; Regime (c), where the Newman-type model is valid, but the microstructures are physically inaccessible; Finally regime (d), where the Newman models are invalid, and the porous microstructures are physically inaccessible. Simulations in regime (a), should be modeled with spatially-resolved numerical methodology, while regime (c) delivers simulations of batteries that would be impossible to manufacture. . . . . . . . . . . . . . . . . . . 29Computing wall-time vs resolution. Circles  $(\bigcirc)$  represent simulation cases. 3.1Solid lines (\_) represent the least-squares regression. The complexity of

Page

27

#### Figure

Active material Li-ion concentration profiles at 1C-rate for graphite NMC 3.3 system. 1C corresponds to  $18.7 \text{ A/m}^2$  or 0.614 A. Inset (a) highlights first 14 minutes of active material Li-ion concentration profile in the NMC electrode. Inset (b) corresponds to Li-ion concentration profile on both electrodes for the full 60 minutes discharge. During the first 2 minutes, Li-ions intercalate in the vicinity of the separator in the positive electrode due to the greater availability of lithium at the intercalating sites of NMC. Such process is followed by an interdiffusion sequence after the first 6 minutes, as intercalation sites become preponderantly occupied in the active material close to separator, and the intercalating reaction is affected by the chemically-induced stresses. The spatial inhomogeneities in the intercalation reaction (see Figure 3.6) develop again after thirty two minutes as a result of the stress contributions and the transport limitations that 44 Stress distribution in graphite NMC system for 1C galvanostatic discharge. 3.41C corresponds to 18.7 A/m<sup>2</sup> or 0.614 A. Inset (a) corresponds to selected instants of the hydrostatic stress during the first 18 minutes of discharge, while inset (b) corresponds to the full 60 minutes discharge. Stress is the result of current collectors and time-dependent chemomechanical expan-46Electrolyte Li-ion concentration profiles at 1C-rate for graphite NMC sys-3.5tem. 1C corresponds to  $18.7 \text{ A/m}^2$  or 0.614 A. Inset (a) highlights the predicted electrolyte Li-ion concentration profile in the NMC electrode during the first 2 minutes of discharge. Inset (b) summarizes electrolyte Li-ion concentration profile for the full 60 minutes of discharge. During the first 11 seconds of discharge, the NMC cathode intercalates lithium faster in the vicinity of the current collector side because of the combined effects of elastic energy and the overpotential drop across the electrode. After 35 seconds, the concentration in the vicinity of the current collector recovers and the intercalation/deintercalation activity relocate to zones close to the separator. 48Spatial distribution of Butler-Volmer flux during 1C discharge for graphite NMC 3.6 system. 1C corresponds to  $18.7 \text{ A/m}^2$  or 0.614 A. Inset (a) corresponds to selected instants during the first 28 minutes of discharge, while inset (b) corresponds to the full 60 minutes discharge. Calculations demonstrate the progressive development of localized heterogeneities zones, aided by the transport limitations of the porous electrode and the stress fields that shift the intercalation reaction. Intercalation is enhanced until the maxi-

#### Page

## Figure

Figu	re	Page
3.7	Concentration frequency histograms for 1C galvanostatic discharge, for selected instants. 1C corresponds to $18.7 \text{ A/m}^2$ or $0.614 \text{ A}$ . Three populations are observed: (i) the lithiation-induced population, (ii) the stress-induced population, and (iii) the diffusion-limited population	. 52
3.8	Concentration frequency histograms for 5C galvanostatic discharge, for selected instants. 5C corresponds to 93.5 A/m <sup>2</sup> or 3.07 A. After $t = 3$ minutes of discharge, three populations are developed: (i) the lithiation-induced population, (ii) the stress-induced population, and (iii) the diffusion limited population.	n- . 52
E.1	Effect of discharge current in the chemically-induced strain of NMC electrodes corresponds to chemically-induced strain calculated from the lattice parameter changes measured experimentally during first cycles of galvanostatic discharge at C/40, as reported by Yabuuchi <i>et al.</i> [94]. $\bigcirc$ identify cases of strain-free concentration or maximum strain	- . 75

## SYMBOLS

- $\mathcal{A}$  Reactive area density
- A Anode
- B Physical property
- c Concentration
- $c_{\max}$  Maximum solid solubility at cathode
- $c_i^0$  Initial concentration of ith phase
- $c_{\varepsilon}$  Stress-free concentration
- $c_{\varepsilon_{\max}}$  Concentration of maximum strain
- C Cathode
- $\stackrel{\leftrightarrow}{\mathcal{C}}$  Stiffness tensor
- D Diffusivity
- E Young modulus
- $\mathcal{F}$  Faraday's constant
- g Gibbs free energy density
- G Gibbs free energy
- I Superficial current density
- $\mathcal{K}$  Interfacial gradient energy penalty
- K Bulk modulus
- $k_r$  Reaction rate constant
- $\ell$  Ions travel path distance
- L Electrode or cell thickness
- $L_{xx}$  Depolarization factor
- M Mobility
- $M_{\rho}$  Electrical mobility

- $\overrightarrow{n}$  Normal vector
- $\mathcal{O}$  Order of the term
- P Pressure
- Q Theoretical charge capacity
- $\mathbf{r}_p$  Radius of the active material particle
- R Universal gas constant
- $R_f$  Film-contact-resistance
- $\mathcal{S}$  Shape factor
- $S^+$  Cation
- T Temperature
- $t_+$  Transference number of Li-ions
- t Time
- $\hat{t}$  Dimensionless time
- $t_{{}_{\mathrm{D}_i}}$  Characteristic diffusion time *i*th phase
- $t_{M_i}$  Characteristic electromigration time *i*th phase
- $t_{\mathbf{R}_i}$  Characteristic heterogeneous reaction time
- $t_{\rm \scriptscriptstyle Ch:}$  Characteristic gradient-energy time  $i{\rm th}$  phase
- $t_{\scriptscriptstyle{\rm Ss}_i}$  Characteristic stress time  $i{\rm th}$  phase
- U\* Characteristic free energy density
- $u_j$  jth component of displacement vector
- $\hat{y}$  Fast spatial variable
- z Charge valence
- $\alpha$  Bruggeman exponent
- $\alpha_c$  Transfer coefficient
- $\beta$  Vegard strain coefficient
- $\stackrel{\leftrightarrow}{\varepsilon}^{T}$  Total strain tensor
- $\varepsilon_{\scriptscriptstyle Che}$  Chemical strain
- $\varepsilon_e$  Elastic strain
- $\eta$  Local surface overpotential

- $\Theta$  Polymer site
- $\epsilon_i$  Volume fraction of the *i*th phase
- $\lambda(\vec{x})$  Position dependent Lagrange multiplier
- $\mu$  Shear modulus
- $\nu$  Poisson ratio
- $\xi$  Scalar
- $\rho$  Electric charge density
- $\stackrel{\leftrightarrow}{\sigma}$  Stress tensor
- $\sigma_T$  Total electrical conductivity
- $\tau_{\rm \tiny R} \qquad {\rm Dimensionless\ reaction\ time}$
- $\tau_{M_i}$  Dimensionless migration time for *i*th phase
- $\tau_{{}_{\mathrm{Ch}_i}}$  Dimensionless gradient energy time for  $i\mathrm{th}$  phase
- $\tau_{\rm \scriptscriptstyle Ss_i}$  Dimensionless stress time for  $i{\rm th}$  phase
- $\phi$  Electric potential
- $\xi$  Closure variable
- $\Omega$  Phase volume

## ABBREVIATIONS

- LIBs Lithium-ion batteries
- $\mathrm{NMC} \qquad \mathrm{Li}_x\mathrm{Ni}_{1/3}\mathrm{Mn}_{1/3}\mathrm{Co}_{1/3}\mathrm{O}_2$
- PVDF Polyvinylidene fluoride
- LFP LiFePO<sub>4</sub>
- MCMB Mesocarbon Microbeads
- LMO  $Li_xMn_2O_4$
- P2D Pseudo-two-dimensional
- PNP Poisson-Nerst-Planck
- GB GigaBytes
- RAM Random Access Memory
- CPU Central Processing Unit
- GPU Graphics Processing Units

## ABSTRACT

Campos, Juan Alfonso Ph.D., Purdue University, August 2020. Generalized Homogenization Theory and its Application to Porous Rechargeable Lithium-ion Batteries. Major Professor: R. Edwin García.

A thermodynamically consistent coarsed-grained phase field model was developed to find the conditions under which a heterogeneous porous electrode can be treated as homogeneous in the description of Li-ions in rechargeable batteries. Four regimes of behavior under which the transport phenomena can be homogenized to describe porous LIBs were identified: regime (a), where the model is inaccurate, for physically accessible particle packings of aspect ratios smaller than c/a = 0.5 and electrode porosities between 0.34 to 0.45; regime (b), where the model is valid, for particles of aspect ratios greater than c/a = 0.7 and electrode porosities greater than 0.35; regime (c), where the model is valid, but the microstructures are physically inaccessible, and correspond to particles with aspect ratios greater than c/a = 0.7 and electrode porosities smaller than 0.34; and regime (d), where the model is invalid and the porous microstructures are physically inaccessible, and correspond to particles with aspect ratios smaller than c/a = 1 and electrode porosities smaller than 0.34.

The developed formulation was applied to the graphite  $|\text{Li}_x \text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3} \text{O}_2$ system to analyze the effect of microstructure and coarsed-grained long-range chemomechanical effects on the electrochemical behavior. Specifically, quantifiable lithium distribution populations in the cathode, as a result of long range interactions of the diffuse interface, charge effects and mechanical stresses were identified: i) diffusion limited population due to negligible composition gradients, ii) stress-induced population as a result of chemically-induced stresses, and iii) lithiation-induced population, as a consequence of the electrochemical potential gradients.

#### 1. INTRODUCTION

#### 1.1 Energy Storage Technology Applications

Traditional energy extraction from fossil fuels generates waste heat and emissions that pollutes and warms up the environment. Renewable energy sources such as water, wind, and sunlight could overcome the world's energy demand without delivering waste heat and operating under low emissions, by powering all productive sectors with secondary energy sources like electricity, [1]. However, weather conditions could impede electricity generation from renewable sources and cause an intermittent supply. Thus, once that primary renewable energy sources are converted into electricity and the electrical demand is covered, the remnant electricity has to be stored. Electricity-based sustainable world will require the conversion of electricity into chemical energy, which can be reserved for later use.

Electronic devices and electric cars are rated and valued according to their battery support performance, [2]. Computer clusters and security systems are as reliable as their energy storage backups. However, current storage technology cannot parallel the rate of progress of computer technology, [3]. Therefore, energy storage systems and in particular rechargeable batteries are fundamental for the environment protection, the economic growth and the technological development.

#### **1.2** Rechargeable Battery Fundamentals

A rechargeable battery consists of two electrodes, anode and cathode, one intermediate membrane separator, and two current collectors, all immersed in ionic conductive liquid (electrolyte), [4–11]. The electrodes are subjected to reversible reactions:

anode: 
$$S_z A \rightleftharpoons z S^+ + A + z e^-$$
  
cathode:  $S_z C \rightleftharpoons z S^+ + C + z e^-$  (1.1)

where S, is the element providing the ions, A, stands for the chemistry in the negative electrode, and C is the chemistry at the positive electrode. This ensemble is called a dual insertion cell or 'rocking chair' [6, 9, 10], in reference to the back and fort movement of ions between cathode and anode as depicted in Figure 1.1.



Figure 1.1. Schematic of charged ions trajectories during cell discharge. The opposite flow occur while charging. The scheme also shows the basic elements of the dual insertion cell. Taken from Ref. [12].

Atoms are deintercalated from the interstitial sites at the host material in the electrode, turned into a positive charged ion (cation), and directed to the opposite electrode through the electrolyte to find a new host, driven by the gradient in free energy. In the context of rechargeable battery systems, the driving force is the electro-chemical potential gradient. The released electrons are carried through the external circuit, following the lowest electrical resistive path between the current collectors,

driven by the electrical potential gradient. Electrons are also identified as negative charged ions (anions).

The membrane between electrodes is meant to be electronically insulating, meanwhile acting as a porous barrier that allows the transport of cations. This ionic permeable membrane is commonly made of polymer and is also soaked in electrolyte of high ionic conductivity. Different mixtures of lithium salts and solvents are used to tailor the electrical conductivity of the electrolyte. Thus, the conductive salt concentration has an impact on the kinetics of battery. In the separator, transport of ions occur through the electrolyte between available sites in the polymer lattice [4,8–11], by a reaction of the form:  $S^+ + \Theta \rightleftharpoons S - \Theta + e^-$ , where  $\Theta$  represent the polymer chain. A summary of common materials used in commercially available rechargeable batteries are listed in table 1.1.

Table 1.1.: Typical materials for rechargeable battery components, [10].

Collector	Electrode	Electrolyte		Separator
		Salt	Solvent	-
Cu	Li	$\mathrm{LiPF}_{6}$	EC: ethylene carbonate	Polyethylene
Al	${\rm LiC}_6$	KOH	DMC: dimethyl carbonate	Polypropylene
	$\rm LiFePO_4$	$LiClO_4$	DEC: diethyl carbonate	Polycarbonate
	$\rm LiMn_2O_4$	LiTFSI	PEO: polyethylene oxide	
	${\rm Li}_4{\rm Ti}_5{\rm O}_{12}$	$AsF_6$	$C_3H_6O_2$ : methyl acetate	
	$LiCoO_2$		$H_2O$	

<sup>†</sup> Not an exhaustive list.

#### **1.3** Transport Properties in Porous Electrodes

The interface area between the solid active particles and the conductive electrolyte plays an essential role in the performance of the battery, because a high surface induces a high reactivity and consequently an increased flux of ions. Pores in the electrodes provide additional surface at the expense of a fraction of solid active material. Additional reactive interface is created if those pores infiltrated with electrolyte are interconnected, so that pathways for high ionic-conductivity allow the transport of cations within the electrode. However, a porous electrode represents a disconnected media for electrons. So, electronic conductive additives such as graphite flakes or carbon needles are dispersed in the electrolyte to create the conductive paths for the anions, [12]. In order to put together solid active particles and fillers as a composite, a polymer such as polyvinylidene fluoride (PVDF) is incorporated to act as binder. Any constituent of the porous electrode is integrated at the expense of a volume fraction of solid active material. Figure 1.2 show the break down of electrode constituents in a percentage basis.



Figure 1.2. Break-down of the multiple phases conforming the composite porous electrode. Volume fraction of the electrolyte in commercially available cathode materials is the range of 30 - 40%. Taken from Ref. [13].

The total interfacial area of a porous electrode is a function of shape and size of the particles of active materials. To calculate an approximate area, two assumptions are usually put in practice: monodispersed distribution of particle size and spherical morphology. The area per unit volume or reactive area density is  $\mathcal{A} = \left(\frac{S \times \epsilon_s}{r_p}\right)$ , where

 $\epsilon_s = \frac{\Omega_{\text{electrolyte}} - \Omega_{\text{fillers}} - \Omega_{\text{binder}}}{\Omega_{\text{total}}}$ , is the volume fraction of the active material,  $\mathcal{S}$  is the shape factor which corresponds to perfect spheres when  $\mathcal{S} = 3$ , and  $r_p$  is the particle radius.

Physical properties such as electrical conductivity and diffusivity are obtained experimentally. Although, in the context of porous electrodes, measurements of these properties differ from point to point due to the obstacles imposed to transport of ions. In a porous media, the effects of porosity and tortuosity over a property value have to be considered. The tortuosity is the ratio of actual travel path of ions,  $\ell$ , to the length of the through-thickness electrode, L,  $\tau = \frac{\ell}{L}$ . Porosity and tortuosity are related by an empirical relation found by Bruggeman, where  $\alpha$  is known as the Bruggeman exponent  $\tau = \frac{1}{\epsilon^{\alpha}}$ , [15].

### 1.4 Overview of the Thesis

A thermodynamically consistent phase field model, based on the contributions to the free energy of the system, is proposed to understand the effects of the complex electrochemical and chemomechanical processes carried through the operation of the battery. In this work, computational models are the keystone for research and one of the intended outcomes. The phase field framework is coarsed-grained with rigorous mathematical techniques in an effort to control the overall investment on computational resources without loosing insight on the phenomena. Chapter 2 introduces the phase field coarsed-grained approach, and the mathematical derivation that allows to assess the validity of the continuum approximation, based on the transport limitations imposed by the electrode microstructure. Specifically, a set of classical Newman-type model definitions of the mass and charge transport equations subjected to diffusion, electromigration and intercalation reaction are derived. For the first time, an experimental microstructural guideline to tailor the secondary active material particles and the electrode porosity to achieve the conditions of validity of the model is introduced. In addition, microstructural analyses on the validity and limitations of coarsed-grained models for commercially and experimentally available electrodes are provided. Chapter 3 makes use of the phase field framework to introduce the contributions of the gradient energy and the mechanical stresses in the battery system, to derive a set of coarsed-grained mass and charge transport equations. The derived equations are applied to a commercially available chemistry,  $\text{Li}_x \text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3} \text{O}_2$ (NMC), and the long range kinetic implications of the additional contributions are reported. Specifically, the overall effect on the macroscopic cell potential and localized effects on position dependent concentration fields of the solid and electrolyte phases. Finally, Chapter 4 presents the future challenges to better and reliably design rechargeable batteries and the opportunities that powerful tools, like those developed in this work, have open to realistically and faithfully engineer the next generation of rechargeable batteries.

## 2. MICROSTRUCTURAL LIMITS AND EXTENSIONS OF POROUS ELECTRODE THEORY

A version of this chapter is currently in preparation for journal publication as: J.A. Campos, I. Battiato, and R.E. García. "Microstructural Limits and Extensions of Porous Electrode Theory."

## 2.1 Introduction

Since its initial commercialization in 1991 [16], the energy density of lithiumion batteries (LIBs) has increased yearly at a rate of 5 - 10% [2], to fulfill the evergoing expectation of longer-lasting electrical power, and has lead to improvements in energy density to more than double in the last two decades [2, 17–19], while its cost decreased by a factor of ten [2, 17, 20]. LIBs currently power a great part of the market of portable devices, 63% [3], while most recently batteries started to be incorporated in the transportation and electrical-grid markets [2, 17–22]. Worldwide, current battery systems are capable to store only 0.02% [23] of the total electrical energy. In order to support the use of intermittent renewable energy sources, or electrically-based transportation, important technological and scientific strides have to occur in the present decade.

The underlying electrochemical processes occurring in rechargeable batteries are a scaled-up, macroscopic, measurable quantities, that are a result of the underlying rechargeable battery microstructural design. Fundamental transport phenomena such as diffusion, electromigration, and reaction have been successfully implemented in porous electrode models through volume-averaged [5,7,8,10,14,24–30], and upscaledhomogenized [31–34] methodologies. Their use and applicability in LIB design is limited by their physical and numerical complexity, and the overall investment on computational and human resources required to better understand or design the device.

Porous electrode theory models developed by a large, well established community, e.g., [5,7,8,10,24], offers a unified, well-thoughtout mean-field approach, where the electrochemically active material phase, processed in granular form, is modeled as perfectly spherical particles, as a step to describe the averaged properties of a representative volume. These models are quite robust and require low computational resources [10,14,27–30]. However, particle-to-particle interactions are not well captured and represent a limitation of the model [35–40]. A representative volume is defined large enough to include every phase, but small enough to assume homogeneity and describe the material as a continuum [5,7,8,10,24]. Here, any scalar, vectorial, or tensorial quantity, B, is averaged over a local representative volume,  $\Omega_i$ , as  $\overline{B}_i \equiv \frac{1}{\Omega} \int_{\Omega_i} B_i d\Omega$ and related to the intrinsic volume average through the relation  $\overline{B}_i = \epsilon_i \langle B \rangle_i$ . The intrinsic volume average is defined as  $\langle B \rangle^i \equiv \frac{1}{\Omega_i} \int_{\Omega} B_i d\Omega$ , for  $i = \{\text{solid, electrolyte}\}$ . Other quantities such as the average of the gradient  $\overline{\nabla B}_i = \nabla \overline{B}_i + \frac{1}{\Omega} \int_S B_i \hat{n}_S dS$ , the average of the divergence  $\overline{\nabla \cdot \vec{B}}_i = \nabla \cdot \vec{B}_i + \frac{1}{\Omega} \int_{S} \vec{B}_i \cdot \hat{n}_{S} dS$ , and the generalized transport theorem  $\frac{d}{dt} \int_{V} BdV = \int_{\Omega} \frac{\partial B}{\partial T} d\Omega + \int_{S} B\vec{v} \cdot \hat{\mathbf{n}} dS$ , enable to define the averaged continuity equations:

$$\frac{\partial \overline{c}_i}{\partial t} + \nabla \cdot \overline{\vec{N}}_i = \overline{R}_{ls}$$

$$\nabla \cdot \overline{\vec{I}}_i = \overline{R}_{ls}$$
(2.1)

Here,  $c_i$  is the concentration of ions, t is time,  $\overline{\vec{I}}_i$  is the averaged electric current density,  $\overline{R}_{ls}$  is the Butler-Volmer relation and i defines the ith component. T is temperature, S corresponds to the closed bounding surface,  $\Omega$  represents the spatial region of interest, and  $\epsilon_i$  is the volume fraction of the ith phase. In a concentrated solution,  $\overline{\vec{N}}_i = -\nu_+ \langle D_i \rangle (1 + H_i^*) \nabla \epsilon_i \langle c_i \rangle + \frac{t_+^*}{z_+ \mathcal{F}} \overline{i}_i$  is the average molar mass flux vector, where  $t_+^*$  is the transference number,  $z_+$  the ionic charge of the cations [24], and  $(1 + H_i^*) = 1/\tau$  is the tortuosity, as introduced by Bruggeman [15]. For porous electrodes, the averaged electrical conductivity and lithium diffusivity are defined as:

$$\langle \sigma \rangle = \frac{\epsilon_i \sigma_0}{\tau}, \quad \text{and} \quad \langle \mathbf{D} \rangle = \frac{\epsilon_i \mathbf{D}_0}{\tau}$$
(2.2)

Porosity and tortuosity are related through the expression  $\tau = \frac{1}{\epsilon_i^{\alpha}}$ , [15]. The microstructural tortuosity is a function of statistical contributions from a representative particle geometry:  $\langle \alpha \rangle = \frac{p + 2pS + 3L(p - 2pS + 2L-2)}{6L(1 - L)}$ , where p is the particle size polydispersity, L is the depolarization factor, and S is the microstructural order parameter, as described by García, [41].

Lai and Ciucci derived a volume-averaged model, by using generalized Poison-Nernst-Planck equations and proposed an interfacial charge transfer equation, where the transfer coefficients depend on electric current and galvanic potential terms [42, 43]. In a follow-up paper, the same authors developed a phase transforming model where the time-dependent motion of the phase boundary was phenomenologically captured [44]. Bazant and collaborators extended Newman's porous electrode theory model to account for phase transforming materials and captured the intercalation kinetics of LiFePO<sub>4</sub> (LFP), [25, 26]. The model predicted the occurrence of voltage spikes due to the discrete filling fraction of lithium in the particles, and demonstrated the spinodal decomposition of lithium in LFP.

In contrast, upscaled-homogenized models define an homogenized property as one that converges to its averaged value, upon applying a multiscale expansion, and have been suitable to be modeled as a periodic structure, [45]. Any variable originally defined as  $B_{\xi}(x,t)$  is recast as a function of all spatial and temporal scales,  $B_{\xi}(x,t) \rightarrow$  $B(x, y, t, t_{R}, t_{M_{e}}, t_{M_{s}})$ , and expanded into powers series:  $B = \sum_{n=0}^{\infty} \xi^{n} B_{n}(x, y, t, t_{R}, t_{M_{e}}, t_{M_{s}})$ , where the scalar  $\xi$  is the ratio of the particle size to the electrode thickness  $\left(\frac{2r_{p}}{L}\right)$ . The expansion, based on the scalar  $\xi \ll 1$ , is carried up to  $\mathcal{O}(\xi^{2})$ , [45–49].

Lai and coworkers [31] developed an upscaled-homogenized model by starting from the Poison-Nernst-Planck equation, whose scales were not fully decoupled by suggesting that diffusion is highly non-linear. Therefore, macroscale equations were set for the solid phase and coupled to spatially-resolved equations on the electrolyte. Golmon and coworkers applied successfully the upscaling-homogenizing technique in porous electrode models to lower the computational burden [32], and reported that the fields of a small spatially-resolved domain are passed up to the coarse-grained model for a second iteration. Battiato and coworkers introduced a method to identify the validity of Newman-type models by considering the chemistry only, [34]. They suggested that the continuum approximation is valid as long as the separation of scales is enforced. This was found to be true when diffusion is dominant (shorter time scale) as compared with other transport process contributions. This was quantified by Péclet and Damköhler numbers:  $\text{Pe}_i = \frac{\text{RT}\sigma_T^*}{(z_i \mathcal{F})^2 \text{D}_i^* c_{\text{max}}}$  and  $\text{Da}_i = \frac{\text{Lk}}{\text{D}_i^*}$ ,  $i = \{\text{electrolyte},$ solid}. Diffusion dominates when the constraints: (a)  $\xi \ll 1$ , (b) Da < 1, (c) Pe < 1, and (d) Da < Pe are enforced.

Table 2.1 summarizes a comparison between the analytical form of the equation terms corresponding to mass accumulation, diffusion, electromigration and reaction processes, as emphasized by each methodology.

Table 2.1.: Summary of relations between spatially-resolved, volume-averaged and upscaled-homogenized terms. Relations used to develop different coarse-grained representations are also highlighted, noting that the upscaling process requires specific relations in addition to the averaging technique.

Spatially-resolved	Averaged	Upscaled-homogenized	
$rac{\partial c_e}{\partial t}$	$\epsilon_i rac{\partial \langle c_e  angle}{\partial t}$	$\epsilon_i rac{\partial \langle \hat{c}_e  angle}{\partial \hat{t}}$	
$rac{\mathrm{D}_e c_e}{2\mathrm{RT}}  abla_x^2 c_e$	$\frac{c_e}{2\mathrm{RT}} \langle \mathrm{D}_e \rangle \nabla_x^2 \langle c_e \rangle$	$rac{\hat{c}_e}{2\mathrm{RT}} \langle \hat{\mathrm{D}}_e  angle \hat{ abla}_x^2 \langle \hat{c}_e  angle$	
$rac{\mathrm{z}_i\mathcal{F}\mathrm{D}_ec_e}{2\mathrm{RT}} abla_x^2\phi_e$	$rac{\langle\sigma_e angle}{{ m z}_i{\cal F}}t_+ abla_x^2\langle\phi_e angle$	$\mathrm{Pe}_{e}t_{+}\langle\hat{\sigma}_{e}\rangle\hat{ abla}_{x}^{2}\langle\hat{\phi}_{e} angle$	
$rac{k}{\mathrm{z}_i\mathcal{F}}\hat{j}_{BV}$	$rac{\epsilon_i k \mathcal{A}}{\mathrm{z}_i \mathcal{F}} \hat{j}_{BV}$	$rac{\epsilon_i \mathrm{Da}_e \mathcal{A}}{\xi} \hat{j}_{BV}$	
$\frac{\mathrm{d}}{\mathrm{dt}} \int_{\Omega} \mathrm{Bd}\Omega = \int_{\Omega} \frac{\partial \mathrm{B}}{\partial \mathrm{T}} \mathrm{d}\Omega$			
$\overline{ abla \cdot ec { m B}}_i =  abla \cdot \overline{ec { m B}}_i + rac{1}{\Omega} \int$	Summary of relations		
$\overline{\nabla \mathbf{B}}_i = \nabla \overline{\mathbf{B}}_i + \frac{1}{\Omega} \int_{\mathbf{S}} \mathbf{B}$	$\overline{\nabla \mathbf{B}}_i = \nabla \overline{\mathbf{B}}_i + \frac{1}{\Omega} \int_{\mathbf{S}} \mathbf{B}_i \hat{\mathbf{n}}_{\mathbf{S}} \mathrm{dS}$		
$\overline{\mathbf{B}}_i \equiv \frac{1}{\Omega} \int_{\Omega_i} \mathbf{B}_i \mathrm{d}\Omega$		averaged equations.	
$\overline{\mathbf{B}}_i = \epsilon_i \langle \mathbf{B} \rangle_i$			
Summary of relations	$\mathbf{B}(x,t) \to \mathbf{I}$	$\mathbf{B}(x,y,t,t_{\mathrm{R}},t_{\mathrm{M}_{e}},t_{\mathrm{M}_{s}})$	
used to develop upscaled-	$\xi = rac{2\mathbf{r}_p}{\mathbf{L}}$		
homogenized equations in	$\mathbf{y} = \xi^{-1} \mathbf{x}$		
addition to the relations also	$\mathbf{B} = \sum_{n=0}^{\infty}$	$\xi^{\mathrm{n}} \ \mathrm{B}_{\mathrm{n}}(x,y,t,t_{\mathrm{\scriptscriptstyle R}},t_{\mathrm{\scriptscriptstyle M}_e},t_{\mathrm{\scriptscriptstyle M}_s})$	
used to volume-averaged	$\hat{ abla}_y \cdot ig( \mathrm{I} + \hat{ abla} ig)$	$V_y\chi\bigr)=0$	
transport equations.	$\hat{\mathbf{n}}\cdotig(\mathrm{I}+\hat{ abla}_y$	$\chi ) = 0$	

The characteristic time of any ionic transport process at the microscopic level is affected by the tortuosity, the reactive area density, and any additional reversible and irreversible physical mechanisms not considered by the classical definition of the macroscale dimensionless numbers. In this context, a modeling methodology based on microstructural criteria that allows to scale-up the different multiphysical aspects of porous LIBs, while providing practical guidelines to determine the extent of validity of the models, is missing. In this paper, a mathematical framework derived from a phase field formulation was developed to allow the incorporation of additional physical contributions that affect the validity guidelines. The microstructural analysis, validity and limitations of Newman-type models for commercially and experimentally available electrodes are also provided.

## 2.2 Theoretical Framework

Define the Gibbs free energy of a material system subjected to chemical, elastic, and electric driving forces as [51–57]:

$$G[\{c_i\}, \rho, u_j; \mathbf{T}_{\circ}] = \int_{\Omega} \left( g(\{c_i\}; \mathbf{T}_{\circ}) + \sum_{i=1}^{N-1} \frac{\mathcal{K}_i}{2} |\nabla c_i|^2 + \frac{1}{2} \overset{\leftrightarrow}{\sigma} \cdot \overset{\leftrightarrow}{\varepsilon}_e + \rho \phi \right) \mathrm{d}\Omega + \int_{\Omega} \lambda(\vec{x}) \left( \rho - \sum_{i=1}^{N} \mathcal{F}z_i c_i \right) \mathrm{d}\Omega$$

$$(2.3)$$

where  $\{c_i\} = \{c_1, \ldots, c_N\}$ , is the set of the concentrations of N electrically charged species,  $u_j$  is the *j*th component of the mechanical displacement vector,  $\overleftrightarrow{\sigma}$  is the mechanical stress tensor,  $\overleftrightarrow{e}_e$  is the elastic strain tensor,  $\varepsilon_{kl} = \frac{1}{2} \left( \frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right)$  describes the relation of geometrical strain and displacement,  $\rho$  is the electric charge density,  $T_{\circ}$ is the temperature,  $\mathcal{K}_i$  is the interfacial gradient energy penalty of the *i*th species,  $\Omega$ is the volume of the phase in consideration,  $z_i$  is the charge valence of the *i*th species,  $\mathcal{F}$  is Faraday's constant, and  $\lambda(\vec{x})$  is a spatially varying Lagrange multiplier, [58].

The resultant variational derivatives are [51, 52, 54, 55]:

$$\frac{\delta G}{\delta c_i} = \frac{\partial g}{\partial c_i} - \mathcal{K}_i \nabla^2 c_i + \lambda \mathcal{F} z_i + \frac{1}{2} \frac{\partial}{\partial c_i} \left( \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}_e \right) 
\frac{\delta G}{\delta \rho} = \phi - \lambda 
\frac{\delta G}{\delta u_j} = \nabla \cdot \overleftrightarrow{\sigma} = \vec{0}$$
(2.4)

Equation set 2.4 constitutes the electrochemomechanical driving force for transport and phase transformations, through the set of coupled Cahn-Hilliard equations:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \mathbf{M}_i \nabla \left( \frac{\delta G}{\delta c_i} \right) = \nabla \cdot \mathbf{M}_i \nabla \left( \frac{\partial g}{\partial c_i} - \mathcal{K}_i \nabla^2 c_i + \frac{1}{2} \frac{\partial}{\partial c_i} \left( \stackrel{\leftrightarrow}{\sigma} \cdot \stackrel{\leftrightarrow}{\varepsilon}_e \right) \right) + \nabla \cdot \mathbf{M}_i \mathcal{F} z_i \nabla \lambda$$

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \mathbf{M}_{\rho} \nabla \left( \frac{\delta G}{\delta \rho} \right) = \nabla \cdot \mathbf{M}_{\rho} \nabla \phi - \nabla \cdot \mathbf{M}_{\rho} \nabla \lambda$$
(2.5)

where  $\lambda(\vec{x}) = \frac{M_{\rho}\phi - \sum_{i=1}^{N} z_i \mathcal{F} M_i \left(\frac{\partial g}{\partial c_i} - \mathcal{K}_i \nabla^2 c_i + \frac{1}{2} \frac{\partial}{\partial c_i} \left(\stackrel{\leftrightarrow}{\sigma} \stackrel{\leftrightarrow}{\varepsilon}_e\right)\right) + \psi(\vec{x})}{M_{\rho} + \sum_{i=1}^{N} (z_i \mathcal{F})^2 M_i}$ , and  $\psi(\vec{x})$  is a solution to the Laplace equation ( $\nabla^2 \psi = 0$ ) that will vanish when substituted in equation set 2.5, in agreement with several authors [51, 58, 59].  $M_i = D_i c_i / RT$ ,  $M_{\rho} = \sum_{i=1}^{N} (z_i \mathcal{F})^2 M_i$ , while  $\sigma_T = \sigma_1 + \ldots + \sigma_N$ , and  $M_{\rho}/2 = \sigma_T$ , [60].

By substituting:

$$\begin{aligned} \frac{\partial c_i}{\partial t} = \nabla_x \cdot \left[ \frac{\mathcal{D}_i c_i (2 - t_i)}{2 \mathrm{RT}} \left( \frac{\partial^2 g}{\partial c_i^2} \nabla_x c_i - \mathcal{K}_i \nabla_x^3 c_i - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c_i} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c_i^2} \nabla_x c_i \right) + \frac{z_i \mathcal{F} \mathcal{D}_i c_i}{2 \mathrm{RT}} \nabla_x \phi \\ + \sum_{j=1, i \neq j}^N \frac{\mathcal{M}_{ij}}{2} \left( \frac{\partial^2 g}{\partial c_j^2} \nabla_x c_j - \mathcal{K}_j \nabla_x^3 c_j - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c_j} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c_j^2} \nabla_x c_j \right) \right] \end{aligned}$$

$$\frac{\partial \rho}{\partial t} = \nabla_x \cdot \left[ \sigma_T \nabla_x \phi + \sum_{i=1}^N \frac{z_i \mathcal{F} \mathcal{D}_i c_i}{2 \mathrm{RT}} \left( \frac{\partial^2 g}{\partial c_i^2} \nabla_x c_i - \mathcal{K}_i \nabla_x^3 c_i - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c_i} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c_i^2} \nabla_x c_i \right) \right]$$
(2.6)

For an intercalating material, strain is imposed on the lattice as a result of the interstitially dissolved lithium [43,44,57,61–63]. The inhomogeneous distribution of solute, results in compositionally-induced stresses. Here, the total (or geometrical) strain,  $\overleftrightarrow{\varepsilon}^{T}$ , is the sum of elastic,  $\overleftrightarrow{\varepsilon}_{e}$ , and the chemical strain,  $\overleftrightarrow{\varepsilon}_{Che}$ , [64–70];  $\overleftrightarrow{\varepsilon}^{T} = \overleftrightarrow{\varepsilon}_{e} + \overleftrightarrow{\varepsilon}_{Che}$ . The stress tensor and the elastic strain are related via Hooke's law,  $\overleftrightarrow{\sigma} = \overleftrightarrow{C} \cdot \overleftrightarrow{\varepsilon}_{e}$ . In agreement with Newman *et al.* [65-67], the Butler-Volmer relation corresponds to:

$$j_{\rm BV} = k c_e^{\alpha_c} (c_{\rm max} - c_s)^{\alpha_c} c_s^{(1-\alpha_c)} \exp\left(-\frac{\overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}_e}{4 \text{RT} c_{\rm max}}\right) \left(\exp\left(\frac{\alpha_c \mathcal{F}}{2 \text{RT}}\eta\right) - \exp\left(-\frac{(1-\alpha_c) \mathcal{F}}{2 \text{RT}}\eta\right)\right)$$
(2.7)

where the local surface overpotential:  $\eta = \left(\phi_s - \phi_e - j_{BV}\mathcal{F}R_f - \frac{1}{2}\frac{\overleftrightarrow{\sigma}\cdot\overleftrightarrow{\varepsilon}_e}{\mathcal{F}c_{\max}}\right)$ . The exponent,  $\alpha_c$ , is the transfer coefficient, k is the reaction rate constant, and  $R_f$  is the interfacial resistance, also known as 'film-contact-resistance'.

Define:

$$\hat{c} = \frac{c}{c_{\max}}, \qquad \hat{x} = \frac{x}{L}, \qquad \hat{\phi} = \frac{z\mathcal{F}\phi}{2R\Gamma}, \qquad \hat{\rho} = \frac{\rho}{z\mathcal{F}c}, \qquad \hat{D} = \frac{D}{D^*} 
\hat{\sigma} = \frac{\sigma}{\sigma^*}, \qquad \hat{\mathcal{K}} = \frac{\mathcal{K}}{\mathcal{K}^*}, \qquad \hat{M} = \frac{M}{M^*}, \qquad \hat{M}_{\rho} = \frac{M_{\rho}}{M_{\rho}^*}, \qquad \hat{t} = \frac{t}{t_{D_e}} 
\nabla = \hat{\underline{\nabla}}, \qquad \frac{\partial}{\partial c} = \frac{1}{c_{\max}}\frac{\partial}{\partial \hat{c}}, \qquad \frac{\partial}{\partial c^2} = \frac{1}{c_{\max}^2}\frac{\partial}{\partial \hat{c}^2}, \qquad \frac{\partial}{\partial t} = \frac{1}{t_{D_e}}\frac{\partial}{\partial \hat{t}} 
\frac{\partial}{\partial x} = \frac{1}{L}\frac{\partial}{\partial \hat{x}}, \qquad \frac{\partial^2}{\partial x^2} = \frac{1}{L^2}\frac{\partial^2}{\partial \hat{x}^2}, \qquad \frac{\partial^3}{\partial x^3} = \frac{1}{L^3}\frac{\partial^3}{\partial \hat{x}^3}$$
(2.8)

which upon substitution into equation set 2.6, results in the following:

$$\begin{split} \frac{\partial \hat{c}}{\partial \hat{t}} = &\hat{\nabla}_x \cdot \left[ \frac{\hat{c}(2-t_+) \mathbf{D}_i^* \hat{\mathbf{D}}_i}{2 \mathbf{R} \mathbf{T} \mathbf{c}_{\max} \mathbf{D}_e^*} \mathbf{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \frac{\mathbf{D}_i^* c \mathcal{K}_i^*}{\mathbf{D}_e^* \mathbf{R} \mathbf{T} \mathbf{L}^2 c_{\max}^2} \frac{(2-t_+)}{2} \hat{\mathbf{D}}_i \hat{\mathcal{K}}_i \hat{\nabla}_x^3 \hat{c} \right. \\ &- \frac{\mathbf{D}_i^* c \sigma^*}{\mathbf{D}_e^* \mathbf{R} \mathbf{T} c_{\max}^2} \frac{(2-t_+)}{2} \hat{\mathbf{D}}_i \left( \frac{\partial \varepsilon_{\text{Che}}}{\partial \hat{c}} \hat{\nabla}_x \hat{\sigma} + \hat{\sigma} \frac{\partial^2 \varepsilon_{\text{Che}}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} \right) + \frac{2 \mathbf{R} \mathbf{T} \sigma_T^* \mathbf{D}_i^*}{(z \mathcal{F})^2 \mathbf{D}_i^* c_{\max} \mathbf{D}_e^*} t_+ \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} \end{split}$$

$$\frac{\partial \hat{\rho}}{\partial \hat{t}} = \hat{\nabla}_{x} \cdot \left[ \frac{2 \mathrm{RT} \sigma_{T}^{*} \mathrm{D}_{i}^{*}}{(z \mathcal{F})^{2} \mathrm{D}_{i}^{*} c_{\max} \mathrm{D}_{e}^{*}} \hat{\sigma}_{T} \hat{\nabla}_{x} \hat{\phi} + \frac{\hat{c} \mathrm{D}_{i}^{*} \mathrm{D}_{i}}{2 \mathrm{RT} \mathrm{c}_{\max} \mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \hat{\nabla}_{x} \hat{c} - \frac{1}{2} \frac{\mathrm{D}_{i}^{*} \hat{c} \mathcal{K}_{i}^{*}}{\mathrm{D}_{e}^{*} \mathrm{RTL}^{2} c_{\max}^{2}} \hat{\mathrm{D}}_{i} \hat{\mathcal{K}}_{i} \hat{\nabla}_{x}^{3} \hat{c} - \frac{1}{2} \frac{\mathrm{D}_{i}^{*} \mathrm{c} \sigma^{*}}{\mathrm{D}_{e}^{*} \mathrm{RTL}^{2} c_{\max}^{2}} \hat{\mathrm{D}}_{i} \hat{\mathcal{K}}_{i} \hat{\nabla}_{x}^{3} \hat{c} + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}^{2}} \hat{\nabla}_{x} \hat{c} \right) \right]$$

$$(2.9)$$

for a pseudobinary system. Here, the following dimensionless numbers are identified:

$$Da_{i} = \frac{Lk}{D_{i}^{*}} \qquad Damköhler number$$

$$Pe_{i} = \frac{RT\sigma_{T}^{*}}{(z_{i}\mathcal{F})^{2}D_{i}^{*}c_{max}} \qquad Péclet number$$

$$Ch_{i} = \frac{c_{i}\mathcal{K}_{i}^{*}}{RTL^{2}c_{max}^{2}} \qquad Cahn number$$

$$Ss_{i} = \frac{c_{i}\sigma^{*}}{RTc_{max}^{2}} \qquad Stress number$$

$$(2.10)$$

where  $i = \{\text{solid}, \text{electrolyte}\}$ . In the solid phase, the electromigration term is negligible in the mass conservation equation (less than half compared with the contribution in the charge conservation equation, assuming  $t_+ = 0.4$ ), while the stress term is negligible in the charge conservation equation (one fourth compared with the contribution in the mass conservation equation, assuming  $t_+ = 0.4$ ), due to the influence of the transference number. Thus, equation set 2.9 reduces to:

$$\begin{aligned} \frac{\partial \hat{c}}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left[ \frac{\hat{c}(2-t_+) \mathcal{D}_s^* \hat{\mathcal{D}}_s}{2 \mathrm{RTc}_{\max} \mathcal{D}_e^*} \mathcal{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \hat{\nabla}_x^3 \hat{c} \\ - \mathrm{Ss} \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}} \hat{\nabla}_x \hat{\sigma} + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} \right) \right] \end{aligned}$$
(2.11)

$$\frac{\partial \hat{\rho}}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left[ \operatorname{Pe}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} + \frac{\hat{c} \mathrm{D}_s^* \hat{\mathrm{D}}_s}{2 \mathrm{RTc}_{\max} \mathrm{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \frac{\mathrm{Ch}_s}{2} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \hat{\mathrm{D}}_s \hat{\mathcal{K}}_s \hat{\nabla}_x^3 \hat{c} \right]$$

For the electrolyte phase, the compositionally-induced mechanical stress terms in the mass and charge conservation equations are negligible, since Young's Modulus is small

(about one to three orders of magnitude smaller than in the solid phase, for plasticized electrolytes and polymer separators, [98]). The resultant simplified equations:

$$\frac{\partial \hat{c}}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left[ \frac{\hat{c}(2-t_+)\hat{D}_e}{2\mathrm{RT}c_{\max}} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \mathrm{Ch}_e \frac{(2-t_+)}{2} \hat{D}_e \hat{\mathcal{K}}_e \hat{\nabla}_x^3 \hat{c} + 2\mathrm{Pe}_e t_+ \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} \right] 
\frac{\partial \hat{\rho}}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left[ 2\mathrm{Pe}_e \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} + \frac{\hat{c}}{2\mathrm{RT}c_{\max}} \hat{D}_e \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \frac{\mathrm{Ch}_e}{2} \hat{D}_e \hat{\mathcal{K}}_e \hat{\nabla}_x^3 \hat{c} \right]$$
(2.12)

By applying the methodology summarized in Appendix A, the upscaled-homogenized transport equations approximated to  $\mathcal{O}(\xi^2)$  in the solid phase are:

$$\epsilon_{s} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})\mathrm{D}_{s}^{*}}{2\mathrm{RT}c_{\max}\mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial \hat{c}^{2}} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\nabla}_{x}^{2} \left\langle \hat{c} \right\rangle - \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{4} \left\langle \hat{c} \right\rangle - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( 2\frac{\partial \left\langle \hat{\sigma} \right\rangle}{\partial \hat{x}} \left\langle \frac{\partial^{2}\varepsilon_{\mathrm{Che}}}{\partial \hat{c}^{2}} \right\rangle \hat{\nabla}_{x} \left\langle \hat{c} \right\rangle + \left\langle \frac{\partial\varepsilon_{\mathrm{Che}}}{\partial \hat{c}} \right\rangle \frac{\partial^{2} \left\langle \hat{\sigma} \right\rangle}{\partial \hat{x}^{2}} \right) - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \left\langle \hat{\sigma} \right\rangle \left\langle \frac{\partial^{2}\varepsilon_{\mathrm{Che}}}{\partial \hat{c}^{2}} \right\rangle \hat{\nabla}_{x}^{2} \left\langle \hat{c} \right\rangle \right) - \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{\epsilon_{s}}{\xi} \mathrm{Da}_{s} \hat{\mathcal{A}} \hat{j}_{BV}$$
(2.13)

$$\begin{aligned} \epsilon_s \frac{\partial \left\langle \hat{\rho} \right\rangle}{\partial \hat{t}} =& 2 \mathrm{Pe}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \left\langle \hat{\sigma}_T \right\rangle \hat{\nabla}_x^2 \hat{\phi} + \frac{\hat{c} \mathrm{D}_s^*}{2 \mathrm{RT} c_{\max} \mathrm{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \left\langle \hat{\mathrm{D}}_s \right\rangle \hat{\nabla}_x^2 \hat{c} \\ &- \frac{\mathrm{Ch}_s}{2} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \left\langle \hat{\mathrm{D}}_s \right\rangle \hat{\mathcal{K}}_s \hat{\nabla}_x^4 \hat{c} - \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{\epsilon_s}{\xi} \mathrm{Da}_s \hat{\mathcal{A}} \hat{j}_{BV} \end{aligned}$$

and in the electrolyte phase:

$$\epsilon_{e} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})}{2 \mathrm{RT} c_{\mathrm{max}}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle - \mathrm{Ch}_{e} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\mathcal{K}}_{e} \hat{\nabla}_{x}^{4} \langle \hat{c} \rangle + 2 \mathrm{Pe}_{e} t_{+} \left\langle \hat{\sigma}_{T} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{\phi} \rangle + \frac{\epsilon_{e}}{\xi} \mathrm{Da}_{e} \hat{\mathcal{A}} \hat{j}_{BV}$$

$$(2.14)$$

$$\begin{split} \epsilon_e \frac{\partial \left\langle \hat{\rho} \right\rangle}{\partial \hat{t}} = & 2 \mathrm{Pe}_e \left\langle \hat{\sigma}_T \right\rangle \hat{\nabla}_x^2 \hat{\phi} + \frac{\hat{c}}{2 \mathrm{RT} c_{\mathrm{max}}} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \left\langle \hat{\mathrm{D}}_e \right\rangle \hat{\nabla}_x^2 \hat{c} \\ & - \frac{\mathrm{Ch}_e}{2} \left\langle \hat{\mathrm{D}}_e \right\rangle \hat{\mathcal{K}} \hat{\nabla}_x^4 \hat{c} + \frac{\epsilon_e}{\xi} \mathrm{Da}_e \hat{\mathcal{A}} \hat{j}_{BV} \end{split}$$

Define the Fourier numbers:  $Fo_s = \frac{D_s^*}{D_e^*}$  and  $Fo_e = \frac{D_e^*}{D_e^*}$ , and recast equation set 2.13 as:

$$\epsilon_{s} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})}{2 \mathrm{RT}c_{\mathrm{max}}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \mathrm{Fo}_{s} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle - \mathrm{Ch}_{s} \mathrm{Fo}_{s} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{4} \langle \hat{c} \rangle - \mathrm{Ss} \mathrm{Fo}_{s} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( 2 \frac{\partial \langle \hat{\sigma} \rangle}{\partial \hat{x}} \left\langle \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}^{2}} \right\rangle \hat{\nabla}_{x} \langle \hat{c} \rangle + \left\langle \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}} \right\rangle \frac{\partial^{2} \langle \hat{\sigma} \rangle}{\partial \hat{x}^{2}} \right) - \mathrm{Ss} \mathrm{Fo}_{s} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \langle \hat{\sigma} \rangle \left\langle \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}^{2}} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle \right) - \frac{\epsilon_{s}}{\xi} \mathrm{Da}_{s} \mathrm{Fo}_{s} \hat{\mathcal{A}} \hat{j}_{BV}$$
(2.15)

$$\epsilon_{s} \frac{\partial \langle \hat{\rho} \rangle}{\partial \hat{t}} = 2 \operatorname{Pe}_{s} \operatorname{Fo}_{s} \langle \hat{\sigma}_{T} \rangle \, \hat{\nabla}_{x}^{2} \hat{\phi} + \operatorname{Fo}_{s} \frac{\hat{c} \mathrm{D}_{s}^{*}}{2 \mathrm{RT} c_{\max} \mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\nabla}_{x}^{2} \hat{c}$$
$$- \operatorname{Ch}_{s} \operatorname{Fo}_{s} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{4} \hat{c} - \frac{\epsilon_{s}}{\xi} \operatorname{Da}_{s} \operatorname{Fo}_{s} \hat{\mathcal{A}} \hat{j}_{BV}$$

Similarly, for equation set 2.14:

$$\epsilon_{e} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})}{2 \mathrm{RT} c_{\mathrm{max}}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \mathrm{Fo}_{e} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle - \mathrm{Ch}_{e} \mathrm{Fo}_{e} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\mathcal{K}}_{e} \hat{\nabla}_{x}^{4} \langle \hat{c} \rangle + 2 \mathrm{Pe}_{e} \mathrm{Fo}_{e} t_{+} \left\langle \hat{\sigma}_{T} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{\phi} \rangle + \frac{\epsilon_{e}}{\xi} \mathrm{Da}_{e} \mathrm{Fo}_{e} \hat{\mathcal{A}} \hat{j}_{BV}$$

$$(2.16)$$

$$\begin{split} \epsilon_e \frac{\partial \left\langle \hat{\rho} \right\rangle}{\partial \hat{t}} =& 2 \mathrm{Pe}_e \mathrm{Fo}_e \left\langle \hat{\sigma}_T \right\rangle \hat{\nabla}_x^2 \hat{\phi} + \mathrm{Fo}_e \frac{\hat{c}}{2 \mathrm{RT} c_{\mathrm{max}}} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \left\langle \hat{\mathrm{D}}_e \right\rangle \hat{\nabla}_x^2 \hat{c} \\ &- \mathrm{Ch}_e \mathrm{Fo}_e \left\langle \hat{\mathrm{D}}_e \right\rangle \hat{\mathcal{K}}_e \hat{\nabla}_x^4 \hat{c} + \frac{\epsilon_e}{\xi} \mathrm{Da}_e \mathrm{Fo}_e \hat{\mathcal{A}} \hat{j}_{BV} \end{split}$$

The dimensionless numbers associated to equation sets 2.15 and 2.16 enable to identify the contribution of each term of the governing equations to the kinetics of the system. A comparison of the magnitude of the dimensionless numbers provides a simple criteria to remove those terms with a negligible contribution to describe the physical phenomena, which in turn leads to simplified equations and thus faster numerical simulations. For example, gradient energy or mechanical stress contributions to the transport of lithium-ions can be removed from the calculation if  $Ss_iFo_i \ll Fo_i$ or  $Ch_iFo_i \ll Fo_i$ , thus accelerating dramatically the computation. Macroscale models adhere to the continuum approximation assumption when homogeneity is preserved, *i.e.*, macro and micro scales remain uncoupled, [34]. Specifically, diffusion-dominated transport enforces homogeneity, thus any other driving force should be smaller in order for the model to be valid. However, fast intercalation, as achieved at high C-rates, induces larger electrochemical and chemomechanical gradients, [71], and consequently loss of fidelity and prediction power of upscaledhomogenized models, [34, 72, 73]. In this context, if the gradient energy contribution is also considered in lithium-ions transport equations, the conditions to enforce separation of scales demand: (a) gradient energy contribution slower than diffusion,  $Ch_iFo_i < Fo_i$ ; (b) electromigration slower than diffusion,  $Pe_iFo_i < Fo_i$ ; (c) intercalation reaction slower than diffusion,  $Da_iFo_i < Fo_i$ ; (d) intercalation reaction slower than gradient energy contribution,  $Da_i < Ch_i$ ; and (e) intercalation reaction slower than electromigration,  $Da_i < Pe_i$ .

The modern description of LIBs that demand to include the mechanical stress contribution to the mass and charge transport equations requires to enforce separation of scales: (a) mechanical stress slower than diffusion,  $Ss_iFo_i < Fo_i$ ; (b) electromigration slower than diffusion,  $Pe_iFo_i < Fo_i$ ; (c) intercalation reaction slower than diffusion,  $Da_iFo_i < Fo_i$ ; (d) intercalation reaction slower than mechanical stress,  $Da_i < Ss_i$ ; and (e) intercalation reaction slower than electromigration,  $Da_i < Pe_i$ . If gradient energy and mechanical stress contributions are simultaneously relevant, the conditions to enforce separation of scales are:  $Fo_i > Pe_i > Ch_i > Ss_i > Da_i$ , where i= {solid, electrolyte}.

In the absence of gradient energy and chemomechanical stresses, equation sets 2.15 and 2.16 reduce to the well-known Newman-type model, when the diffusivity is setup as independent of concentration and transference number:  $\frac{\hat{c}(2-t_+)}{2\mathrm{RT}c_{\max}}\mathrm{U}^*\frac{\partial^2\hat{g}}{\partial\hat{c}^2} = 1$  and  $\frac{(2-t_+)}{2}$ . For the solid phase:

$$\epsilon_s \frac{\partial \langle \hat{c}_s \rangle}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left( \operatorname{Fo}_s \epsilon^{1+\alpha} \hat{\nabla}_x \langle \hat{c}_s \rangle \right) + \frac{\epsilon_s}{\xi} \hat{\mathcal{A}} \operatorname{Da}_s \operatorname{Fo}_s \hat{j}_{BV}$$

$$0 = \nabla_x \cdot \left( 2\operatorname{Pe}_s \operatorname{Fo}_s \epsilon^{1+\alpha} \hat{\nabla}_x \langle \hat{\phi}_s \rangle \right) + \frac{\epsilon_s}{\xi} \hat{\mathcal{A}} \operatorname{Da}_s \operatorname{Fo}_s \hat{j}_{BV}$$

$$(2.17)$$

and for the electrolyte phase:

$$\epsilon_{e} \frac{\partial \langle \hat{c}_{e} \rangle_{\mathcal{B}}}{\partial \hat{t}} = \hat{\nabla}_{x} \cdot \left( \epsilon^{1+\alpha} \operatorname{Fo}_{e} \hat{\nabla}_{x} \langle \hat{c}_{e} \rangle + 2\operatorname{Pe}_{e} \operatorname{Fo}_{e} t_{+} \epsilon^{1+\alpha} \hat{\nabla}_{x} \langle \hat{\phi}_{e} \rangle \right) + \frac{\epsilon_{e}}{\xi} \hat{\mathcal{A}} \operatorname{Da}_{e} \operatorname{Fo}_{e} \hat{j}_{BV}$$

$$0 = \hat{\nabla}_{x} \cdot \left( 2\operatorname{Pe}_{e} \operatorname{Fo}_{e} \epsilon^{1+\alpha} \hat{\nabla}_{x} \langle \hat{\phi}_{e} \rangle \right) + \frac{\epsilon_{e}}{\xi} \hat{\mathcal{A}} \operatorname{Da}_{e} \operatorname{Fo}_{e} \hat{j}_{BV}$$

$$(2.18)$$

These two sets of equations are equivalent to those reported by Battiato et al. [34].

From equation sets 2.17 and 2.18, define the extended dimensionless numbers:

$$Fo_{\mu} = Fo \ \epsilon^{1+\alpha}$$

$$Pe_{\mu} = Pe \ \epsilon^{1+\alpha}$$

$$Da_{\mu} = Da \ \hat{\mathcal{A}}\epsilon_{i}$$
(2.19)

as the microstructural Fourier, Péclet and Damköhler numbers, and lead to the following revised constraints to enforce scale separation by including the effect of microstructure:

$$\xi = \frac{2\mathbf{r}_p}{\mathbf{L}} \ll 1 \tag{2.20}$$

$$\mathrm{Da}_{\mu}\mathrm{Fo} < \mathrm{Fo}_{\mu} \tag{2.21}$$

$$Pe_{\mu}Fo < Fo_{\mu} \tag{2.22}$$

$$\mathrm{Da}_{\mu} < \mathrm{Pe}_{\mu} \tag{2.23}$$

Following Battiato *et al.* [34], microstructural Fourier, Péclet, and Damköhler parameters expressed as a power of the scalar  $\xi$  are: Fo<sub> $\mu$ </sub> =  $\xi^{-\delta}$ , Pe<sub> $\mu$ </sub> =  $\xi^{\beta}$ , and Da<sub> $\mu$ </sub> =  $\xi^{\gamma}$ . <sup>1</sup> Equation 2.21 is satisfied for any  $\gamma < \left(-\delta - \frac{\ln{(Fo)}}{\ln(\xi)}\right)$ . Equation 2.22 is satisfied for any  $\beta < \left(-\delta - \frac{\ln{(Fo)}}{\ln(\xi)}\right)$ . In the limit of  $\gamma = -\beta$ , Pe<sub> $\mu$ </sub> = Da<sub> $\mu$ </sub> and equation 2.23 is satisfied for any  $\gamma > -\beta$ .

<sup>&</sup>lt;sup>1</sup>The minus sign for the  $\delta$  exponent is required for orthogonal plots in equations 2.21 and 2.22. Similarly, a minus sign in the  $\beta$  exponent will be required to plot equation 2.23, in agreement with Battiato *et al.*, [34].

## 2.3 Implementation for Example Chemistries and Porous Microstructures

To determine the limits of microstructural validity of Newman-type models, analytical symbolic calculations were performed in Mathematica, version 10.4.0.0, [74], where extended dimensionless numbers and physical constraints (equations 2.20, to 2.23) were enforced.

The markers in Figures 2.1 and 2.3, represent the relation  $\gamma = f(-\beta)$ , where  $\gamma$ and  $\beta$  are the exponents in the expressions that relate the scaling parameter,  $\xi$ , to the dimensionless numbers. For microstructure-enhanced dimensionless numbers the relations are: Fo<sub> $\mu$ </sub> =  $\xi^{-\delta}$ , Pe<sub> $\mu$ </sub> =  $\xi^{\beta}$ , and Da<sub> $\mu$ </sub> =  $\xi^{\gamma}$ , while for microstructure-free are: Fo =  $\xi^{-\delta}$ , Pe =  $\xi^{\beta}$ , and Da =  $\xi^{\gamma}$ .

Figure 2.2 represents an extension of the relation  $\gamma = f(-\beta)$ , that determines the range of the function due to subsidiary functional relations. Thus,  $\text{Da}_{\mu} = f(\epsilon, \alpha, \hat{\mathcal{A}})$ , and  $\text{Pe}_{\mu} = f(\epsilon, \alpha)$ , where  $\alpha = f(\text{L}_{xx})$ ,  $\hat{\mathcal{A}} = f(\epsilon, \text{r}_a)$ , and  $\text{L}_{xx} = f(\text{r}_a)$ . Full descriptions of the dimensionless reactive area density,  $\hat{\mathcal{A}}$ , the Bruggeman exponent,  $\alpha$ , and the through-thickness depolarization factor for fully aligned particles,  $\text{L}_{xx}$ , are available in the literature, [41].

Figure 2.4, represents the inequality  $\text{Pe } \epsilon^{\alpha} \geq -\text{Da } \hat{\mathcal{A}}$ , where the functional relations  $\alpha = f(\mathcal{L}_{xx} = f(\mathbf{r}_a))$ , and  $\hat{\mathcal{A}} = f(\epsilon, \mathbf{r}_a)$  were applied. Table 2.2 summarizes the properties used to calculate dimensionless numbers for typical commercial batteries.
	$\mathbf{r}_p$	L	k	$D_e$	$\sigma^e_T$	$c_{\max}$	$D_s$	$\sigma_T^s$	
Chemistry	[m]	[m]	$\left[\frac{\mathrm{m}}{\mathrm{s}}\right]$	$\left[\frac{\mathrm{m}^2}{\mathrm{s}}\right]$	$\left[\frac{1}{\Omega \text{ m}}\right]$	$\left[\frac{mol}{m^3}\right]$	$\left[\frac{\mathrm{m}^2}{\mathrm{s}}\right]$	$\left[\frac{1}{\Omega \ m}\right]$	Ref.
	$\times 10^{-6}$	$5 \times 10^{-5}$	$5 \times 10^{-9}$	$\times 10^{-10}$	)	$\times 10^4$	$\times 10^{-15}$		
${ m LiC}_6$	12	9.3	7.7	2.9	1.1	2.82	100	100	[75, 76]
$\rm LiFePO_4$	11	9.2	5.9	2.3	1.3	2.64	1.2	0.01	[77]
$\rm LiMn_2O_4$	1.7	5.0	76.0	3.2	1.83	2.29	6.0	10	[78, 79]
$\mathrm{Li}_4\mathrm{Ti}_5\mathrm{O}_{12}$	0.01	6.6	150.0	2.0	0.28	2.28	6.8	100	[80]
$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	5.0	4.6	8.3	2.7	0.98	3.62	30.0	3.8	[28, 29]
$\operatorname{Li}_{x}\operatorname{Ni}_{y}\operatorname{Co}_{z}\operatorname{Al}_{1-y-z}\operatorname{O}_{2}$	2.5	5.0	23.0	3.2	0.87	4.95	100	10	[78]
$\rm LiCoO_2$	10	8.0	4.5	2.6	1.0	5.10	10	100	[30, 39]

Table 2.2.: Macroscale parameters, solid particle size and electrode size; as reported in the literature for the different Li-ion chemistries [28–30, 39, 75–80]. These values are used to calculate the transport numbers as listed in the Table B.1.

#### 2.4 Results and Discussion

Figure 2.1 summarizes the effect of the microstructure on Péclet and Damköhler numbers in the electrolyte, for selected chemistries. Values of dimensionless numbers are reported in Table B.1 in appendix B. In the absence of mechanical stresses and gradient energy contributions, the shaded area corresponds to the region of validity of a Newman-type model, and encloses the constraints to enforce separation of scales, where a coarse-grained description of the transport at the macroscopic level is decoupled from the microscopic description.

Figure 2.1 demonstrates that the validity of a Newman-type model to describe the electrolyte phase is very sensitive to the morphology of secondary particles of active material. For example, the platelet-shaped morphology of LiFePO<sub>4</sub> with aspect ratio of c/a ~ 0.3, induces a high dimensionless reactive area density,  $\hat{\mathcal{A}} = 3.7$ , and consequently a high intercalation reaction. Its corresponding Bruggeman exponent,  $\alpha = 3.01$ , causes a high through-thickness tortuosity of  $\tau = 37.5$  with an assumed porosity of  $\epsilon_e = 0.3$ . Tortuosity greatly decreases the effective ionic conductivity and, accordingly, the electromigration contribution. Thus, the intercalation reaction, in LiFePO<sub>4</sub>-based electrode layers, dominates over the electromigration process. In this case, the intrinsic microstructure impedes the validity of the model.

An essential assumption on Newman-type models is the expected spherical morphology of secondary particles. However, spherically-shaped particles of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ chemistry are shown outside the region of validity in Figure 2.1, and thus coarsegrained models are not useful. This situation is avoided if hypothetical prolate-shaped  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  particles with aspect ratios,  $c/a \sim 5.0$ , and electrode porosity of  $\epsilon_e = 0.88$  is modeled instead. Here, the dimensionless reactive area density drops from  $\hat{\mathcal{A}} = 2.14$ to  $\hat{\mathcal{A}} = 0.31$ , and the Bruggeman exponent of  $\alpha = 0.06$  decreases the tortuosity 0.47% to  $\tau \sim 1$ .

LiC<sub>6</sub>, the most widely used material in rechargeable LIBs, is typically used in platelet form with aspect ratios c/a ~ 0.3 and electrode porosity of  $\epsilon_e \sim 0.3$ , naturally placing it in the non-valid regime. A simple change of the particle aspect ratio to c/a ~ 0.5, favors a decrease in tortuosity from  $\tau = 10.5$  to  $\tau = 3.8$ , enabling the electromigration to dominate over the intercalation reaction, bringing the Newmantype model back to validity for this chemistry.



Figure 2.1. Effect of the microstructure on the model validity for Li-ion transport in the electrolyte phase as a function of Péclet and Damköhler numbers. Open symbols represent microstructure free chemistries:  $\triangleright$  LiC<sub>6</sub>,  $\triangle$  LiFePO<sub>4</sub>,  $\bigcirc$  LiMn<sub>2</sub>O<sub>4</sub>,  $\square$  Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>,  $\diamondsuit$  LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>,  $\Leftrightarrow$  LiNi<sub>0.8</sub>Co<sub>0.2-x</sub>Al<sub>x</sub>O<sub>2</sub>,  $\triangledown$  LiCoO<sub>2</sub>. Filled symbols describe the effect of microstructure:  $\blacktriangleright$  LiC<sub>6</sub>,  $\triangle$  LiFePO<sub>4</sub>,  $\bigcirc$  LiNi<sub>0.8</sub>Co<sub>0.2-x</sub>Al<sub>x</sub>O<sub>2</sub>,  $\bigstar$  LiCoO<sub>2</sub>. The shaded-region above the diagonal line corresponds to the regime where Newman-type models are valid. Model predicts that Newman approaches will only be valid when diffusion dominates over reaction and the electromigration processes.

For a LiMn<sub>2</sub>O<sub>4</sub>-based electrode, Figure 2.2 (a) highlights the region where the constraint  $Da_{\mu} < Pe_{\mu}$  is satified. Basically, intercalation reaction is slower than electromigration for electrodes with porosity  $\epsilon_e \geq 0.3$  for a wide range of particle shapes. Figure 2.2 (b) shows electrode microstructures that satisfy the constraint,  $Da_{\mu}Fo < Fo_{\mu}$ . Results demonstrate that the model is valid for a wide range of combinations of particle shapes and porosity values, except for platelet-shaped particles and porosities  $\epsilon_e < 0.3$ . LiMn<sub>2</sub>O<sub>4</sub> particles, with octahedral-like shape [79, 81, 82] tailored to aspect ratios ranging  $0.1 \leq c/a \leq 10$ , are valid for cases with porosities  $\epsilon_e \geq 0.3$  and aspect ratios  $c/a \geq 1$  or porosities  $\epsilon_e \geq 0.45$  and aspect ratios  $0.5 \leq c/a \leq 1$ . Another range of validity includes porosities  $\epsilon_e \geq 0.7$  and aspect ratios  $0.2 \leq c/a \leq 0.5$ .

For highly aligned particles of high aspect ratios, the Bruggeman exponent,  $\alpha$ , increases far above 0.5 [41], and the microstructural Péclet number reaches the asymptote  $\operatorname{Pe}_{\mu} \rightarrow \left(\frac{\operatorname{RT}\sigma_e}{\mathcal{F}^2 \operatorname{D}_e c_{\max}}\right)$  in the limit  $\epsilon \rightarrow 1$ . Because both dimensionless numbers, Fo<sub>µ</sub> and Pe<sub>µ</sub>, have the same microstructural dependence ( $\epsilon^{1+\alpha}$ ), the validity condition Pe<sub>µ</sub> < Fo<sub>µ</sub>, reduces to Pe < 1, as reported in previous work [34].



Figure 2.2. Regions of validity as a function of porosity in the electrolyte and secondary particle aspect ratio for LiMn<sub>2</sub>O<sub>4</sub>-based battery electrodes. — correspond to constant values of electrode porosity as particle aspect ratio change values,  $0.1 \leq c/a \leq 10$ . — correspond to constant values of particle aspect ratio for electrode porosity moving in the range  $0.1 \leq \epsilon \leq$ 1. ( $\triangleright$ ,  $\blacktriangle$ ,  $\bigcirc$ ,  $\blacksquare$ ,  $\diamondsuit$ ,  $\bigstar$ ,  $\blacktriangledown$ ) correspond to different tailored microstructures of LiMn<sub>2</sub>O<sub>4</sub>-based battery electrodes. The shaded-region corresponds to the validity regime. Inset (a) demonstrates that intercalation reaction is slower than electromigration for electrodes with  $\epsilon_e \geq 0.3$  and  $c/a \geq$ 1. Inset (b) reveals that the intercalation reaction is slower than diffusion except for  $\epsilon_e < 0.3$  and  $c/a \leq 0.3$ . Aspect ratio isocontours asymptotically collapse into a vertical green line | as the porosity,  $\epsilon$ , approximates 1. Aspect ratios, c/a > 1 generate overlapping curves.

Figure 2.3 summarizes the space of validity of porous electrode theory models to describe lithium-ion transport inside the particles of active material. Results demonstrate that for all existing particle shapes and sizes, the numerical homogenized description of lithium transport inside secondary particles with internal microstructure is not valid because lithium-ion diffusivity in the solid phase is five orders of magnitude smaller than in the electrolyte phase. In addition, spinodal decomposition and stress-induced kinetics are mechanisms that should be included, as reported by several authors [25, 54, 57, 59, 69]



Figure 2.3. Effect of microstructure on the validity of the description of the Li-ion transport in the solid phase as a function of Péclet and Damköhler numbers for the porous electrode model. Empty symbols represent microstructure free chemistries:  $\triangleright$  LiC<sub>6</sub>,  $\triangle$  LiFePO<sub>4</sub>,  $\bigcirc$  LiMn<sub>2</sub>O<sub>4</sub>,  $\Box$  Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>,  $\diamond$  LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>,  $\thickapprox$  LiNi<sub>0.8</sub>Co<sub>0.2-x</sub>Al<sub>x</sub>O<sub>2</sub>,  $\nabla$  LiCoO<sub>2</sub>. Filled symbols demonstrate the effect of microstructure for the same chemistries:  $\triangleright$  LiC<sub>6</sub>,  $\triangle$  LiFePO<sub>4</sub>,  $\bigcirc$  LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>,  $\bigstar$  LiOO<sub>2</sub>. Filled symbols demonstrate the effect of microstructure for the same chemistries:  $\triangleright$  LiC<sub>6</sub>,  $\triangle$  LiFePO<sub>4</sub>,  $\bigcirc$  LiMn<sub>2</sub>O<sub>4</sub>,  $\blacksquare$  Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>,  $\blacklozenge$  LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>,  $\bigstar$  LiNi<sub>0.8</sub>Co<sub>0.2-x</sub>Al<sub>x</sub>O<sub>2</sub>,  $\bigtriangledown$  LiCoO<sub>2</sub>). The shaded-region corresponds to the validity regime. Considering porous electrode theory's model will only be valid when diffusion dominate, most (if not all) of the existing chemistries require to spatially describe the effect of the internal microstructural features of the active solid particles.

The overall validity of classic porous electrode theory models as a function of porosity and secondary particle aspect ratio is summarized in Figure 2.4. Here, a physically accessible maximal random packaging limit, [84] (red line), defines an additional physical constraint that is not directly included in the formulation. The blue line represents the constraint  $Da_{\mu} = Pe_{\mu}$  for inset (i), and  $Da_{\mu}Fo = Fo_{\mu}$  for inset (ii).  $Da_{\mu} = Pe_{\mu}$ is more restrictive and supersedes  $Da_{\mu}Fo = Fo_{\mu}$ . Four regimes are identified: regime (a), which defines the valid range of aspect ratios and porosities where porous electrode theory models can be used; regime (b), where spatially-resolved models are best suited to describe porous battery electrodes; regimes (c) and (d), which are physically inaccessible because it is topologically impossible to pack secondary particles of active material at the specified aspect ratio and porosity.

Figure 2.4 was derived for LiMn<sub>2</sub>O<sub>4</sub>-based porous electrodes, but the methodology that results on the proposed guidelines can be easily extended to assess in general the validity of Newman-type models for commercially available LIBs. Thus, for most chemistries (LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub>, LiNi<sub>0.8</sub>Co<sub>0.2-x</sub>Al<sub>x</sub>O<sub>2</sub>, LiCoO<sub>2</sub>, etc.), the electrodes with typical porosity of  $\epsilon_e \sim 0.36$  and aspect ratios  $c/a \ge 0.7$  can be faithfully described by Newman-type models. LiFePO<sub>4</sub> electrodes with a typical porosity of  $\epsilon_e$  $\sim 0.36$  and platelet-shaped particles with a spect ratios c/a  $\sim 0.2$  are not accurately described by porous electrode theory models. Aspect ratios above c/a = 0.3 would enable a valid calculation. Similarly,  $LiC_6$  electrodes of platelet-shaped particles of aspect ratios c/a  $\leq 0.3$  and porosity  $\epsilon_e \sim 0.36$  are not well described, but if c/a = 0.4 the validity of Newman-type models would be restored, e.g., models with  $LiC_6$ -Mesocarbon Microbeads (MCMB) anodes are accurate as long as the electrode porosity remains high,  $\epsilon_e \geq 0.36$ . This adds an additional limitation to the design of advanced LIBs because the community aims to the manufacturing of lower porosity electrodes, and particles displaying aspect ratios and alignments that differ greatly from the spherical limit.



Figure 2.4. Regions of validity for Newman-type model of LiMn<sub>2</sub>O<sub>4</sub>. — corresponds to maximal random packing of ellipsoids as reported by Torquato *et al.* [84]. Validity of the homogenized Newman-type model corresponds to the region above the blue line —. For inset (i), the blue line represent  $Da_{\mu} = Pe_{\mu}$ , while for inset (ii) represents  $Da_{\mu}Fo = Fo_{\mu}$ . Four regimes of behavior are observed: Regime (a), where the Newmantype model simulation would be inaccurate, even for physically accessible particle packing configurations and porosities; Regime (b), where the Newman-type model is valid; Regime (c), where the Newman-type model is valid, but the microstructures are physically inaccessible; Finally regime (d), where the Newman models are invalid, and the porous microstructures are physically inaccessible. Simulations in regime (a), should be modeled with spatially-resolved numerical methodology, while regime (c) delivers simulations of batteries that would be impossible to manufacture.

## 2.5 Summary and Conclusions

A free energy variational principle was used as a starting point to derive transport equations, that incorporate multiphysical contributions such as the gradient energy and the mechanical stresses in a thermodynamically consistent way. The resultant phase field formulation was used as a starting point to develop an homogenized description of the kinetic equations, including the conditions to enforce separation of scales, requiring diffusion to dominate over electromigration, gradient energy, mechanical stresses, and intercalation reaction terms.

A set of practical, numerically quantifiable microstructural guidelines to define the validity of the generality of porous electrode theory models were defined. These were consolidated into four regimes of behavior: regime (a), which defines the valid range of aspect ratios and porosities where porous electrode theory models can be used; regime (b), where spatially-resolved models are best suited to describe porous battery electrodes; regimes (c) and (d), which are physically inaccessible because it is topologically impossible to pack secondary particles of active material at the specified aspect ratio and porosity. Specifically, the spherically-shaped active particles approximation is neither representative of real porous microstructures, nor it guarantees the validity of a porous electrode theory model. Size, aspect ratio, and morphological texture of the secondary particles, as well as the porosity and reactive area density, all have to be taken into consideration to accurately define a physical model to describe the generality of porous battery materials, and to design advanced LIBs.

# 3. COARSE-GRAINED ELECTROCHEMOMECHANICAL EFFECTS IN POROUS RECHARGEABLE LITHIUM-ION BATTERIES

A version of this chapter is currently in preparation for journal publication as: J.A. Campos, A. Deva, J. Lund, A. Jana, I. Battiato, and R.E. García. "Coarse-grained Electrochemical Effects in Porous Rechargeable Lithium-ion Batteries."

## 3.1 Introduction

For large scale applications, such as those used to support the electric grid, transportation systems, and electric vehicles, the  $\text{Li}_x \text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3} \text{O}_2$  (NMC) chemistry has recently emerge as the preferred cathode chemistry due to its ease in fabrication and scalability [21], cycle stability at temperatures as high as 50 °C, and its high reversible specific capacity  $\sim 234 \text{ mAh/g}$ , [85], it became very rapidly, a popular alternative to expensive LiCoO<sub>2</sub>, a cobalt-based-only cathode material. Electrochemical models developed to understand this cathode material include the work of Christensen and coworkers [87], who coupled a heat transfer model to assess the temperature heterogeneities of NMC-based batteries, as used in transportation systems, finding that for prismatic cells at discharge rates higher than 4C, the thermal runway was slower by approximately 50% as compared to cylindrical cells. Vazquez and coworkers conducted a sensitivity analysis over the pseudo-two-dimensional porous electrode model (P2D) parameters for an NMC-based pouch battery [27], identifying the volume fractions of the solid phases as the sources of higher variability of the cell potential. Dees, Abraham, et al. studied the electronic conductivity effects in Mn-rich oxides with a modified volume-averaged model that incorporated capacitive terms in parallel with the Butler-Volmer reaction and the contact-resistance, [88]. Smekens and coworkers derived a conventional porous electrode theory model by starting from irreversible thermodynamics principles to describe the transport of multiple species in the electrolyte, [29]. Danner, Latz, and coworkers, simulated thick NMC-based electrodes, larger than 300  $\mu$ m, with a three-dimensional microstructurally resolved model aided with kinetic parameters estimated with a 1+1D supplementary model [28], finding strong transport limitations and high losses in capacity.

A few electrochemomechanical models focused on NMC-based cathodes, including the work of Ko, Lindbergh, and coworkers, studied the stress effects with a P2D model, [89]. Here, the change in chemical potential was formulated through a change in the equilibrium potential, and two mechanisms were identified: the inter-particle kinetic lithium exchange, and the intra-particle lithium diffusion. These descriptions considered short-range effects within the active particle, or inside a representative volume element.

Despite of great the advances in the electrochemical modeling of NMC-based LIBs, currently available models are based on adapting Poison-Nerst-Plank (PNP) equations, and sets of diffusion equations with a source, and are not derived from thermodynamic principles. Thus, the addition of novel physical phenomena into existing models is not guaranteed to be in agreement with the laws of thermodynamics or to be physically consistent. Furthermore, the existing averaging methodology complicates the description of the generality of transport and phase transitions in multiphase heterogeneous electrodes. In this paper, a fully homogenized phase field model that starts from well established thermodynamic principles is presented. The formulation was developed for the graphite|NMC system, and demonstrates elastic and gradient energy contributions. The effects of the different driving forces favoring or limiting power density were assessed.

# 3.2 Theoretical Framework

Define the Gibbs free energy of a material system subjected to chemical, elastic, and electric driving forces as [51–57]:

$$G[\{c_i\}, \rho, u_j; \mathbf{T}_{\circ}] = \int_{\Omega} \left( g(\{c_i\}; \mathbf{T}_{\circ}) + \sum_{i=1}^{N-1} \frac{\mathcal{K}_i}{2} |\nabla c_i|^2 + \frac{1}{2} \overset{\leftrightarrow}{\sigma} \cdot \overset{\leftrightarrow}{\varepsilon}_e + \rho \phi \right) \mathrm{d}\Omega + \int_{\Omega} \lambda(\vec{x}) \left( \rho - \sum_{i=1}^{N} \mathcal{F}z_i c_i \right) \mathrm{d}\Omega$$

$$(3.1)$$

where  $\{c_i\} = \{c_1, \ldots, c_N\}$ , is the set of the concentrations of N electrically charged species,  $u_j$  is the *j*th component of the mechanical displacement vector,  $\overleftrightarrow{\sigma}$  is the mechanical stress tensor,  $\overleftrightarrow{\varepsilon}_e$  is the total strain tensor,  $\varepsilon_{kl} = \frac{1}{2} \left( \frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k} \right)$  describes the relation of geometrical strain and displacement,  $\rho$  is the electric charge density,  $T_{\circ}$ is the temperature,  $\mathcal{K}_i$  is the interfacial gradient energy penalty of the *i*th species,  $\Omega$ is the volume of the phase in consideration,  $z_i$  is the charge valence of the *i*th species,  $\mathcal{F}$  is Faraday's constant, and  $\lambda(\vec{x})$  is a spatially varying Lagrange multiplier [58].

The resultant variational derivatives are [50–52, 54, 55]:

$$\frac{\delta G}{\delta c_i} = \frac{\partial g}{\partial c_i} - \mathcal{K}_i \nabla^2 c_i + \lambda \mathcal{F} z_i + \frac{1}{2} \frac{\partial}{\partial c_i} \left( \overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}_e \right) 
\frac{\delta G}{\delta \rho} = \phi - \lambda 
\frac{\delta G}{\delta u_i} = \nabla \cdot \overleftrightarrow{\sigma} = \vec{0}$$
(3.2)

Equation set 3.2 constitutes the electrochemomechanical driving force for transport and phase transformations, through the set of coupled Cahn-Hilliard equations:

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \mathbf{M}_i \nabla \left( \frac{\delta G}{\delta c_i} \right) = \nabla \cdot \mathbf{M}_i \nabla \left( \frac{\partial g}{\partial c_i} - \mathcal{K}_i \nabla^2 c_i + \frac{1}{2} \frac{\partial}{\partial c_i} \left( \stackrel{\leftrightarrow}{\sigma} \cdot \stackrel{\leftrightarrow}{\varepsilon}_e \right) \right) + \nabla \cdot \mathbf{M}_i \mathcal{F} z_i \nabla \lambda$$

$$\frac{\partial \rho}{\partial t} = \nabla \cdot \mathbf{M}_\rho \nabla \left( \frac{\delta G}{\delta \rho} \right) = \nabla \cdot \mathbf{M}_\rho \nabla \phi - \nabla \cdot \mathbf{M}_\rho \nabla \lambda$$
(3.3)

where  $\lambda(\vec{x}) = \frac{M_{\rho}\phi - \sum_{i=1}^{N} z_i \mathcal{F} M_i \left(\frac{\partial g}{\partial c_i} - \mathcal{K}_i \nabla^2 c_i + \frac{1}{2} \frac{\partial}{\partial c_i} \left(\overleftrightarrow{\sigma} \cdot \overleftrightarrow{\varepsilon}_e\right)\right) + \psi(\vec{x})}{M_{\rho} + \sum_{i=1}^{N} (z_i \mathcal{F})^2 M_i}$ , and  $\psi(\vec{x})$  is a solution to the Laplace equation ( $\nabla^2 \psi = 0$ ) that will vanish when substituted in equation set 3.3, in agreement with several authors [51, 58, 59].  $M_i = D_i c_i / RT$  is the chemical mobility, and  $M_{\rho} = \sum_{i=1}^{N} (z_i \mathcal{F})^2 M_i$  is the electrical mobility, where  $\sigma_T = \sigma_1 + \sigma_2 + ... + \sigma_N$ , and  $M_{\rho}/2 = \sigma_T$ , [60].

By substituting:

$$\frac{\partial c_i}{\partial t} = \nabla_x \cdot \left[ \frac{\mathcal{D}_i c_i (2 - t_i)}{2 \mathrm{RT}} \left( \frac{\partial^2 g}{\partial c_i^2} \nabla_x c_i - \mathcal{K}_i \nabla_x^3 c_i - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c_i} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c_i^2} \nabla_x c_i \right) + \frac{z_i \mathcal{F} \mathcal{D}_i c_i}{2 \mathrm{RT}} \nabla_x \phi + \sum_{j=1, i \neq j}^N \frac{\mathcal{M}_{ij}}{2} \left( \frac{\partial^2 g}{\partial c_j^2} \nabla_x c_j - \mathcal{K}_j \nabla_x^3 c_j - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c_j} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c_j^2} \nabla_x c_j \right) \right]$$

$$\frac{\partial \rho}{\partial t} = \nabla_x \cdot \left[ \sigma_T \nabla_x \phi + \sum_{i=1}^N \frac{z_i \mathcal{F} \mathcal{D}_i c_i}{2 \mathrm{RT}} \left( \frac{\partial^2 g}{\partial c_i^2} \nabla_x c_i - \mathcal{K}_i \nabla_x^3 c_i - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c_i} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c_i^2} \nabla_x c_i \right) \right]$$
(3.4)

For an intercalating material, strain is imposed in the lattice as a result of the interstitially dissolved lithium [43, 44, 57, 61–63]. The inhomogeneous distribution of solute, results in compositionally-induced stresses. Here, the total (or geometrical) strain,  $\overleftrightarrow{\varepsilon}^{T}$ , is the sum of elastic,  $\overleftrightarrow{\varepsilon}_{e}$ , and the chemical strain,  $\overleftrightarrow{\varepsilon}_{Che}$ , [64–70],  $\overleftrightarrow{\varepsilon}^{T} = \overleftrightarrow{\varepsilon}_{e} + \overleftrightarrow{\varepsilon}_{Che}$ . The stress tensor and the elastic strain are related via Hooke's law,  $\overleftrightarrow{\sigma} = \overleftrightarrow{C} \cdot \overleftrightarrow{\varepsilon}_{e}$ .

In agreement with Newman *et al.* [65–67], the Butler-Volmer relation corresponds to:

$$j_{\rm BV} = kc_e^{\alpha}(c_{\rm max} - c_s)^{\alpha}c_s^{(1-\alpha)}\exp\left(-\frac{\overleftrightarrow{\sigma}\cdot\overleftrightarrow{\varepsilon}_e}{4{\rm RT}c_{\rm max}}\right)\left(\exp\left(\frac{\alpha\mathcal{F}}{2{\rm RT}}\eta\right) - \exp\left(-\frac{(1-\alpha)\mathcal{F}}{2{\rm RT}}\eta\right)\right)$$
(3.5)

where the local surface overpotential:  $\eta = \left(\phi_s - \phi_e - j_{BV} \mathcal{F} \mathbf{R}_f - \frac{1}{2} \frac{\overrightarrow{\sigma} \cdot \overrightarrow{\varepsilon}_e}{\mathcal{F} c_{\max}}\right)$ . The exponent,  $\alpha_c$ , is the transfer coefficient, k is the reaction rate constant, and  $\mathbf{R}_f$  is the interfacial resistance, also known as 'film-contact-resistance'.

Define:

$$\hat{c} = \frac{c}{c_{\max}}, \qquad \hat{x} = \frac{x}{L}, \qquad \hat{\phi} = \frac{z\mathcal{F}\phi}{2R\Gamma}, \qquad \hat{\rho} = \frac{\rho}{z\mathcal{F}c}, \qquad \hat{D} = \frac{D}{D^*} 
\hat{\sigma} = \frac{\sigma}{\sigma^*}, \qquad \hat{\mathcal{K}} = \frac{\mathcal{K}}{\mathcal{K}^*}, \qquad \hat{M} = \frac{M}{M^*}, \qquad \hat{M}_{\rho} = \frac{M_{\rho}}{M_{\rho}^*}, \qquad \hat{t} = \frac{t}{t_{D_{\rho}}} 
\hat{g} = \frac{g}{U}, \qquad \nabla = \frac{\hat{\nabla}}{L}, \qquad \frac{\partial}{\partial c} = \frac{1}{c_{\max}}\frac{\partial}{\partial \hat{c}}, \qquad \frac{\partial}{\partial c^2} = \frac{1}{c_{\max}^2}\frac{\partial}{\partial \hat{c}^2}, \qquad \frac{\partial}{\partial t} = \frac{1}{t_{D_{\rho}}}\frac{\partial}{\partial \hat{t}} 
\frac{\partial}{\partial x} = \frac{1}{L}\frac{\partial}{\partial \hat{x}}, \qquad \frac{\partial^2}{\partial x^2} = \frac{1}{L^2}\frac{\partial^2}{\partial \hat{x}^2}, \qquad \frac{\partial^3}{\partial x^3} = \frac{1}{L^3}\frac{\partial^3}{\partial \hat{x}^3}$$
(3.6)

which upon substitution into equation set 3.4, results in the following:

$$\begin{split} \frac{\partial \hat{c}}{\partial \hat{t}} = &\hat{\nabla}_x \cdot \left[ \frac{\hat{c}(2-t_+) \mathbf{D}_s^* \hat{\mathbf{D}}_s}{2 \mathbf{R} \mathbf{T} \mathbf{c}_{\max} \mathbf{D}_e^*} \mathbf{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \frac{\mathbf{D}_s^* c \mathcal{K}_s^*}{\mathbf{D}_e^* \mathbf{R} \mathbf{T} \mathbf{L}^2 c_{\max}^2} \frac{(2-t_+)}{2} \hat{\mathbf{D}}_s \hat{\mathcal{K}}_s \hat{\nabla}_x^3 \hat{c} \right. \\ &- \frac{\mathbf{D}_s^* c \sigma^*}{\mathbf{D}_e^* \mathbf{R} \mathbf{T} c_{\max}^2} \frac{(2-t_+)}{2} \hat{\mathbf{D}}_s \left( \frac{\partial \varepsilon_{\text{Che}}}{\partial \hat{c}} \hat{\nabla}_x \hat{\sigma} + \hat{\sigma} \frac{\partial^2 \varepsilon_{\text{Che}}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} \right) + \frac{2 \mathbf{R} \mathbf{T} \sigma_T^*}{(z \mathcal{F})^2 \mathbf{D}_e^* c_{\max}} t_+ \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} \bigg] \end{split}$$

$$\frac{\partial \hat{\rho}}{\partial \hat{t}} = \hat{\nabla}_{x} \cdot \left[ \frac{2 \mathrm{RT} \sigma_{T}^{*} \mathrm{D}_{s}^{*}}{(z\mathcal{F})^{2} \mathrm{D}_{s}^{*} c_{\max} \mathrm{D}_{e}^{*}} \hat{\sigma}_{T} \hat{\nabla}_{x} \hat{\phi} + \frac{\hat{c} \mathrm{D}_{s}^{*} \hat{\mathrm{D}}_{s}}{2 \mathrm{RT} \mathrm{c}_{\max} \mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \hat{\nabla}_{x} \hat{c} - \frac{1}{2} \frac{\mathrm{D}_{s}^{*} \hat{c} \mathcal{K}_{s}^{*}}{\mathrm{D}_{e}^{*} \mathrm{RTL}^{2} c_{\max}^{2}} \hat{\mathrm{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{3} \hat{c} - \frac{1}{2} \frac{\mathrm{D}_{s}^{*} \mathrm{c} \sigma^{*}}{\mathrm{D}_{e}^{*} \mathrm{RTL}^{2} c_{\max}^{2}} \hat{\mathrm{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{3} \hat{c} - \frac{1}{2} \frac{\mathrm{D}_{s}^{*} \mathrm{c} \sigma^{*}}{\mathrm{D}_{e}^{*} \mathrm{RTL}^{2} c_{\max}^{2}} \hat{\mathrm{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{3} \hat{c} \right]$$

$$(3.7)$$

for a pseudobinary system. Here, the following dimensionless transport numbers are identified:  $\mathbf{I} \ k$ 

$$Da_{i} = \frac{L\kappa}{D_{i}^{*}} \qquad Damköhler number$$

$$Pe_{i} = \frac{RT\sigma_{T}^{*}}{(z_{i}\mathcal{F})^{2}D_{i}^{*}c_{max}} \qquad Péclet number$$

$$Ch_{i} = \frac{c_{i}\mathcal{K}_{i}^{*}}{RTL^{2}c_{max}^{2}} \qquad Cahn number$$

$$Ss_{i} = \frac{c_{i}\sigma^{*}}{RTc_{max}^{2}} \qquad Stress number$$

$$(3.8)$$

where  $i = \{\text{solid, electrolyte}\}$ . In the solid phase, the electromigration term is negligible in the mass conservation equation (less than half compared with the contribution in the charge conservation equation, assuming  $t_+ = 0.4$ ), while the stress term is negligible in the charge conservation equation (one fourth compared with the contri-

bution in the mass conservation equation, assuming  $t_{+} = 0.4$ ), due to the influence of the transference number. Thus, equation set 3.7 reduces to:

$$\frac{\partial \hat{c}}{\partial \hat{t}} = \hat{\nabla}_{x} \cdot \left[ \frac{\hat{c}(2-t_{+})\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RTc}_{\max}\mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial\hat{c}^{2}} \hat{\nabla}_{x}\hat{c} - \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{3} \hat{c} - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial\hat{c}} \hat{\nabla}_{x} \hat{\sigma} + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial\hat{c}^{2}} \hat{\nabla}_{x} \hat{c} \right) \right]$$

$$(3.9)$$

$$\frac{\partial \hat{\rho}}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left[ \operatorname{Pe}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} + \frac{\hat{c} \mathrm{D}_s^* \hat{\mathrm{D}}_s}{2\mathrm{RTc}_{\max} \mathrm{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \frac{\mathrm{Ch}_s}{2} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \hat{\mathrm{D}}_s \hat{\mathcal{K}}_s \hat{\nabla}_x^3 \hat{c} \right]$$

For the electrolyte phase, the compositionally-induced mechanical stress terms in the mass and charge conservation equations are negligible, since Young's Modulus is small (about one to three orders of magnitude smaller than in the solid phase, for plasticized electrolytes and polymer separators, [98])). The simplified equations are:

$$\frac{\partial \hat{c}}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left[ \frac{\hat{c}(2-t_+)\hat{D}_e}{2RTc_{\max}} U^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - Ch_e \frac{(2-t_+)}{2} \hat{D}_e \hat{\mathcal{K}}_e \hat{\nabla}_x^3 \hat{c} + 2Pe_e t_+ \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} \right]$$

$$\frac{\partial \hat{\rho}}{\partial \hat{t}} = \hat{\nabla}_x \cdot \left[ 2Pe_e \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} + \frac{\hat{c}}{2RTc_{\max}} \hat{D}_e U^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \frac{Ch_e}{2} \hat{D}_e \hat{\mathcal{K}}_e \hat{\nabla}_x^3 \hat{c} \right]$$
(3.10)

By applying the methodology reported in the Appendix A, the upscaled-homogenized transport equations approximated to  $\mathcal{O}(\xi^2)$  in the solid phase are:

$$\epsilon_{s} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})\mathrm{D}_{s}^{*}}{2\mathrm{RT}c_{\mathrm{max}}\mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial \hat{c}^{2}} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle - \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{4} \langle \hat{c} \rangle - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( 2 \frac{\partial \langle \hat{\sigma} \rangle}{\partial \hat{x}} \left\langle \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}^{2}} \right\rangle \hat{\nabla}_{x} \langle \hat{c} \rangle + \left\langle \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}} \right\rangle \frac{\partial^{2} \langle \hat{\sigma} \rangle}{\partial \hat{x}^{2}} \right) - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \left\langle \hat{\sigma} \right\rangle \left\langle \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}^{2}} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle \right) - \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{\epsilon_{s}}{\xi} \mathrm{Da}_{s} \mathcal{A} \hat{j}_{\mathrm{BV}}$$
(3.11)

$$\epsilon_{s} \frac{\partial \langle \hat{\rho} \rangle}{\partial \hat{t}} = 2 \operatorname{Pe}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \left\langle \hat{\sigma}_{T} \right\rangle \hat{\nabla}_{x}^{2} \hat{\phi} + \frac{\hat{c} \mathrm{D}_{s}^{*}}{2 \mathrm{RT} c_{\max} \mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\nabla}_{x}^{2} \hat{c} \\ - \frac{\operatorname{Ch}_{s}}{2} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{4} \hat{c} - \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{\epsilon_{s}}{\xi} \mathrm{Da}_{s} \hat{\mathcal{A}} \hat{j}_{\mathrm{BV}}$$

And in the electrolyte:

$$\epsilon_{e} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})}{2 \mathrm{RT} c_{\mathrm{max}}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}^{2}} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle - \mathrm{Ch}_{e} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\mathcal{K}}_{e} \hat{\nabla}_{x}^{4} \langle \hat{c} \rangle + 2 \mathrm{Pe}_{e} \mathrm{t}_{+} \left\langle \hat{\sigma}_{T} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{\phi} \rangle + \frac{\epsilon_{e}}{\xi} \mathrm{Da}_{e} \mathcal{A} \hat{j}_{\mathrm{BV}}$$

$$(3.12)$$

$$\begin{split} \epsilon_e \frac{\partial \left\langle \hat{\rho} \right\rangle}{\partial \hat{t}} = & 2 \mathrm{Pe}_e \left\langle \hat{\sigma}_T \right\rangle \hat{\nabla}_x^2 \hat{\phi} + \frac{\hat{c}}{2 \mathrm{RT} c_{\mathrm{max}}} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \left\langle \hat{\mathrm{D}}_e \right\rangle \hat{\nabla}_x^2 \hat{c} \\ & - \frac{\mathrm{Ch}_e}{2} \hat{\mathrm{D}}_e \left\langle \hat{\mathcal{K}}_e \right\rangle \hat{\nabla}_x^4 \hat{c} + \frac{\epsilon_e}{\xi} \mathrm{Da}_e \mathcal{A} \hat{j}_{\mathrm{BV}} \end{split}$$

## 3.3 Implementation and Numerical Setup

Discretization of the partial differential equations that describe the mass and charge transport of Li-ions in the graphite|NMC system was performed with the python-based library FiPy, version 3.4.1, [92].

Compositionally-induced mechanical stresses were calculated based on averaged mechanical properties, as formulated in Appendix F, in a three-dimensional uniformgrid mesh. The side length of the squared cross-section  $(y \times z)$  perpendicular to the x direction is ten times larger than the battery cell through-thickness. Stresses calculated at the center column of the 3D-mesh are mapped into a one-dimensional stress field variable, to update the values of the stress terms in the one-dimensional transport equations. Similarly, the updated one-dimensional concentration field is used as feedback to recalculate the three-dimensional stress field variable in the next time step. Time steps passed between updates on stress and concentration fields, are controlled by the user to allow management of computational resources.

Applied boundary conditions in the one-dimensional domain consist of fixed current  $\vec{I}(x,t) \cdot \vec{n} = I$ , and zero mass flux  $\vec{J}(x,t) \cdot \vec{n} = 0$ , at the current collectors: x = 0 and x = L. Also, the reference potential was set to zero,  $\phi_0 = 0$ , in the interface of the negative electrode and the current collector. At the three-dimensional domain, zero displacement boundary conditions,  $u_x = 0$ , were applied at the surfaces of the current collectors facing the electrodes, x = 0 and x = L.

Initial conditions of the solid and electrolyte concentrations,  $c_s = c_s^0$  and  $c_e = c_e^0$ , were set to the values reported in Table 3.1, and the initial electrode potentials set to zero,  $\phi_e^0 = \phi_s^0 = 0$  in the one-dimensional and three-dimensional domains. For the NMC phase, the chemical strain was set as reported by Yabuuchi and coworkers [94], see Appendix E. The stress-free concentration was set to  $\hat{c}_{\varepsilon_1} \sim 1/3$ . Similarly, for the graphite phase were determined by using Vegard's law, assuming stress free condition when fully depleted.

The resultant linear systems of equations were solved using GMRES, as implemented by Trilinos, [93]. The iterative solution is performed to a relative tolerance of  $1 \times 10^{-6}$ . The one-dimensional regular mesh of 120 voxels requires 2 to 3 iterations per time step to be solved, while the three-dimensional regular mesh of  $3 \times 10^5$ voxels, requires 2 iterations per time step. The overall performance of the system is related to the resolution  $n = (n_x \times n_y \times n_z)^{\frac{1}{3}}$  of the three-dimensional domain, where the complexity is of the order of  $\mathcal{O}(n)$ , where n is the number of voxels. A simulation ten times larger will require ten times more wall-time to compute. The system is numerically stable if  $\Delta t \leq \Delta x^2/(2D_e)$ .



Figure 3.1. Computing wall-time vs resolution. Circles ( $\bigcirc$ ) represent simulation cases. Solid lines ( $\_$ ) represent the least-squares regression. The complexity of the simulations is on the order  $\mathcal{O}(n)$ .

The chemomechanical part of the calculation is on the order of  $3.7 \times 10^4$  voxels, and required approximately 3.2 GB of RAM and 27.6 minutes of wall time for one CPU core, and required 4.5 GB of RAM and 10.4 minutes of wall time for eight CPU cores. The electrochemical part of the 1D calculation is on the order of 120 voxels in 1D arrangement and required 2.2 MB of RAM and 50 seconds of wall time for one CPU core, and 40 seconds of wall time and 2.5 MB of RAM for eight CPU cores. Computations were performed on a 2.0 GHz, 32 CPU cores, Linux Ubuntu (14.04.5) server with 128 GB RAM. By updating the chemomechanical calculation from every time step to every ten time steps, the one CPU core wall time decreases to 4.2 minutes, and the eight CPU cores wall time decreases to a total of 2.3 minutes.

Table 3.1.: Physical parameters used in the coarsed-grained model [27–29, 68, 94–97]. The free energy definitions as well as equilibrium potentials for NMC, Graphite and EC:DMC electrolyte, can be found in the Appendix C.

Parameter	Cathode	Ref.	Separator	Ref.	Anode	Ref.	Units
$\hat{\mathcal{A}}$	1.9	‡	-	-	4.3	‡	-
$\mathrm{c}_e^0$	$1.0 \times 10^{3}$	[28]	$1.0 \times 10^{3}$	[28]	$1.0 \times 10^{3}$	[28]	$mol/m^3$
$c_{max}$	$3.6 \times 10^4$	[29]	$1.4 \times 10^{3}$	‡	$3.01 \times 10^{4}$	[29]	$mol/m^3$
$c_s^0$	$1.3 \times 10^{4}$	‡	$1 \times 10^{-5}$	‡	$1.9{ imes}10^4$	‡	$mol/m^3$
$\mathrm{D}^*_s$	$3.4 \times 10^{-14}$	[27]	$1 \times 10^{-16}$	‡	$3.9 \times 10^{-14}$	[95]	$m^2/s$
$\mathbf{D}_e^*$	$2.7 \times 10^{-10}$	[96]	$2.7 \times 10^{-10}$	[96]	$2.7 \times 10^{-10}$	[96]	$m^2/s$
Ε	120	[97]	0.7	[98]	12	[68]	GPa
Ι	18.7	[29]	18.7	[29]	18.7	[29]	$A/m^2$
$\mathbf{k}_r$	$6.9 \times 10^{-8}$	‡	-	-	$1.1 \times 10^{-7}$	‡	m/s
$\mathcal{K}_e^*$	$4.4 \times 10^{-4}$	‡	$4.4 \times 10^{-4}$	‡	$4.4 \times 10^{-4}$	‡	$J/m^1$
$\mathcal{K}^*_s$	$2.1 \times 10^{-2}$	‡	-	-	-	-	$J/m^1$
L	$46 \times 10^{-6}$	[29]	$20 \times 10^{-6}$	[29]	$52 \times 10^{-6}$	[29]	m
Q	279	‡	-	-	372	‡	mAh/g
$\mathrm{R}_{f}$	0.15	‡	-	-	0.15	‡	$\Omega \ { m m}^2$
$\mathbf{r}_p$	$5.5 \times 10^{-6}$	[28]	-	-	$12.0 \times 10^{-6}$	[28]	m
$t_+$	0.6	[28]	-	-	0.4	[28]	-
eta	0.104	[99]	-	-	-	-	-
$\epsilon_e$	0.27	[29]	0.4	[29]	0.34	[29]	-
ν	0.3	[97]	0.33	[66]	0.3	[68]	-
ho	4.77	[94]	-	-	2.11	[27]	$g/cm^3$
$\sigma^*_s$	0.023	[28]	-	-	100	[28]	S/m
$\sigma_e^*$	0.98	[96]			0.98	[96]	S/m
au	$\epsilon^{1.5}$	‡			$\epsilon^{1.5}$	‡	-

<sup>‡</sup> Estimated values.

## 3.4 **Results and Discussion**

For selected fixed current densities, the simulated cell potential of the graphite|NMC cell was compared against experimental data as reported by Smekens and coworkers, [29], see Figure 3.2. For a 1C-rate of 18.7 A/m<sup>2</sup> or 0.614 A, the maximum attained time-dependent capacity was ~ 57% of the theoretical capacity, 159 Ah/g. Results demonstrate that the ~ 9.2% of the macroscopic cell potential corresponds to the contributions of the stresses, and is equivalent to a contribution from film-contact-resistance, ~ 10.2%. The exclusion of either, the mechanical stresses or the ohmic losses, leads to a cell potential mismatch with the experimental potential curve because both contributions slow down the lithium intercalation by the reduction on the local overpotential. Thus, models not accounting for the contribution of mechanical stresses require unrealistically higher values of the film-contact-resistance to match experimental values, inaccurately describing the physical system, particularly at high C-rates.

Simulations show that the effect of the gradient energy term on the cell potential is small,  $\sim 1.5\%$ . The main effect of the gradient energy term is shown at the interface with the separator.



Figure 3.2. Comparison of simulated cell potential \_ in graphite|NMC system versus experimental data  $\bullet$  as reported by Smekens *et al.* [29], subjected to selected fixed current densities.\_ simulation without mechanical stress effect discharges ~ 9.2% faster, \_ simulation without film-contact-resistance effect discharges ~ 10.2% faster, \_ simulation without gradient energy contribution effect minimally delays discharge by ~ 1.5% . 1C corresponds to 18.7 A/m<sup>2</sup> or 0.614 A.

Figure 3.3 (a) shows that during the first two minutes of discharge, the greater availability of Li-ions and intercalation sites in the vicinity of the cathode-separator interface, induces local lithium accumulation. During the first six minutes of discharge, Figure 3.3 (a) showed spatial inhomogeneities in the intercalation reaction developed as a result of the mechanical stresses in the composite electrode (polymer matrix + NMC particles), until the strain-free concentration of the individual NMC particles,  $c_{\varepsilon} \sim 1.45 \times 10^4 \text{ mol/m}^3$ , was reached at 5  $\mu$ m away from the separator after eighteen minutes. Immediately after, the mechanical stresses in the composite electrode became progressively less compressive and lead to a continued reduction of the concentration gradients, as shown in Figure 3.3 (b). Lithium intercalation was affected by less-compressive mechanical stresses by means of the reduced local overpotential, which entirely flattened the concentration gradients except at those positions closer to the separator. After 32 minutes, the intercalated lithium exceeded the concentration value for maximum chemical strain inside individual NMC particles,  $c_{\varepsilon_{max}} \sim 2.31 \times 10^4 \text{ mol/m}^3$ . As a result, the magnitude of the mechanical stresses at the composite electrode level decreased and spatial inhomogeneities were developed again until the end of the galvanostatic discharge.



Figure 3.3. Active material Li-ion concentration profiles at 1C-rate for graphite|NMC system. 1C corresponds to  $18.7 \text{ A/m}^2$  or 0.614 A. Inset (a) highlights first 14 minutes of active material Li-ion concentration profile in the NMC electrode. Inset (b) corresponds to Li-ion concentration profile on both electrodes for the full 60 minutes discharge. During the first 2 minutes, Li-ions intercalate in the vicinity of the separator in the positive electrode due to the greater availability of lithium at the intercalating sites of NMC. Such process is followed by an interdiffusion sequence after the first 6 minutes, as intercalation sites become preponderantly occupied in the active material close to separator, and the intercalating reaction is affected by the chemically-induced stresses. The spatial inhomogeneities in the intercalation reaction (see Figure 3.6) develop again after thirty two minutes as a result of the stress contributions and the transport limitations that result because of the porosity of the electrode.

As shown in Figure 3.4 (a), at the start of the galvanostatic discharge, the initial hydrostatic stresses in the cathode,  $\sigma_h \sim -37$  MPa, were compressive and spatially uniform because the starting lithium concentration was smaller than the NMC particle strain-free concentration and the imposed (fixed displacement) boundary conditions. However, initial inhomogeneous intercalation in the vicinity of the cathode-separator interface developed an initial localized region of higher compressive stress that was progressively mitigated as the concentration gradients diminished. After eighteen minutes of discharge, the average mechanical stress reached  $\sigma_h \sim -47.5$  MPa, the maximum compressive stress. Shortly after, the concentration of lithium in the solid phase was greater than the strain-free concentration. From t = 19 minutes to t = 31minutes the stress profile remained flat until at t = 32 minutes when the concentration of lithium in the solid phase reached the condition for maximum NMC lattice strain. As the compositional strain decreased, long range stress heterogeneities developed, see Figure 3.4 (b). This was because the intercalating sites in the vicinity of the separator became available. The mechanical stresses developed in graphite electrode showed moderate heterogeneity due to small concentration gradients in the solid phase at the region close to the separator. For current densities greater than 1C, the NMC electrode will remain in compression because chemically-induced stress never have the opportunity to relax.

The porous separator develops small elastic stresses, due to its small Young's Modulus, E = 0.7 GPa, [98], in comparison to the Young's Modulus of the graphite particles, E = 12 GPa, [68], or the NMC particles, E = 120 GPa, [97].



Figure 3.4. Stress distribution in graphite|NMC system for 1C galvanostatic discharge. 1C corresponds to 18.7 A/m<sup>2</sup> or 0.614 A. Inset (a) corresponds to selected instants of the hydrostatic stress during the first 18 minutes of discharge, while inset (b) corresponds to the full 60 minutes discharge. Stress is the result of current collectors and time-dependent chemomechanical expansion of the porous electrode layers.

Figure 3.5 (a) shows that after eleven seconds of discharge, chemical gradients developed in the vicinity of the separator in the electrolyte, favored by the higher intercalation rate in those particles exposed to a higher magnitude of overpotential.

Because Li-ions in the electrolyte had a one minute recovery time, the steady-state profile of the electrolyte concentration developed after thirty minutes, as shown in Figure 3.5 (b), because there was a small number of available sites at the surface of particles of active material, less lithium was intercalated from the electrolyte, while lithium accumulated in the anode-separator region.



Figure 3.5. Electrolyte Li-ion concentration profiles at 1C-rate for graphite NMC system. 1C corresponds to  $18.7 \text{ A/m}^2$  or 0.614 A. Inset (a) highlights the predicted electrolyte Li-ion concentration profile in the NMC electrode during the first 2 minutes of discharge. Inset (b) summarizes electrolyte Li-ion concentration profile for the full 60 minutes of discharge. During the first 11 seconds of discharge, the NMC cathode intercalates lithium faster in the vicinity of the current collector side because of the combined effects of elastic energy and the overpotential drop across the electrode. After 35 seconds, the concentration in the vicinity of the current collector recovers and the intercalation/deintercalation activity relocate to zones close to the separator.

In agreement with Figures 3.3 to 3.5, for a 1C-rate, the Butler-Volmer flux underwent a transient the first four minutes, after which it decreased uniformly and continuously until the end of discharge, see Figure 3.6 (a). The gradient energy contribution in the solid phase, induced a region of high heterogeneity in the vicinity of the separator, that is visible after twenty four minutes of discharge, and is about 5  $\mu$ m wide. Thereafter, the localized zone of heterogeneities grew towards the current collector until t = 42 minutes. Afterwards, the exchange current density became dominated by the electrical contributions of the overpotential because the chemicallyinduced stresses decreased.

The magnitude of the local overpotential in the negative electrode was larger in the vicinity of the separator, as compared to the overpotential displayed in the positive electrode in the equivalent region. As shown in Figure 3.6 (b), the Butler-Volmer flux in the cathode is greater at the interface with the current collector.



Figure 3.6. Spatial distribution of Butler-Volmer flux during 1C discharge for graphite|NMC system. 1C corresponds to  $18.7 \text{ A/m}^2$  or 0.614 A. Inset (a) corresponds to selected instants during the first 28 minutes of discharge, while inset (b) corresponds to the full 60 minutes discharge. Calculations demonstrate the progressive development of localized heterogeneities zones, aided by the transport limitations of the porous electrode and the stress fields that shift the intercalation reaction. Intercalation is enhanced until the maximum stress is reach after 18 minutes.

Figure 3.7 quantifies the lithium distribution populations in the NMC layer. For a 1C-rate, after one minute of discharge, two out of three populations were identified: i) the diffusion-limited population, which is a result of the negligible composition gradients, and is identified by the first sharp peak of concentration; ii) the stress-induced population, as a result of chemically-induced expansion of the lattice and characterized by a second and smaller peak. After fourteen to eighteen minutes of discharge, the stress-induced population collapsed into a single concentration population as a result of particles transitioning from being below the stress-free concentration to above it. A third population iii) arose to the left of the first (diffusion-limited) population peak, as a consequence of the lithiation induced by the gradient energy term. After 44 minutes, the total stresses kept moving towards the zero stress, as advised by the flattening of the spatial concentration profile. At the end of discharge, the stress-induced population merged with the diffusion-limited population, for t = 60minutes.

Figure 3.8 summarizes the effects on the lithium distribution populations in the NMC layer at a 5C-rate. The three frequency populations became evident after 3 minutes of galvanostatic discharge. Due to the high electrical current, the calculation demonstrates that the stress-induced population dominated the kinetics of the system.



Figure 3.7. Concentration frequency histograms for 1C galvanostatic discharge, for selected instants. 1C corresponds to  $18.7 \text{ A/m}^2$  or 0.614 A. Three populations are observed: (i) the lithiation-induced population, (ii) the stress-induced population, and (iii) the diffusion-limited population.



Figure 3.8. Concentration frequency histograms for 5C galvanostatic discharge, for selected instants. 5C corresponds to 93.5 A/m<sup>2</sup> or 3.07 A. After t = 3 minutes of discharge, three populations are developed: (i) the lithiation-induced population, (ii) the stress-induced population, and (iii) the diffusion-limited population.

## 3.5 Summary and Conclusions

A coarsed-grained thermodynamically consistent phase field model, based on the electrical, chemical, and elastic energy contributions to the total free energy of the system, was developed to investigate the transport limitations and the long range effects imposed by the related mechanisms on the kinetics of LIBs. The numerical implementation of the mathematical model was applied to the commercial chemistry,  $\text{Li}_x \text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3} \text{O}_2$ , and validated against experimental data available in the literature, [29].

Results demonstrate that mechanical stresses have a comparable effect to that of the ohmic losses as imposed by the film-contact-resistance, demonstrating that such effects cannot be ignored during battery design and manufacturing, in order to optimize performance, and minimize long-term degradation. Further, three distinguishable lithium distribution populations were identified in the cathode: i) the diffusion-limited population as a result of the negligible composition gradients, ii) the stress-induced population as a result of chemically-induced stresses, and iii) the lithiation-induced population, as a result of the lithiation induced gradient energy contribution. The stress-controlled population dominates the kinetics of lithiation at high C-rates.

Self-induced, compressive mechanical stresses developed as a result of the chemical strain and the externally imposed boundary conditions. These stresses enhance the intercalation reaction process by increasing the local overpotential, even though the magnitude of the interfacial reaction can be greatly suppressed (see Equation 5). Thus, it is desirable for the mechanical stresses contribution to Li-ion transport, as quantified by its dimensionless number,  $Ss_s$ , to be comparable to the intercalation reaction driving force contribution,  $Ss_s \sim Da_s$ . Further, the design of LIBs whose initial state of charge favors compressive stresses, so that  $Da_s \leq Ss_s < Pe_s$ , will result in improved performance. However, even though it was not the focus of this work, the induced chemomechanical stresses might also favor the development of irreversible (degradation) reactions, as well as chemomechanical (cycling) fatigue.

## 4. FUTURE WORK

The developed phase field framework allows the addition of multiple driving forces to the free energy of the system. Also, the interactions between multiple charged species can be described by enabling the "wind energy" term in the transport equations. In this context, the theoretical framework has ample capabilities to support a broad range of future research projects.

In the short term, tasks related with the work presented in Chapters 2 and 3 have been identified:

- 1. Continue the effort to provide experimental guidelines that help to engineer the microstructure of chemically active materials, and comply with the conditions of validity for porous electrode theory models.
- 2. Extend the comparison of dimensionless numbers to determine the regions of predominance of each transport process. Specifically, those derived from the contribution of gradient energy and elastic energy driving forces:
  - gradient energy contribution slower than the diffusion process  $(Ch_i Fo_i < Fo_i)$
  - electromigration process slower than diffusion process  $(Pe_iFo_i < Fo_i)$
  - intercalation reaction slower than diffusion process  $(Da_iFo_i < Fo_i)$
  - intercalation reaction slower than gradient energy contribution  $(Da_i < Ch_i)$
  - intercalation reaction slower than electromigration process  $(Da_i < Pe_i)$
  - mechanical stress contribution slower than diffusion process  $(Ss_iFo_i < Fo_i)$
  - electromigration process slower than diffusion process ( $Pe_iFo_i < Fo_i$ )
  - intercalation reaction slower than diffusion process  $(Da_iFo_i < Fo_i)$
  - intercalation reaction slower than mechanical stress contribution  $(Da_i < Ss_i)$

- intercalation reaction slower than electromigration process  $(Da_i < Pe_i)$
- 3. Parallel computing capability through GPU's.
- 4. Publication of the numerical implementation of the developed model. [91].

In the long term, projects related to extensions of the theoretical framework:

- Describe phase transforming materials.
- Incorporate additional contributions to the free energy functional.
- Apply to charged species different than Lithium-ions.
- Apply to systems with more than one charged species.
- Explore the life cycle of rechargeable batteries.
### APPENDIX A. HOMOGENIZATION METHODOLOGY

Coarse-grained models approximate the transport phenomena occurring at the molecular level into a macroscopic scale continuum. The multiple-scale expansion requires a scalar  $\xi = 2r_p/L \ll 1$ , and an additional spatial variable  $\hat{y} = \hat{x}/\xi$  named 'fast space' variable, to relate macroscale and microscale spatial dimensions. As identified earlier, this battery model considers five processes. Therefore, the following seven variables of time are defined:

$$\begin{split} \tau_{\rm R} &= \frac{t}{t_{\rm R}} = {\rm Da}_e \hat{t} & \text{reaction} \\ \tau_{\rm M_s} &= \frac{t}{t_{\rm M_s}} = {\rm Pe}_s \frac{{\rm Da}_e}{{\rm Da}_s} \hat{t} & \text{migration at solid} \\ \tau_{\rm M_e} &= \frac{t}{t_{\rm M_e}} = {\rm Pe}_e \hat{t} & \text{migration at electrolyte} \\ \tau_{\rm Ch_s} &= \frac{t}{t_{\rm Ch_s}} = {\rm Ch}_s \hat{t} & \text{gradient energy at solid} \\ \tau_{\rm Ch_e} &= \frac{t}{t_{\rm Ch_e}} = {\rm Ch}_e \hat{t} & \text{gradient energy at electrolyte} \\ \tau_{\rm Ss_s} &= \frac{t}{t_{\rm Ss_s}} = {\rm Ss}_s \hat{t} & \text{stress at solid} \\ \tau_{\rm Ss_e} &= \frac{t}{t_{\rm Ss_e}} = {\rm Ss}_e \hat{t} & \text{stress at electrolyte} \end{split}$$

where  $\hat{t} = t/t_{D_e}$  is the dimensionless time. As a result of the introduction of new spatial and temporal variables, the functional relation for any field variable B (*e.g.* concentration, stress, potential), involved in the physical formulation, has to be recast from one spatial and one temporal variables:  $B_{\xi}(x,t)$ , into two spatial and eight time variables  $B(x, y, t, \tau_R, \tau_{M_s}, \tau_{M_e}, \tau_{Ch_s}, \tau_{Ch_e}, \tau_{Ss}, \tau_{Ss})$ . Accordingly, the spatial and temporal operators become:

$$\nabla_{\xi} = \nabla_x + \xi^{-1} \nabla_y \tag{A.2}$$

$$\frac{\partial_{\xi}}{\partial t} = \frac{\partial}{\partial t} + \mathrm{Da}_{e} \frac{\partial}{\partial \tau_{\mathrm{R}}} + \mathrm{Pe}_{s} \frac{\partial}{\partial \tau_{\mathrm{M}_{s}}} \frac{\mathrm{Da}_{e}}{\mathrm{Da}_{s}} + \mathrm{Pe}_{e} \frac{\partial}{\partial \tau_{\mathrm{M}_{e}}} + \mathrm{Ch}_{s} \frac{\partial}{\partial \tau_{\mathrm{Ch}_{s}}} + \mathrm{Ch}_{e} \frac{\partial}{\partial \tau_{\mathrm{Ch}_{e}}} + \mathrm{Ss}_{s} \frac{\partial}{\partial \tau_{\mathrm{Ss}_{s}}} + \mathrm{Ss}_{e} \frac{\partial}{\partial \tau_{\mathrm{Ss}_{$$

Moreover, any recast variable  $B(x, y, t, \tau_{R}, \tau_{M_{s}}, \tau_{M_{e}}, \tau_{Ch_{s}}, \tau_{Ch_{e}}, \tau_{Ss_{s}}, \tau_{Ss_{e}})$  has to be expressed as an asymptotic series, in integer powers of the scalar  $\xi$  as:

$$\mathbf{B} = \sum_{n=0}^{\infty} \xi^{n} \mathbf{B}_{n}(x, y, t, \tau_{\mathbf{R}}, \tau_{\mathbf{M}_{s}}, \tau_{\mathbf{M}_{e}}, \tau_{\mathbf{Ch}_{s}}, \tau_{\mathbf{Ch}_{e}}, \tau_{\mathbf{Ss}_{s}}, \tau_{\mathbf{Ss}_{e}}) \quad \mathbf{n} = 0, 1, 2...$$
(A.4)

and any field constant will be re-defined as a power of the scalar  $\xi$ :

$$\begin{aligned} &\operatorname{Pe}_{s} = \xi^{-\beta}, \quad \operatorname{Da}_{s} = \xi^{\gamma}, \quad \operatorname{Ch}_{s} = \xi^{\delta}, \quad \operatorname{Ss}_{s} = \xi^{\zeta} \\ &\operatorname{Pe}_{e} = \xi^{-\iota}, \quad \operatorname{Da}_{e} = \xi^{\upsilon}, \quad \operatorname{Ch}_{e} = \xi^{o}, \quad \operatorname{Ss}_{e} = \xi^{\omega} \end{aligned}$$
(A.5)

where the values of the exponents  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\zeta$ ,  $\iota$ ,  $\upsilon$ , o, and  $\omega$  are constrained to the domain of the real numbers  $\mathcal{R}$ . Lithium-ion transport equations can be homogenized up to a desired order approximation, by the number of terms used from the power expansion. Thus, to homogenize the transport equations with an error of  $\mathcal{O}(\xi^2)$ , the physical variables are expanded:

$$c_i = \xi^0 c_{i,0} + \xi c_{i,1} + \mathcal{O}(\xi^2)$$
(A.6)

$$\phi_i = \xi^0 \phi_{i,0} + \xi \phi_{i,1} + \mathcal{O}(\xi^2)$$
(A.7)

$$\rho_i = \xi^0 \rho_{i,0} + \xi \rho_{i,1} + \mathcal{O}(\xi^2)$$
 (A.8)

$$\sigma_i = \xi^0 \sigma_{i,0} + \xi \sigma_{i,1} + \mathcal{O}(\xi^2) \tag{A.9}$$

The conservation equations for mass and charge, when applied in volume elements containing solid and electrolyte phases, are coupled to the interfacial condition:

$$\vec{n} \cdot \left[\frac{\mathrm{D}c(2-t_{+})}{2\mathrm{R}\mathrm{T}} \left(\frac{\partial^2 g}{\partial c^2} \nabla_x c - \mathcal{K} \nabla_x^3 c - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c^2} \nabla_x c\right) + \frac{z\mathcal{F}\mathrm{D}c}{2\mathrm{R}\mathrm{T}} \nabla_x \phi\right] = j_{BV}$$
(A.10)

$$\vec{n} \cdot \left[ \sigma_T \nabla_x \phi + \frac{z \mathcal{F} \mathrm{D}c}{2\mathrm{RT}} \left( \frac{\partial^2 g}{\partial c^2} \nabla_x c - \frac{\mathcal{K}}{2} \nabla_x^3 c - \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial c} \nabla_x \sigma - \sigma \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial c^2} \nabla_x c \right) \right] = \mathcal{F} j_{BV} \quad (A.11)$$

By applying 2.8 to equations A.10 and A.11 leads to:

$$\vec{n} \cdot \left[ \frac{\hat{c}(2-t_{+})\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RT}c_{\max}\mathrm{D}_{e}^{*}} \mathrm{U}^{*}\frac{\partial^{2}\hat{g}}{\partial\hat{c}^{2}}\hat{\nabla}_{x}\hat{c} - \frac{\mathrm{D}_{s}^{*}c\mathcal{K}_{s}^{*}}{\mathrm{D}_{e}^{*}\mathrm{RT}\mathrm{L}^{2}c_{\max}^{2}} \frac{(2-t_{+})}{2}\hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s}\hat{\nabla}_{x}^{3}\hat{c} - \frac{\mathrm{D}_{s}^{*}c\sigma^{*}}{\mathrm{D}_{e}^{*}\mathrm{RT}\mathrm{L}^{2}c_{\max}^{2}} \frac{(2-t_{+})}{2}\hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s}\hat{\nabla}_{x}^{3}\hat{c} - \frac{\mathrm{D}_{s}^{*}c\sigma^{*}}{\mathrm{D}_{e}^{*}\mathrm{RT}c_{\max}^{2}}\hat{\mathrm{D}}_{s}\hat{\mathrm{C}}^{*}\hat{\mathrm{C}}_{\mathrm{che}}\hat{\nabla}_{x}\hat{\sigma} + \hat{\sigma}\frac{\partial^{2}\varepsilon_{\mathrm{Che}}}{\partial\hat{c}^{2}}\hat{\nabla}_{x}\hat{c}\right) \right] = \frac{Lk}{\mathrm{D}_{s}^{*}}\frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}}c_{\max}^{\alpha_{c}}\hat{j}_{BV}$$

$$(A.12)$$

$$\vec{n} \cdot \left[ \frac{2\text{RT}\sigma_T^* \text{D}_s^*}{(z\mathcal{F})^2 \text{D}_s^* c_{\max} \text{D}_e^*} \hat{\sigma}_T \hat{\nabla}_x \hat{\phi} + \frac{\hat{c} \text{D}_s^* \hat{D}_s}{2\text{RT} c_{\max} \text{D}_e^*} \text{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \hat{\nabla}_x \hat{c} - \frac{1}{2} \frac{\text{D}_s^* \hat{c} \mathcal{K}_s^*}{\text{D}_e^* \text{RTL}^2 c_{\max}^2} \hat{D}_s \hat{\mathcal{K}}_s \hat{\nabla}_x^3 \hat{c} \right]$$
$$= \frac{Lk}{\text{D}_s^*} \frac{\text{D}_s^*}{\text{D}_e^*} c_{\max}^{\alpha_c} \mathcal{F} \frac{\hat{j}_{BV}}{k}$$
(A.13)

from there, the dimensionless numbers are identified:

$$\vec{n} \cdot \left[ \frac{\hat{c}(2-t_{+})\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RT}c_{\max}\mathrm{D}_{e}^{*}} \mathrm{U}^{*}\frac{\partial^{2}\hat{g}}{\partial\hat{c}^{2}}\hat{\nabla}_{x}\hat{c} - \mathrm{Ch}_{s}\frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}}\frac{(2-t_{+})}{2}\hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s}\hat{\nabla}_{x}^{3}\hat{c} - \mathrm{Ss}\frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}}\frac{(2-t_{+})}{2}\hat{\mathrm{D}}_{s}\left(\frac{\partial\varepsilon_{\mathrm{Che}}}{\partial\hat{c}}\hat{\nabla}_{x}\hat{\sigma} + \hat{\sigma}\frac{\partial^{2}\varepsilon_{\mathrm{Che}}}{\partial\hat{c}^{2}}\hat{\nabla}_{x}\hat{c}\right) \right] = \mathrm{Da}_{s}\frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}}c_{\max}^{\alpha_{c}}\frac{\hat{j}_{BV}}{k}$$

$$\vec{n} \cdot \left[\mathrm{Pe}_{s}\frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}}\hat{\sigma}_{T}\hat{\nabla}_{x}\hat{\phi} + \frac{\hat{c}\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RT}c_{\max}\mathrm{D}_{e}^{*}}\mathrm{U}^{*}\frac{\partial^{2}\hat{g}}{\partial\hat{c}^{2}}\hat{\nabla}_{x}\hat{c} - \frac{\mathrm{Ch}_{s}}{2}\frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}}\hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s}\hat{\nabla}_{x}^{3}\hat{c}\right] = \mathrm{Da}_{s}\frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}}c_{\max}^{\alpha_{c}}\mathcal{F}\frac{\hat{j}_{BV}}{k}$$

$$(A.14)$$

$$(A.14)$$

Applying equations A.2 through A.5 to the mass conservation equation 2.11 at the solid phase:

$$\begin{aligned} \frac{\partial c_s}{\partial t} &+ \xi^{\gamma} \frac{\partial c_s}{\partial \tau_{\rm R}} + \xi^{-\beta} \bigg( \xi^{\nu-\gamma} \frac{\partial c_s}{\partial \tau_{\rm M_s}} \bigg) + \xi^{-\iota} \frac{\partial c_s}{\partial \tau_{\rm M_e}} + \xi^{\delta} \frac{\partial c_s}{\partial \tau_{\rm Ch_s}} + \xi^{o} \frac{\partial c_s}{\partial \tau_{\rm Ch_e}} + \xi^{\zeta} \frac{\partial c_s}{\partial \tau_{\rm Ss_s}} + \xi^{\omega} \frac{\partial c_s}{\partial \tau_{\rm Ss_s}} \\ &= \hat{\nabla}_x \cdot \bigg[ \frac{\hat{c}_s (2 - t_+) \mathcal{D}_s^* \hat{\mathcal{D}}_s}{2 \mathrm{RT} c_{\mathrm{max}} \mathcal{D}_e^*} \mathcal{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \bigg( \hat{\nabla}_x \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \bigg) \\ &- \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2 - t_+)}{2} \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \bigg( \hat{\nabla}_x^3 \hat{c}_s + \xi^{-1} \hat{\nabla}_y^3 \hat{c}_s \bigg) \\ &- \mathrm{Ss} \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2 - t_+)}{2} \hat{\mathcal{D}}_s \bigg( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \bigg( \hat{\nabla}_x \hat{\sigma} + \xi^{-1} \hat{\nabla}_y \hat{\sigma} \bigg) + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \bigg( \hat{\nabla}_x \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \bigg) \bigg) \bigg] \\ &+ \xi^{-1} \hat{\nabla}_y \cdot \bigg[ \frac{\hat{c}_s (2 - t_+) \mathcal{D}_s^* \hat{\mathcal{D}}_s}{2 \mathrm{RT} c_{\mathrm{max}} \mathcal{D}_e^*} \mathcal{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \bigg( \hat{\nabla}_x \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \bigg) \\ &- \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2 - t_+)}{2} \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \bigg( \hat{\nabla}_x^3 \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \bigg) \\ &- \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} (2 - t_+) \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \bigg( \hat{\nabla}_x^3 \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \bigg) \end{aligned} \right)$$

$$(A.16)$$

then, applying equations A.6 and A.9 to equation A.16:

$$\begin{aligned} \frac{\partial c_{s,0}}{\partial t} + \xi \frac{\partial c_{s,1}}{\partial t} + \xi^{\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\rm R}} + \xi^{\gamma+1} \frac{\partial c_{s,1}}{\partial \tau_{\rm R}} + \xi^{-\beta} \left( \xi^{\nu-\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\rm M_s}} + \xi^{\nu-\gamma+1} \frac{\partial c_{s,1}}{\partial \tau_{\rm M_s}} \right) + \xi^{-\iota} \frac{\partial c_{s,0}}{\partial \tau_{\rm M_e}} \\ + \xi^{-\iota+1} \frac{\partial c_{s,1}}{\partial \tau_{\rm M_e}} + \xi^{\delta} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ch_s}} + \xi^{\delta+1} \frac{\partial c_{s,1}}{\partial \tau_{\rm Ch_s}} + \xi^{\rho} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ch_e}} + \xi^{\rho+1} \frac{\partial c_{s,1}}{\partial \tau_{\rm Ch_e}} + \xi^{\zeta} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ss_s}} + \xi^{\zeta+1} \frac{\partial c_{s,1}}{\partial \tau_{\rm Ss_s}} \\ + \xi^{\omega} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ss_e}} + \xi^{\omega+1} \frac{\partial c_{s,1}}{\partial \tau_{\rm Ss_e}} \\ = \hat{\nabla}_x \cdot \left[ \frac{\hat{c}_s(2-t_+) D_s^* \hat{D}_s}{2 \mathrm{RT} c_{\rm max} D_e^*} U^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_{s,0} + \xi \hat{\nabla}_x \hat{c}_{s,1} + \xi^{-1} \hat{\nabla}_y \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \right) \\ - \mathrm{Ch}_s \frac{D_s^*}{D_e^*} \frac{(2-t_+)}{2} \hat{D}_s \hat{\mathcal{K}}_s \left( \hat{\nabla}_x^3 \hat{c}_{s,0} + \xi \hat{\nabla}_x \hat{c}_{s,1} + \xi^{-1} \hat{\nabla}_y \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \right) \\ - \mathrm{Ss} \frac{D_s^*}{D_e^*} \frac{(2-t_+)}{2} \hat{D}_s \left( \frac{\partial \varepsilon_{\rm Che}}{\partial \hat{c}_s} \left( \hat{\nabla}_x \hat{\sigma}_{s,0} + \xi \hat{\nabla}_x \hat{\sigma}_{s,1} + \xi^{-1} \hat{\nabla}_y \hat{\sigma}_{s,0} + \hat{\nabla}_y \hat{\sigma}_{s,1} \right) \\ + \hat{\sigma} \frac{\partial^2 \hat{c}_e}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_{s,0} + \xi \hat{\nabla}_x \hat{c}_{s,0} + \xi \hat{\nabla}_x \hat{\sigma}_{s,1} + \xi^{-2} \hat{\nabla}_y \hat{\sigma}_{s,0} + \hat{\nabla}_y \hat{\sigma}_{s,1} \right) \\ - \mathrm{Ch}_s \frac{D_s^*}{D_e^*} \frac{(2-t_+)}{2} \hat{D}_s \left( \frac{\partial \varepsilon_{\rm Che}}{\partial \hat{c}_s} \left( \xi^{-1} \hat{\nabla}_x \hat{\sigma}_{s,0} + \hat{\nabla}_x \hat{\sigma}_{s,1} + \xi^{-2} \hat{\nabla}_y \hat{\sigma}_{s,0} + \xi^{-1} \hat{\nabla}_y \hat{\sigma}_{s,1} \right) \right) \right] \\ + \hat{\sigma} \frac{\partial^2 \hat{c}_e}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_x \hat{\sigma}_{s,1} + \xi^{-2} \hat{\nabla}_y \hat{\sigma}_{s,0} + \xi^{-1} \hat{\nabla}_y \hat{\sigma}_{s,1} \right) \\ - \mathrm{Ss} \frac{D_s^*}{D_e^*} \frac{(2-t_+)}{2} \hat{D}_s \hat{\mathcal{K}}_s \left( \xi^{-1} \hat{\nabla}_x \hat{\sigma}_{s,0} + \hat{\nabla}_x \hat{\sigma}_{s,1} + \xi^{-2} \hat{\nabla}_y \hat{\sigma}_{s,0} + \xi^{-1} \hat{\nabla}_y \hat{\sigma}_{s,1} \right) \\ - \mathrm{Ss} \frac{D_s^*}{D_e^*} \frac{(2-t_+)}{2} \hat{D}_s \left( \frac{\partial \varepsilon_{\rm Che}}{\partial \hat{c}_s} \left( \xi^{-1} \hat{\nabla}_x \hat{\sigma}_{s,0} + \hat{\nabla}_x \hat{\sigma}_{s,1} + \xi^{-2} \hat{\nabla}_y \hat{\sigma}_{s,0} + \xi^{-1} \hat{\nabla}_y \hat{\sigma}_{s,1} \right) \right) \right] \right]$$
(A.17)

Collecting terms of  $\mathcal{O}(\xi)$ :

$$\begin{split} & \left\{ \frac{\partial c_{s,1}}{\partial t} + \xi^{\gamma} \frac{\partial c_{s,1}}{\partial \tau_{\mathrm{R}}} + \xi^{-\beta} \left( \xi^{\nu-\gamma} \frac{\partial c_{s,1}}{\partial \tau_{\mathrm{M}_{s}}} \right) + \xi^{-\iota} \frac{\partial c_{s,1}}{\partial \tau_{\mathrm{M}_{e}}} + \xi^{\delta} \frac{\partial c_{s,1}}{\partial \tau_{\mathrm{Ch}_{s}}} + \xi^{o} \frac{\partial c_{s,1}}{\partial \tau_{\mathrm{Ch}_{e}}} + \xi^{\zeta} \frac{\partial c_{s,1}}{\partial \tau_{\mathrm{Ss}_{s}}} \right. \\ & \left. + \xi^{\omega} \frac{\partial c_{s,1}}{\partial \tau_{\mathrm{Ss}_{e}}} \right] \\ & = \hat{\nabla}_{x} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+}) \mathrm{D}_{s}^{*} \hat{\mathrm{D}}_{s}}{2\mathrm{RT} c_{\mathrm{max}} \mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{x} \hat{c}_{s,1} - \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{3} \hat{c}_{s,1} \right. \end{split}$$
(i)  
$$& \left. - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}} \hat{\nabla}_{x} \hat{\sigma}_{s,1} + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{x} \hat{c}_{s,1} \right) \right] \bigg\} \end{split}$$

Collecting terms of  $\mathcal{O}(\xi^0)$ :

$$\begin{split} &\xi^{0} \Biggl\{ \frac{\partial c_{s,0}}{\partial t} + \xi^{\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{R}}} + \xi^{-\beta} \Biggl( \xi^{v-\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{M}_{s}}} \Biggr) + \xi^{-\iota} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{M}_{e}}} + \xi^{\delta} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ch}_{s}}} + \xi^{\sigma} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ch}_{e}}} + \xi^{\zeta} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ss}_{s}}} \\ &+ \xi^{\omega} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ss}_{e}}} \Biggr] \\ &= \hat{\nabla}_{x} \cdot \Biggl[ \frac{\hat{c}_{s}(2-t_{+})\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RT}c_{\mathrm{max}}\mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial \hat{c}_{s}^{2}} \Biggl( \hat{\nabla}_{x}\hat{c}_{s,0} + \hat{\nabla}_{y}\hat{c}_{s,1} \Biggr) \Biggr] \\ &- \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*} (2-t_{+})}{\mathrm{D}_{e}^{*}} \hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s} \Biggl( \hat{\nabla}_{x}^{3}\hat{c}_{s,0} + \hat{\nabla}_{y}\hat{c}_{s,1} \Biggr) \Biggr] \\ &- \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \Biggl( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}} \Biggl( \hat{\nabla}_{x}\hat{\sigma}_{s,0} + \hat{\nabla}_{y}\hat{\sigma}_{s,1} \Biggr) + \hat{\sigma} \frac{\partial^{2}\varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}^{2}} \Biggl( \hat{\nabla}_{x}\hat{c}_{s,0} + \hat{\nabla}_{y}\hat{c}_{s,1} \Biggr) \Biggr] \Biggr] \\ &+ \hat{\nabla}_{y} \cdot \Biggl[ \frac{\hat{c}_{s}(2-t_{+})\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RT}c_{\mathrm{max}}\mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{x}\hat{c}_{s,1} - \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s}\hat{\nabla}_{x}^{3}\hat{c}_{s,1} \Biggr] \Biggr] \Biggr\}$$

$$(\mathrm{ii})$$

Collecting terms of  $\mathcal{O}(\xi^{-1})$ :

$$\begin{split} \xi^{-1} \Biggl\{ 0 &= \hat{\nabla}_x \cdot \left[ \frac{\hat{c}_s(2-t_+) \mathcal{D}_s^* \hat{\mathcal{D}}_s}{2 \mathrm{RT} c_{\max} \mathcal{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \hat{\nabla}_y \hat{c}_{s,0} - \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \hat{\nabla}_y^3 \hat{c}_{s,0} \right. \\ &- \mathrm{Ss} \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \hat{\nabla}_y \hat{\sigma}_{s,0} + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \hat{\nabla}_y \hat{c}_{s,0} \right) \Biggr] \\ &+ \hat{\nabla}_y \cdot \left[ \frac{\hat{c}_s(2-t_+) \mathcal{D}_s^* \hat{\mathcal{D}}_s}{2 \mathrm{RT} c_{\max} \mathcal{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \right) \right. \\ &- \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \left( \hat{\nabla}_x^3 \hat{c}_{s,0} + \hat{\nabla}_y^3 \hat{c}_{s,1} \right) \\ &- \mathrm{Ss} \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \left( \hat{\nabla}_x \hat{\sigma}_{s,0} + \hat{\nabla}_y \hat{\sigma}_{s,1} \right) + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \right) \right) \Biggr] \Biggr\}$$
(iii)

Collecting terms of  $\mathcal{O}(\xi^{-2})$ :

$$\xi^{-2} \Biggl\{ 0 = \hat{\nabla}_{y} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+}) \mathcal{D}_{s}^{*} \hat{\mathcal{D}}_{s}}{2 \mathrm{RT} c_{\max} \mathcal{D}_{e}^{*}} \mathcal{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{y} \hat{c}_{s,0} - \mathrm{Ch}_{s} \frac{\mathcal{D}_{s}^{*}}{\mathcal{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathcal{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{y}^{3} \hat{c}_{s,0} - \mathrm{Sh}_{s} \frac{\mathcal{D}_{s}^{*}}{\mathcal{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathcal{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{y}^{3} \hat{c}_{s,0} - \mathrm{Sh}_{s} \frac{\mathcal{D}_{s}^{*}}{\mathcal{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathcal{D}}_{s} \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}} \hat{\nabla}_{y} \hat{\sigma}_{s,0} + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{y} \hat{c}_{s,0} \right) \Biggr] \Biggr\}$$
(iv)

Now, applying equation A.2 to the left-hand-side of equation A.14:

$$\begin{split} \vec{n} \cdot \left[ \frac{\hat{c}_s(2-t_+)\mathrm{D}_s^*\hat{\mathrm{D}}_s}{2\mathrm{RT}c_{\max}\mathrm{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \right) \\ &- \mathrm{Ch}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \hat{\mathcal{K}}_s \left( \hat{\nabla}_x^3 \hat{c}_s + \xi^{-1} \hat{\nabla}_y^3 \hat{c}_s \right) \\ &- \mathrm{Ss} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \left( \hat{\nabla}_x \hat{\sigma} + \xi^{-1} \hat{\nabla}_y \hat{\sigma} \right) + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \right) \right) \right] \\ &+ \xi^{-1} \hat{\nabla}_y \cdot \left[ \frac{\hat{c}_s(2-t_+)\mathrm{D}_s^* \hat{\mathrm{D}}_s}{2\mathrm{RT}c_{\max}\mathrm{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \right) \right. \\ &- \mathrm{Ch}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \hat{\mathcal{K}}_s \left( \hat{\nabla}_x^3 \hat{c}_s + \xi^{-1} \hat{\nabla}_y^3 \hat{c}_s \right) \\ &- \mathrm{Ss} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \left( \hat{\nabla}_x \hat{\sigma} + \xi^{-1} \hat{\nabla}_y \hat{\sigma} \right) + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_s + \xi^{-1} \hat{\nabla}_y \hat{c}_s \right) \right] \end{split}$$

(A.18)

then, applying equations A.6 and A.9 to equation A.18:

$$\vec{n} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+})\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RT}c_{\max}\mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial\hat{c}_{s}^{2}} \left( \hat{\nabla}_{x}\hat{c}_{s,0} + \xi\hat{\nabla}_{x}\hat{c}_{s,1} + \xi^{-1}\hat{\nabla}_{y}\hat{c}_{s,0} + \hat{\nabla}_{y}\hat{c}_{s,1} \right) \right. \\ \left. - \operatorname{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s} \left( \hat{\nabla}_{x}^{3}\hat{c}_{s,0} + \xi\hat{\nabla}_{x}\hat{c}_{s,1} + \xi^{-1}\hat{\nabla}_{y}^{3}\hat{c}_{s,0} + \hat{\nabla}_{y}^{3}\hat{c}_{s,0} \right) \right. \\ \left. - \operatorname{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \frac{\partial\varepsilon_{\operatorname{Che}}}{\partial\hat{c}_{s}} \left( \hat{\nabla}_{x}\hat{\sigma}_{s,0} + \xi\hat{\nabla}_{x}\hat{\sigma}_{s,1} + \xi^{-1}\hat{\nabla}_{y}\hat{\sigma}_{s,0} + \hat{\nabla}_{y}\hat{\sigma}_{s,1} \right) \right. \\ \left. + \hat{\sigma} \frac{\partial^{2}\varepsilon_{e}}{\partial\hat{c}_{s}^{2}} \left( \hat{\nabla}_{x}\hat{c}_{s,0} + \xi\hat{\nabla}_{x}\hat{c}_{s,1} + \xi^{-1}\hat{\nabla}_{y}\hat{c}_{s,0} + \hat{\nabla}_{y}\hat{c}_{s,1} \right) \right) \right] \\ \left. + \hat{\nabla}_{y} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+})\mathrm{D}_{s}^{*}\hat{\mathrm{D}}_{s}}{2\mathrm{RT}c_{\max}\mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial\hat{c}_{s}^{2}} \left( \xi^{-1}\hat{\nabla}_{x}\hat{c}_{s,0} + \hat{\nabla}_{x}\hat{c}_{s,1} + \xi^{-2}\hat{\nabla}_{y}\hat{c}_{s,0} + \xi^{-1}\hat{\nabla}_{y}\hat{c}_{s,1} \right) \right. \\ \left. - \operatorname{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s}\hat{\mathcal{K}}_{s} \left( \xi^{-1}\hat{\nabla}_{x}\hat{c}_{s,0} + \hat{\nabla}_{x}\hat{c}_{s,1} + \xi^{-2}\hat{\nabla}_{y}\hat{c}_{s,0} + \xi^{-1}\hat{\nabla}_{y}\hat{c}_{s,1} \right) \\ \left. - \operatorname{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \frac{\partial\varepsilon_{\operatorname{Che}}}{\partial\hat{c}_{s}} \left( \xi^{-1}\hat{\nabla}_{x}\hat{\sigma}_{s,0} + \hat{\nabla}_{x}\hat{\sigma}_{s,1} + \xi^{-2}\hat{\nabla}_{y}\hat{\sigma}_{s,0} + \xi^{-1}\hat{\nabla}_{y}\hat{\sigma}_{s,1} \right) \right. \\ \left. + \hat{\sigma} \frac{\partial^{2}\varepsilon_{\operatorname{Che}}}{\mathrm{D}_{e}^{*}} \left( \xi^{-1}\hat{\nabla}_{x}\hat{c}_{s,0} + \hat{\nabla}_{x}\hat{c}_{s,1} + \xi^{-2}\hat{\nabla}_{y}\hat{c}_{s,0} + \xi^{-1}\hat{\nabla}_{y}\hat{\sigma}_{s,1} \right) \right) \right]$$

$$(A.19)$$

The exponential part of  $\hat{j}_{BV}$ , at the right-hand-side of equation A.14, can be expanded by substitution of the equations A.7, A.9, and the identity  $2*\sinh(x)=e^x-e^{-x}$ . Define:

$$x = \left(\hat{\phi}_s^0 - \hat{\phi}_e^0 - \hat{j}_{BV}^0 \hat{R}_f - \hat{\sigma}^0 \varepsilon_e + \xi (\hat{\phi}_s^1 - \hat{\phi}_e^1 - \hat{j}_{BV}^1 \hat{R}_f - \hat{\sigma}^1 \varepsilon_e)\right),$$

$$2 * \sinh(x) = \exp(\hat{\phi}_{s}^{0} - \hat{\phi}_{e}^{0} - \hat{j}_{BV}^{0} \hat{R}_{f} - \hat{\sigma}^{0} \varepsilon_{e} + \xi(\hat{\phi}_{s}^{1} - \hat{\phi}_{e}^{1} - \hat{j}_{BV}^{1} \hat{R}_{f} - \hat{\sigma}^{1} \varepsilon_{e})) - \exp(-(\hat{\phi}_{s}^{0} - \hat{\phi}_{e}^{0} - \hat{j}_{BV}^{0} \hat{R}_{f} - \hat{\sigma}^{0} \varepsilon_{e} + \xi(\hat{\phi}_{s}^{1} - \hat{\phi}_{e}^{1} - \hat{j}_{BV}^{1} \hat{R}_{f} - \hat{\sigma}^{1} \varepsilon_{e}))) + \mathcal{O}(\xi^{2})$$
(A.20)

Then, simplify the trigonometric identity,  $\sinh(a + b) = \sinh(a) \cosh(b) + \cosh(a)$  $\sinh(b)$ , by approximating  $\sinh(a) \sim a$ , and assuming that  $\xi(\hat{\phi}_s^1 - \hat{\phi}_e^1 - \hat{j}_{BV}^1 \hat{R}_f - \hat{\sigma}^1 \varepsilon_e)$  $\sim 0$ , is negligible. Thus,  $\cosh(\xi(\hat{\phi}_s^1 - \hat{\phi}_e^1 - \hat{j}_{BV}^1 \hat{R}_f - \hat{\sigma}^1 \varepsilon_e)) = 1$ , and  $\sinh(a + b)$  can be expanded to  $\mathcal{O}(\xi^2)$ .

Define:

$$a = (\hat{\phi}_{s}^{0} - \hat{\phi}_{e}^{0} - \hat{j}_{BV}^{0} \hat{R}_{f} - \hat{\sigma}^{0} \varepsilon_{e}),$$
  
$$b = (\xi (\hat{\phi}_{s}^{1} - \hat{\phi}_{e}^{1} - \hat{j}_{BV}^{1} \hat{R}_{f} - \hat{\sigma}^{1} \varepsilon_{e}),$$
  
(A.21)

$$2 * \sinh(a+b) = \sinh(\hat{\phi}_s^0 - \hat{\phi}_e^0 - \hat{j}_{BV}^0 \hat{R}_f - \hat{\sigma}^0 \varepsilon_e) + \xi (\hat{\phi}_s^1 - \hat{\phi}_e^1 - \hat{j}_{BV}^1 \hat{R}_f - \hat{\sigma}^1 \varepsilon_e) \cosh(\hat{\phi}_s^0 - \hat{\phi}_e^0 - \hat{j}_{BV}^0 \hat{R}_f - \hat{\sigma}^0 \varepsilon_e)$$

Similarly, the expansion up to  $\mathcal{O}(\xi^2)$  of the coefficient of  $\hat{j}_{BV}$  in the right-hand-side of equation A.14 is:

$$(\hat{c}_{e}\hat{c}_{s}(\hat{c}_{\max}-\hat{c}_{s}))^{\frac{1}{2}} = \left[ (\hat{c}_{e}^{0}+\xi\hat{c}_{e}^{1})(\hat{c}_{s}^{0}+\xi\hat{c}_{s}^{1})(1-(\hat{c}_{s}^{0}+\xi\hat{c}_{s}^{1})) \right]^{\frac{1}{2}}$$

$$= \left\{ \hat{c}_{e}^{0}\hat{c}_{s}^{0}(1-\hat{c}_{s}^{0})\left[ 1+\xi\left(\frac{\hat{c}_{s}^{1}}{\hat{c}_{s}^{0}}+\frac{\hat{c}_{e}^{1}}{\hat{c}_{e}^{0}}-\frac{\hat{c}_{s}^{1}}{(1-\hat{c}_{s}^{0})}\right) \right] \right\}^{\frac{1}{2}}$$
(A.22)

From equations A.21 and A.22, the following terms can be identified:

$$A_{0} = \sinh(\hat{\phi}_{s}^{0} - \hat{\phi}_{e}^{0} - \hat{j}_{BV}^{0}\hat{R}_{f} - \hat{\sigma}^{0}\varepsilon_{e})$$

$$A_{1} = (\hat{\phi}_{s}^{1} - \hat{\phi}_{e}^{1} - \hat{j}_{BV}^{1}\hat{R}_{f} - \hat{\sigma}^{1}\varepsilon_{e})\cosh(\hat{\phi}_{s}^{0} - \hat{\phi}_{e}^{0} - \hat{j}_{BV}^{0}\hat{R}_{f} - \hat{\sigma}^{0}\varepsilon_{e})$$

$$B_{1} = \left(\hat{c}_{e}^{0}\hat{c}_{s}^{0}(1 - \hat{c}_{s}^{0})\right)^{\frac{1}{2}}$$

$$B_{0} = \left[1 + \xi \left(\frac{\hat{c}_{s}^{1}}{\hat{c}_{s}^{0}} + \frac{\hat{c}_{e}^{1}}{\hat{c}_{e}^{0}} - \frac{\hat{c}_{s}^{1}}{(1 - \hat{c}_{s}^{0})}\right)\right]^{\frac{1}{2}}$$
(A.23)

Re-organizing terms,  $\hat{j}_{BV}$  up to  $\mathcal{O}(\xi^2)$  can be re-written as:

$$\hat{j}_{BV} = (A_0 + \xi A_1)(B_0 B_1) = A_0 B_0 B_1 + \xi A_1 B_0 B_1 + \mathcal{O}(\xi^2)$$
(A.24)

Now, both sides of equation A.14 are expanded, and the terms can be re-organized. Collecting terms of  $\mathcal{O}(\xi)$ :

$$\begin{split} \xi \Biggl\{ \vec{n} \cdot \Biggl[ \frac{\hat{c}_s(2-t_+) \mathbf{D}_s^* \hat{\mathbf{D}}_s}{2 \mathbf{R} \mathbf{T} c_{\max} \mathbf{D}_e^*} \mathbf{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} (\hat{\nabla}_x \hat{c}_{s,1}) - \mathbf{Ch}_s \frac{\mathbf{D}_s^*}{\mathbf{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathbf{D}}_s \hat{\mathcal{K}}_s \left( \hat{\nabla}_x^3 \hat{c}_{s,1} \right) \\ &- \mathbf{Ss} \frac{\mathbf{D}_s^*}{\mathbf{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathbf{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \left( \hat{\nabla}_x \hat{\sigma}_{s,1} \right) + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \left( \xi \hat{\nabla}_x \hat{c}_{s,1} \right) \right) \Biggr] \tag{v} \\ &= \mathbf{Da}_s \frac{\mathbf{D}_s^*}{\mathbf{D}_e^*} c_{\max}^{\alpha_c} \mathbf{A}_1 \mathbf{B}_0 \mathbf{B}_1 \Biggr\} \end{split}$$

Collecting terms of  $\mathcal{O}(\xi^0)$ :

$$\begin{split} \xi^{0} \Biggl\{ \vec{n} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+}) \mathbf{D}_{s}^{*} \hat{\mathbf{D}}_{s}}{2 \mathbf{R} \mathbf{T} c_{\max} \mathbf{D}_{e}^{*}} \mathbf{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \left( \hat{\nabla}_{x} \hat{c}_{s,0} + \hat{\nabla}_{y} \hat{c}_{s,1} \right) \\ &- \mathbf{C} \mathbf{h}_{s} \frac{\mathbf{D}_{s}^{*}}{\mathbf{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathbf{D}}_{s} \hat{\mathcal{K}}_{s} \left( \hat{\nabla}_{x}^{3} \hat{c}_{s,0} + \hat{\nabla}_{y}^{3} \hat{c}_{s,1} \right) \\ &- \mathbf{S} \mathbf{s} \frac{\mathbf{D}_{s}^{*}}{\mathbf{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathbf{D}}_{s} \left( \frac{\partial \varepsilon_{\text{Che}}}{\partial \hat{c}_{s}} \left( \hat{\nabla}_{x} \hat{\sigma}_{s,0} + \hat{\nabla}_{y} \hat{\sigma}_{s,1} \right) \right) \\ &+ \hat{\sigma} \frac{\partial^{2} \varepsilon_{\text{Che}}}{\partial \hat{c}_{s}^{2}} \left( \hat{\nabla}_{x} \hat{c}_{s,0} + \hat{\nabla}_{y} \hat{c}_{s,1} \right) \right) \Biggr]$$
(vi)  
$$&+ \hat{\nabla}_{y} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+}) \mathbf{D}_{s}^{*} \hat{\mathbf{D}}_{s}}{2 \mathbf{R} \mathbf{T} c_{\max} \mathbf{D}_{e}^{*}} \mathbf{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{x} \hat{c}_{s,1} - \mathbf{C} \mathbf{h}_{s} \frac{\mathbf{D}_{s}^{*}}{\mathbf{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathbf{D}}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{3} \hat{c}_{s,1} \\ &- \mathbf{S} \mathbf{s} \frac{\mathbf{D}_{s}^{*}}{\mathbf{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathbf{D}}_{s} \left( \frac{\partial \varepsilon_{\text{Che}}}{\partial \hat{c}_{s}} \hat{\nabla}_{x} \hat{\sigma}_{s,1} + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\text{Che}}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{x} \hat{c}_{s,1} \right) \Biggr] \Biggr] \\ &= \mathbf{D} \mathbf{a}_{s} \frac{\mathbf{D}_{s}^{*}}{\mathbf{D}_{e}^{*}} c_{\max}^{\alpha_{c}} \mathbf{A}_{0} \mathbf{B}_{0} \mathbf{B}_{1} \Biggr\}$$

Collecting terms of  $\mathcal{O}(\xi^{-1})$ :

$$\begin{split} \xi^{-1} \Biggl\{ \vec{n} \cdot \Biggl[ \frac{\hat{c}_s(2-t_+) \mathcal{D}_s^* \hat{\mathcal{D}}_s}{2 \mathrm{RT} c_{\max} \mathcal{D}_e^*} \mathcal{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \hat{\nabla}_y \hat{c}_{s,0} - \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \hat{\nabla}_y^3 \hat{c}_{s,0} \\ &- \mathrm{Ss} \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \Biggl( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \hat{\nabla}_y \hat{\sigma}_{s,0} + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \hat{\nabla}_y \hat{c}_{s,0} \Biggr) \Biggr] \\ &+ \hat{\nabla}_y \cdot \Biggl[ \frac{\hat{c}_s(2-t_+) \mathcal{D}_s^* \hat{\mathcal{D}}_s}{2 \mathrm{RT} c_{\max} \mathcal{D}_e^*} \mathcal{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \Biggl( \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \Biggr) \\ &- \mathrm{Ch}_s \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \hat{\mathcal{K}}_s \Biggl( \hat{\nabla}_x^3 \hat{c}_{s,0} + \hat{\nabla}_y^3 \hat{c}_{s,1} \Biggr) \\ &- \mathrm{Ss} \frac{\mathcal{D}_s^*}{\mathcal{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathcal{D}}_s \Biggl( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \Biggl( \hat{\nabla}_x \hat{\sigma}_{s,0} + \hat{\nabla}_y \hat{\sigma}_{s,1} \Biggr) \\ &+ \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \Biggl( \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \Biggr) \Biggr] = 0 \Biggr\} \end{split}$$

Homogeneity of equation iv guarantees independence of 'y' in the variable  $c_0$ : *i.e.*  $\hat{c}_0(x, t, \tau_{\rm R}, \tau_{{\rm M}_s}, \tau_{{\rm M}_e}, \tau_{{\rm Ch}_s}, \tau_{{\rm Ch}_e}, \tau_{{\rm Ss}_s}, \tau_{{\rm Ss}_e})$  is independent of y if:

$$\hat{\nabla}_y \hat{c}_0 = 0 \tag{A.25}$$

Similarly,  $\hat{\phi}_0(x, t, \tau_{\text{\tiny R}}, \tau_{\text{\tiny Ms}}, \tau_{\text{\tiny Me}}, \tau_{\text{\tiny Chs}}, \tau_{\text{\tiny Che}}, \tau_{\text{\tiny Sss}}, \tau_{\text{\tiny Sse}})$  is independent of y if:

$$\hat{\nabla}_y \hat{\phi}_0 = 0 \tag{A.26}$$

Lastly,  $\hat{\sigma}_0(x,t,\tau_{\rm\scriptscriptstyle R},\tau_{\scriptscriptstyle\rm M_{\it S}},\tau_{\scriptscriptstyle\rm M_{\it e}},\tau_{\scriptscriptstyle\rm Ch_{\it s}},\tau_{\scriptscriptstyle\rm Ch_{\it e}},\tau_{\scriptscriptstyle\rm Ss_{\it s}},\tau_{\scriptscriptstyle\rm Ss_{\it e}})$  is independent of y if:

$$\hat{\nabla}_y \hat{\sigma}_0 = 0 \tag{A.27}$$

Applying A.25, A.26 and A.27 to equation iii

$$0 = \hat{\nabla}_{y} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+})\mathbf{D}_{s}^{*}\mathbf{D}_{s}}{2\mathrm{RT}c_{\max}\mathbf{D}_{e}^{*}} \mathbf{U}^{*} \frac{\partial^{2}\hat{g}}{\partial\hat{c}_{s}^{2}} \left( \hat{\nabla}_{x}\hat{c}_{s,0} + \hat{\nabla}_{y}\hat{c}_{s,1} \right) - \mathrm{Ch}_{s} \frac{\mathbf{D}_{s}^{*}}{\mathbf{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathbf{D}}_{s}\hat{\mathcal{K}}_{s} \left( \hat{\nabla}_{x}^{3}\hat{c}_{s,0} + \hat{\nabla}_{y}^{3}\hat{c}_{s,1} \right) - \mathrm{Ss} \frac{\mathbf{D}_{s}^{*}}{\mathbf{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathbf{D}}_{s} \left( \frac{\partial\varepsilon_{\mathrm{Che}}}{\partial\hat{c}_{s}} \left( \hat{\nabla}_{x}\hat{\sigma}_{s,0} + \hat{\nabla}_{y}\hat{\sigma}_{s,1} \right) + \hat{\sigma} \frac{\partial^{2}\varepsilon_{\mathrm{Che}}}{\partial\hat{c}_{s}^{2}} \left( \hat{\nabla}_{x}\hat{c}_{s,0} + \hat{\nabla}_{y}\hat{c}_{s,1} \right) \right) \right]$$
(A.28)

Applying A.25, A.26 and A.27 to equation vi

$$\vec{n} \cdot \left[ \frac{\hat{c}_s(2-t_+) \mathbf{D}_s^* \hat{\mathbf{D}}_s}{2 \mathrm{RT} c_{\max} \mathbf{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \right) - \mathrm{Ch}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \hat{\mathcal{K}}_s \left( \hat{\nabla}_x^3 \hat{c}_{s,0} + \hat{\nabla}_y^3 \hat{c}_{s,1} \right) - \mathrm{Ss} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \left( \hat{\nabla}_x \hat{\sigma}_{s,0} + \hat{\nabla}_y \hat{\sigma}_{s,1} \right) + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \left( \hat{\nabla}_x \hat{c}_{s,0} + \hat{\nabla}_y \hat{c}_{s,1} \right) \right) \right] \\ + \hat{\nabla}_y \cdot \left[ \frac{\hat{c}_s(2-t_+) \mathrm{D}_s^* \hat{\mathrm{D}}_s}{2 \mathrm{RT} c_{\max} \mathrm{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}_s^2} \hat{\nabla}_x \hat{c}_{s,1} - \mathrm{Ch}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \hat{\mathcal{K}}_s \hat{\nabla}_x^3 \hat{c}_{s,1} - \mathrm{Ss} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{(2-t_+)}{2} \hat{\mathrm{D}}_s \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s} \hat{\nabla}_x \hat{\sigma}_{s,1} + \hat{\sigma} \frac{\partial^2 \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_s^2} \hat{\nabla}_x \hat{c}_{s,1} \right) \right] = \mathrm{Da}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} c_{\max}^{\alpha_c} \mathrm{A}_0 \mathrm{B}_0 \mathrm{B}_1$$

$$(A.29)$$

Substituting equation A.29 into equation A.28:

$$0 = \hat{\nabla}_y \cdot [\text{DaA}_0 \text{B}_0 \text{B}_1] \tag{A.30}$$

therefore,  $A_0B_0B_1 = 0$ .

Now, proposing solutions of the form:

$$\hat{c}_{1}(x, y, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}}) = \chi_{1}(y) \hat{\nabla}_{x} \hat{c}_{0}(x, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}}) + \bar{\hat{c}}_{1}(x, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}})$$

$$\hat{\phi}_{1}(x, y, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}}) = \chi_{2}(y)\hat{\nabla}_{x}\hat{\phi}_{0}(x, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}}) + \overline{\hat{\phi}}_{1}(x, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}})$$

$$(A.32)$$

$$\hat{\sigma}_{1}(x, y, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}}) = \chi_{3}(y)\hat{\nabla}_{x}\hat{\sigma}_{0}(x, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}})$$

$$+ \overline{\hat{\sigma}}_{1}(x, t, \tau_{\rm R}, \tau_{{\rm M}_{s}}, \tau_{{\rm M}_{e}}, \tau_{{\rm Ch}_{s}}, \tau_{{\rm Ch}_{e}}, \tau_{{\rm Ss}_{s}}, \tau_{{\rm Ss}_{e}})$$

(A.33)

and substituting equations A.31 and A.33 into equation ii:

$$\begin{aligned} \frac{\partial c_{s,0}}{\partial t} + \xi^{\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\rm R}} + \xi^{-\beta} \left( \xi^{\nu-\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\rm M_{s}}} \right) + \xi^{-\iota} \frac{\partial c_{s,0}}{\partial \tau_{\rm M_{e}}} + \xi^{\delta} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ch_{s}}} + \xi^{\sigma} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ch_{e}}} + \xi^{\zeta} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ss_{s}}} + \xi^{\omega} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ss_{s}}} \right. \\ &= \hat{\nabla}_{x} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+}) D_{s}^{*} \hat{D}_{s}}{2 R T c_{\rm max} D_{e}^{*}} U^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \left( I + \hat{\nabla}_{y} \chi_{1} \right) \left( \hat{\nabla}_{x} \hat{c}_{s,0} \right) \right. \\ &- \left. Ch_{s} \frac{D_{s}^{*}}{D_{e}^{*}} \frac{(2-t_{+})}{2} \hat{D}_{s} \hat{\mathcal{K}}_{s} \left( I + \hat{\nabla}_{y}^{3} \chi_{1} \right) \left( \hat{\nabla}_{x}^{3} \hat{c}_{s,0} \right) \right. \\ &- \left. Ss \frac{D_{s}^{*}}{D_{e}^{*}} \frac{(2-t_{+})}{2} \hat{D}_{s} \left( \frac{\partial \varepsilon_{\rm Che}}{\partial \hat{c}_{s}} \left( I + \hat{\nabla}_{y} \chi_{3} \right) \left( \hat{\nabla}_{x} \hat{\sigma}_{s,0} \right) + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\rm Che}}{\partial \hat{c}_{s}^{2}} \left( I + \hat{\nabla}_{y} \chi_{1} \right) \left( \hat{\nabla}_{x} \hat{c}_{s,0} \right) \right) \right] \\ &+ \hat{\nabla}_{y} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+}) D_{s}^{*} \hat{D}_{s}}{2 R T c_{\rm max} D_{e}^{*}} U^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{x} \hat{c}_{s,1} - Ch_{s} \frac{D_{s}^{*}}{D_{e}^{*}} \frac{(2-t_{+})}{2} \hat{D}_{s} \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{3} \hat{c}_{s,1} \\ &- \left. Ss \frac{D_{s}^{*}}{D_{e}^{*}} \frac{(2-t_{+})}{2} \hat{D}_{s} \left( \frac{\partial \varepsilon_{\rm Che}}{\partial \hat{c}_{s}} \hat{\nabla}_{x} \hat{\sigma}_{s,1} + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\rm Che}}{\partial \hat{c}_{s}^{2}} \hat{\nabla}_{x} \hat{c}_{s,1} \right) \right] \end{aligned} \tag{iiA}$$

Similarly, substituting equation v into equation iiA:

$$\begin{aligned} \frac{\partial c_{s,0}}{\partial t} + \xi^{\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\rm R}} + \xi^{-\beta} \left( \xi^{\nu-\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\rm Ms}} \right) + \xi^{-\iota} \frac{\partial c_{s,0}}{\partial \tau_{\rm Me}} + \xi^{\delta} \frac{\partial c_{s,0}}{\partial \tau_{\rm Chs}} + \xi^{o} \frac{\partial c_{s,0}}{\partial \tau_{\rm Che}} + \xi^{\zeta} \frac{\partial c_{s,0}}{\partial \tau_{\rm Sss}} + \xi^{\omega} \frac{\partial c_{s,0}}{\partial \tau_{\rm Sse}} \\ &= \hat{\nabla}_{x} \cdot \left[ \frac{\hat{c}_{s}(2-t_{+}) D_{s}^{*} \hat{D}_{s}}{2 R T c_{\rm max} D_{e}^{*}} U^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \left( I + \hat{\nabla}_{y} \chi_{1} \right) \left( \hat{\nabla}_{x} \hat{c}_{s,0} \right) \right. \\ &- \left. Ch_{s} \frac{D_{s}^{*}}{D_{e}^{*}} \frac{(2-t_{+})}{2} \hat{D}_{s} \hat{\mathcal{K}}_{s} \left( I + \hat{\nabla}_{y}^{3} \chi_{1} \right) \left( \hat{\nabla}_{x}^{3} \hat{c}_{s,0} \right) \right. \\ &- \left. Ss \frac{D_{s}^{*}}{D_{e}^{*}} \frac{(2-t_{+})}{2} \hat{D}_{s} \left( \frac{\partial \varepsilon_{\rm Che}}{\partial \hat{c}_{s}} \left( I + \hat{\nabla}_{y} \chi_{3} \right) \left( \hat{\nabla}_{x} \hat{\sigma}_{s,0} \right) + \hat{\sigma} \frac{\partial^{2} \varepsilon_{\rm Che}}{\partial \hat{c}_{s}^{2}} \left( I + \hat{\nabla}_{y} \chi_{1} \right) \left( \hat{\nabla}_{x} \hat{c}_{s,0} \right) \right) \right] \\ &+ \hat{\nabla}_{y} \cdot \left[ Da_{s} \frac{D_{s}^{*}}{D_{e}^{*}} c_{\rm max}^{\alpha} A_{1} B_{0} B_{1} \right] \end{aligned} \tag{iiB}$$

now, multiplying equation iiB by  $\xi,$  integrating w.r.t. y, and recalling equation A.3:

$$\begin{split} \xi \int_{S} \left( \frac{\partial c_{s,0}}{\partial t} + \xi^{\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{R}}} + \xi^{-\beta} \left( \xi^{\nu-\gamma} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{M}s}} \right) + \xi^{-\iota} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{M}e}} + \xi^{\delta} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ch}s}} + \xi^{o} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ch}e}} + \xi^{\zeta} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ss}s}} \right) dy \\ &+ \xi^{\omega} \frac{\partial c_{s,0}}{\partial \tau_{\mathrm{Ss}e}} \right) dy = \frac{\hat{c}_{s}(2-t_{+}) \mathrm{D}_{s}^{*} \hat{\mathrm{D}}_{s}}{2\mathrm{RT} c_{\mathrm{max}} \mathrm{D}_{e}^{*}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{s}^{2}} \xi \int_{S} \left(\mathrm{I} + \hat{\nabla}_{y} \chi_{1}\right) \left(\hat{\nabla}_{x}^{2} \hat{c}_{s,0}\right) dy \\ &- \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \hat{\mathcal{K}}_{s} \xi \int_{S} \left(\mathrm{I} + \hat{\nabla}_{y} \chi_{1}\right) \left(\hat{\nabla}_{x}^{4} \hat{c}_{s,0}\right) dy \\ &- \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}} \xi \int_{S} \left(\mathrm{I} + \hat{\nabla}_{y} \chi_{3}\right) \left(\hat{\nabla}_{x}^{2} \hat{\sigma}_{s,0}\right) dy \\ &+ \hat{\sigma} \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{s}^{2}} \xi \int_{S} \left(\mathrm{I} + \hat{\nabla}_{y} \chi_{1}\right) \left(\hat{\nabla}_{x}^{2} \hat{c}_{s,0}\right) dy \right) \\ &+ \xi \int_{S} \hat{\nabla}_{y} \cdot \left[ \mathrm{Da}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} c_{\mathrm{max}}^{\alpha c} \mathrm{A}_{1} \mathrm{B}_{0} \mathrm{B}_{1} \right] dy \end{split}$$

$$(\mathrm{iiC})$$

Considering:

where the closure variable  $\chi(y)_i$  has zero mean  $\langle \chi \rangle = 0$ , and is the solution to:

$$\hat{\nabla}_{y} \cdot \left( \mathbf{I} + \hat{\nabla}_{y} \chi \right) = 0$$

$$\vec{n} \cdot \left( \mathbf{I} + \hat{\nabla}_{y} \chi \right) = 0$$
(A.35)

The integral w.r.t. y is performed over the volume domain, S, although the intercalation reaction occurs only at surface domain, dS. Thus a volume-to-surface conversion is required:

$$\int_{dS} \hat{\nabla}_y \cdot \left[ \mathrm{Da}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} c_{\max}^{\alpha_c} \mathrm{A}_1 \mathrm{B}_0 \mathrm{B}_1 \right] \mathrm{d}y = \frac{|A|}{|V|} \times \int_S \hat{\nabla}_y \cdot \left[ \mathrm{Da}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} c_{\max}^{\alpha_c} \mathrm{A}_1 \mathrm{B}_0 \mathrm{B}_1 \right] \mathrm{d}y \quad (A.36)$$

Recasting equations A.6 and A.9 as:

$$\hat{c}_{s} = \xi^{0} \hat{c}_{s,0} + \xi \hat{c}_{s,1} + \mathcal{O}(\xi^{2})$$

$$\xi \hat{c}_{s} = \xi \hat{c}_{s,0} + \mathcal{O}(\xi^{2})$$
(A.37)

$$\hat{\sigma}_s = \xi^0 \hat{\sigma}_{s,0} + \xi \hat{\sigma}_{s,1} + \mathcal{O}(\xi^2)$$

$$\xi \hat{\sigma}_s = \xi \hat{\sigma}_{s,0} + \mathcal{O}(\xi^2)$$
(A.38)

Substituting equations A.37 and A.38 into equation iiC, using equation A.24, A.30, and the dimensionless reactivity definition  $(\hat{\mathcal{A}} = \frac{|\mathcal{A}|}{|V|})$ , the upscaled-homogenized mass transport equation for the solid phase, approximated to  $\mathcal{O}(\xi^2)$  is:

$$\epsilon_{s} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})\mathrm{D}_{s}^{*}}{2\mathrm{RT}c_{\max}\mathrm{D}_{e}^{*}}\mathrm{U}^{*} \frac{\partial^{2}\hat{g}}{\partial \hat{c}^{2}} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle - \mathrm{Ch}_{s} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{s} \right\rangle \hat{\mathcal{K}}_{s} \hat{\nabla}_{x}^{4} \langle \hat{c} \rangle - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*}}{\mathrm{D}_{e}^{*}} \frac{(2-t_{+})}{2} \hat{\mathrm{D}}_{s} \left( 2\frac{\partial \langle \hat{\sigma} \rangle}{\partial \hat{x}} \left\langle \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{i}^{2}} \right\rangle \hat{\nabla}_{x} \langle \hat{c}_{i} \rangle + \left\langle \frac{\partial \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{i}} \right\rangle \frac{\partial^{2} \langle \hat{\sigma} \rangle}{\partial \hat{x}^{2}} \right) - \mathrm{Ss} \frac{\mathrm{D}_{s}^{*} (2-t_{+})}{\mathrm{D}_{e}^{*}} \hat{\mathrm{D}}_{s} \left( \left\langle \hat{\sigma} \right\rangle \left\langle \frac{\partial^{2} \varepsilon_{\mathrm{Che}}}{\partial \hat{c}_{i}^{2}} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c}_{i} \rangle \right) - \frac{\mathrm{D}_{s}^{*} \epsilon_{s}}{\mathrm{D}_{e}^{*} \xi} \mathrm{Da}_{s} \hat{\mathcal{A}} \hat{j}_{BV}$$
(A.39)

Following the process for the charge transport equation in equation set 2.11:

$$\epsilon_s \frac{\partial \langle \hat{\rho} \rangle}{\partial \hat{t}} = 2 \operatorname{Pe}_s \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \left\langle \hat{\sigma}_T \right\rangle \hat{\nabla}_x^2 \hat{\phi} + \frac{\hat{c} \mathrm{D}_s^*}{2 \mathrm{RT} c_{\max} \mathrm{D}_e^*} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \left\langle \hat{\mathrm{D}}_s \right\rangle \hat{\nabla}_x^2 \hat{c} \\ - \frac{\mathrm{Ch}_s}{2} \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \left\langle \hat{\mathrm{D}}_s \right\rangle \hat{\mathcal{K}}_s \hat{\nabla}_x^4 \hat{c} - \frac{\mathrm{D}_s^*}{\mathrm{D}_e^*} \frac{\epsilon_s}{\xi} \operatorname{Da}_s \hat{\mathcal{A}} \hat{j}_{BV}$$
(A.40)

Similarly, the mass and charge transport equations for the electrolyte are given by:

$$\epsilon_{e} \frac{\partial \langle \hat{c} \rangle}{\partial \hat{t}} = \frac{\hat{c}(2-t_{+})}{2 \mathrm{RT} c_{\mathrm{max}}} \mathrm{U}^{*} \frac{\partial^{2} \hat{g}}{\partial \hat{c}_{i}^{2}} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{c} \rangle - \mathrm{Ch}_{e} \frac{(2-t_{+})}{2} \left\langle \hat{\mathrm{D}}_{e} \right\rangle \hat{\mathcal{K}}_{e} \hat{\nabla}_{x}^{4} \langle \hat{c} \rangle + 2 \mathrm{Pe}_{e} t_{+} \left\langle \hat{\sigma}_{T} \right\rangle \hat{\nabla}_{x}^{2} \langle \hat{\phi} \rangle + \frac{\epsilon_{e}}{\xi} \mathrm{Da}_{e} \hat{\mathcal{A}} \hat{j}_{BV}$$

$$(A.41)$$

$$\begin{split} \epsilon_e \frac{\partial \left\langle \hat{\rho} \right\rangle}{\partial \hat{t}} &= 2 \mathrm{Pe}_e \left\langle \hat{\sigma}_T \right\rangle \hat{\nabla}_x^2 \hat{\phi} + \frac{\hat{c}}{2 \mathrm{RT} c_{\max}} \mathrm{U}^* \frac{\partial^2 \hat{g}}{\partial \hat{c}^2} \left\langle \hat{\mathrm{D}}_e \right\rangle \hat{\nabla}_x^2 \hat{c} \\ &- \frac{\mathrm{Ch}_e}{2} \left\langle \hat{\mathrm{D}}_e \right\rangle \hat{\mathcal{K}} \hat{\nabla}_x^4 \hat{c} + \frac{\epsilon_e}{\xi} \mathrm{Da}_e \hat{\mathcal{A}} \hat{j}_{BV} \end{split}$$

## APPENDIX B. DIMENSIONLESS NUMBERS

Table B.1.: Estimated values of transport numbers at the electrolyte phase and at the solid electrode particle for different chemistries. The first section (columns 2 to 8) presents the microstructural dependent transport numbers. Transport numbers dependent only on the chemistry are given in the second section (columns 9 to 15).

Chemistry		$Da^e_\mu$	$\mathrm{Pe}^e_\mu$	$\mathrm{Fo}^e_\mu$	$\mathrm{Da}^s_\mu$	$\mathrm{Pe}^s_\mu$	$\mathrm{Fo}^s_\mu$		$Da^e$	$\mathrm{Pe}^{e}$	$\mathrm{Fo}^e$	$\mathrm{Da}^{s}$	$\mathrm{Pe}^{s}$	$\mathrm{Fo}^s$
		$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-1}$	$\times 10^2$	$ imes 10^2$	$\times 10^{-5}$		$\times 10^{-3}$	$\times 10^{-3}$		$\times 10^2$	$ imes 10^2$	$ imes 10^{-4}$
$\mathrm{LiC}_{6}$		2.76	1.04	0.28	0.19	450	0.98		2.5	37.0	1	0.07	16000	3.44
$LiFePO_4$		3.46	0.46	0.08	14.9	0.006	0.004	$ \Delta $	2.4	58.0	1	4.34	0.81	0.05
$\rm LiMn_2O_4$	ullet	6.3	15.3	2.33	7.91	45.2	0.43	0	11.7	65.9	1	6.3	194	0.19
$\mathrm{Li}_4\mathrm{Ti}_5\mathrm{O}_{12}$		31.9	2.6	1.58	21.9	272	0.53		49.8	16.3	1	14.7	1700	0.34
${\rm LiNi}_{1/3}{\rm Mn}_{1/3}{\rm Co}_{1/3}{\rm O}_2$	•	0.9	4.19	1.58	0.19	1.45	1.77	$\diamond$	1.4	26.5	1	0.13	9.18	1.12
$LiNi_{0.8}Co_{0.2-x}Al_xO_2$	★	1.73	4.06	2.79	0.013	0.15	86.5	☆	3.4	14.5	1	0.01	0.54	31.0
$LiCoO_2$	▼	1.03	2.22	1.11	0.063	5.77	4.26		1.4	20.1	1	0.04	52.2	3.85

Assumed values of  $\epsilon=0.3$ 

### APPENDIX C. ELECTROCHEMICAL DATA

The Gibbs free energy density for  $\text{Li}_x \text{Ni}_{1/3} \text{Mn}_{1/3} \text{Co}_{1/3} \text{O}_2$  was defined as:

$$g(c) = c(\Delta g_b - \Delta g_a) + \Delta g_a + \operatorname{RT}(c\ln(c) + (1-c)\ln(1-c)) + c(1-c)(L_0 + L_1(2c-1)) + L_2(2c-1)^2 + L_3(2c-1)^3 + L_4(2c-1)^4)$$
(C.1)

where  $\Delta g_b - \Delta g_a = -396000 \text{ J/mol}$ ,  $L_0 = -60000 \text{ J/mol}$ ,  $L_1 = 20500 \text{ J/mol}$ ,  $L_2 = 18000 \text{ J/mol}$ ,  $L_3 = -20000 \text{ J/mol}$ , and  $L_4 = -16000 \text{ J/mol}$ . The equilibrium potential was derived as  $\phi_{\text{OCP}} = -\frac{1}{z\mathcal{F}}\frac{\partial g}{\partial c}$ , and the second derivative as:  $\frac{\partial^2 g}{\partial c^2} = -z\mathcal{F}\frac{\partial \phi_{\text{OCP}}}{\partial c}$ .

The Gibbs free energy density for EC:DMC electrolyte was defined as:

$$g(c) = \frac{\mathrm{RT}}{\Omega} (c \ln(c) + (1-c) \ln(1-c)) + (c(1-c)(\mathrm{L}_0 + \mathrm{L}_1(2c-1) + \mathrm{L}_2(2c-1)^2))$$
(C.2)

where  $\Omega = 6.93 \times 10^{-5} \text{ m}^3/\text{mol}$ ,  $L_0 = -4.35 \times 10^8 \text{ J/m}^3$ ,  $L_1 = 0$ ,  $L_2 = -4.40 \times 10^8 \text{ J/m}^3$ .

The open circuit potential for Graphite used in this paper was reported by Safari and coworkers [95]:

$$\phi_{\text{OCP}} = (0.6379 + 0.5416 \exp(-305.5309c) + 0.044(\tanh(-(c - 0.1958)/0.1088) - 0.1978 \tanh((c - 1.0571)/0.0854) - 0.6875 \tanh((c + 0.0117)/0.0529) - 0.0175 \tanh((c - 0.5692)/0.0875))$$
(C.3)

Considering  $\frac{\partial g}{\partial c} = -z\mathcal{F}\phi_{\text{OCP}}$ , the second derivative is defined as:  $\frac{\partial^2 g}{\partial c^2} = -z\mathcal{F}\frac{\partial\phi_{\text{OCP}}}{\partial c}$ .

# APPENDIX D. CHARACTERISTIC TIME SCALES

Five characteristic times related to diffusion, electromigration, heterogeneous reaction, gradient energy, and stress were identified:

$$t_{\mathrm{D}_i} = \frac{\mathrm{L}^2}{\mathrm{D}_i^*} \tag{D.1}$$

$$t_{\mathbf{M}_i} = \frac{(z_i \mathcal{F})^2 \mathbf{L}^2 c_{\max}}{\mathbf{R} \mathbf{T} \sigma_T^*} \tag{D.2}$$

$$t_{\rm R} = \frac{\rm L}{k} \tag{D.3}$$

$$t_{\mathrm{Ch}_i} = \frac{\mathrm{RTL}^4 c_{\mathrm{max}}^2}{\mathrm{D}_i^* c_i \mathcal{K}_i^*} \tag{D.4}$$

$$t_{\rm \scriptscriptstyle Ss_{\it i}} = \frac{{\rm RTL}^2 c_{\rm max}^2}{{\rm D}_i^* c_i \sigma^*} \tag{D.5}$$

and  $i = \{ solid, electrolyte \}$ .

### APPENDIX E. NMC CHEMICAL STRAIN

In-plane and out-of-plane chemical strain as a function of concentration [94]:

$$\varepsilon_{xx}^{\text{Che}}(\hat{c}) = 0.0119 - 0.0454\hat{c} + 0.028\hat{c}^2 + 0.0065\hat{c}^3$$
 (E.1)

$$\varepsilon_{zz}^{\text{Che}}(\hat{c}) = -0.012 - 0.0012(1. - \hat{c}) + 0.204(1. - \hat{c})^2 - 0.2513(1. - \hat{c})^3$$
(E.2)



Figure E.1. Effect of discharge current in the chemically-induced strain of NMC electrodes. — corresponds to chemically-induced strain calculated from the lattice parameter changes measured experimentally during first cycles of galvanostatic discharge at C/40, as reported by Yabuuchi *et al.* [94].  $\bigcirc$  identify cases of strain-free concentration or maximum strain.

### APPENDIX F. ELECTRICAL AND MECHANICAL PROPERTIES

Macroscopic physical quantities such as electrical conductivity and chemical diffusivity are related to porosity and tortuosity through the well-known expressions [5,7,8,10,24,42]:

$$\langle \sigma \rangle = \frac{\epsilon \sigma_{\circ}}{\tau}, \text{ and } \langle \mathbf{D} \rangle = \frac{\epsilon \mathbf{D}_{\circ}}{\tau}$$
 (F.1)

Porosity and tortuosity are connected through the Bruggeman relation  $\tau = \frac{1}{\epsilon^{\alpha}}$  [15].

Similarly, the average mechanical properties are given by [101]:

$$\langle \mathbf{E} \rangle = \frac{9 \langle \mathbf{K} \rangle}{1 + 3 \langle \mathbf{K} \rangle / \langle \mu \rangle}$$
(F.2)

where the average values of the bulk (K) and the shear  $(\mu)$  modulus are derived from a variational formulation known as Hashin-Shtrikman bounds [100]. The lower bound is defined as:

$$\langle \mathbf{K} \rangle = \mathbf{K}_m + (1 - \epsilon) \left[ \frac{1}{\mathbf{K}_p - \mathbf{K}_m} + \frac{3\epsilon}{3\mathbf{K}_m + 4\mu_m} \right]^{-1}$$
 (F.3)

$$\langle \mu \rangle = \mu_m + (1 - \epsilon) \left[ \frac{1}{\mu_p - \mu_m} + \frac{6\epsilon (\mathbf{K}_m + 2\mu_m)}{5\mu_m (3\mathbf{K}_m + 4\mu_m)} \right]^{-1}$$
(F.4)

K is the bulk modulus and  $\mu$  the shear modulus, such that:

$$\mu = \frac{E}{2(1+\nu)} \qquad K = \frac{E}{3(1-2\nu)}$$
(F.5)

Here, m stands for matrix and p for embedded particles.

Similarly, the average of the differential chemical strain  $\partial \varepsilon_e / \partial \hat{c}$  is:

$$\left\langle \frac{\partial \epsilon_{e}}{\partial \hat{c}_{i}} \right\rangle = \left[ \frac{\left( \frac{\partial \epsilon_{e}}{\partial \hat{c}_{i}} \right)_{m} \epsilon \mathbf{K}_{m} + \left( \frac{\partial \epsilon_{e}}{\partial \hat{c}_{i}} \right)_{p} (1 - \epsilon) \mathbf{K}_{p}}{\epsilon \mathbf{K}_{m} + (1 - \epsilon) \mathbf{K}_{p}} \right]$$
(F.6)

in analogy to the thermal expansion formulation [101].

#### REFERENCES

- M.Z. Jacobson, M.A. Delucchi, Z.A.F. Bauer, S.C. Goodman, W.E. Chapman, M.A. Cameron, . . . , A.S. Yachanin, 100% Clean and Renewable Wind, Water, and Sunlight All-Sector Energy Roadmaps for 139 Countries of the World, Joule, 1, 108-121, 2017.
- [2] G. Crabtree, E. K\u00f9cs, and L. Trahey, The energy-storage frontier: Lithium-ion batteries and beyond, MRS BULLETIN, 40, 1067-1076, 2015.
- [3] J.-M. Tarascon, and M. Armand, Issues and challenges facing rechargeable lithium batteries, Nature, 414, 359-366, 2001.
- [4] J. Newman, and K.E. Thomas-Alyea, *Electrochemical systems*, 3rd Edition, Hoboken, N. Y.: John Wiley & Sons, 1999.
- [5] J. Newman and W. Tiedemann, *Porous electrode theory with battery applications*, AIChE Journal, 21, 25–41, 1975.
- [6] J.M. Tarascon, and D. Guyomard, The Li<sub>1+x</sub>Mn<sub>2</sub>O<sub>4</sub>/C rocking-chair system: a review, Electrochimica Acta, 38, 9, 1221-1231, 1993.
- [7] M. Doyle, J. Newman, A. S. Gozdz, C. N. Schmutz, and J. M. Tarascon, Comparison of modeling predictions with experimental data from plastic lithium ion cells, Journal of the Electrochemical Society, 143 (6), 1890–1903, 1996.
- [8] M. Doyle, T.F. Fuller, and J. Newman, Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion Cell, Journal of the Electrochemical Society, 140 (6), 1526–1533, 1993.
- [9] T.F. Fuller, M. Doyle, and J. Newman, Simulation and optimization of the dual Lithium ion insertion cell, Journal of the Electrochemical Society, 141 (1), 1-9, 1994.
- [10] C.M. Doyle, Design and Simulation of lithium rechargeable batteries, PhD dissertation, University of California, Energy and Environmental Division Lawrence Berkeley National Laboratory, 1996, Retrieved from http://www.escholarship.org/uc/item/6j87z0sp
- [11] P. Arora, M. Doyle, and R.E. White, Mathematical modeling of the lithium deposition overcharge reaction in Lithium-ion batteries using carbon-based negative electrodes, Journal of the Electrochemical Society, 146 (10), 3543-3555, 1999.
- [12] M. Park, X. Zhang, M. Chung, G.B. Less, and A.M. Sastry, A review of conduction phenomena in Li-ion batteries, Journal of Power Sources, 195, 7904-7929, 2010.

- [13] Y.-H. Chen, C.-W. Wang, X. Zhang, and A.M. Sastry, Porous cathode optimization for lithium cells: Ionic and electronic conductivity, capacity, and selection of materials, Journal of Power Sources, 195, 2851-2862, 2010.
- [14] D. Miranda, C.M. Costa, and S. Lanceros-Mendez, Lithium ion rechargeable batteries: State of the art and future needs of microscopic theoretical models and simulations, Journal of Electroanalytical Chemistry, 739, 97-110, 2015.
- [15] D. A. G. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen, Annalen der Physik, 24, 636-664, 1935.
- [16] T. Nagaura and K. Tazawa, Prog. Batteries Solar Cells, 9, 20, 1990.
- [17] M.Li, J. Lu, Z. Chen, and K. Amine, 30 years of lithium-ion batteries, Advanced Materials, 30, 1800561, 2018.
- [18] B. Scrosati, K.M. Abraham, W. van-Schalkwijk, and J. Hassoun, *Lithium bat*teries: advanced technologies and applications, 1st Edition, Hoboken, New Jersey, John Wiley & Sons, Inc., 2013.
- [19] M. Yoshio, R.J. Brodd, and A.Kozawa Lithium-ion batteries, New York, Springer, 2009, pp. xix
- [20] B. Nykvist, and M. Nilsson, *Rapidly falling costs of battery packs for electric vehicles*, Nature Climate Change 5, 329-332, 2015.
- [21] D. Deng, Li-ion batteries: basics, progress, and challenges, Energy Science & Engineering, 3 (5), 385-418, 2015.
- [22] S. Chu, Y. Cui, and N. Liu, the path towards sustainable energy, Nature materials, 16, 16-22, 2017.
- [23] D. Larcher, and J.-M. Tarascon, Towards greener and more sustainable batteries for electrical energy storage, Nature Chemistry, 7, 19-29, 2015.
- [24] P. De Vidts, and R.E. White, *Governing equations for transport in porous electrodes*, Journal of the Electrochemical Society, 144 (4), 1343–1353, 1997.
- [25] T.R. Ferguson, and M.Z. Bazant, *Nonequilibrium thermodynamics of Porous electrodes*, Journal of the Electrochemical Society, 159 (12), A1967-A1985, 2012.
- [26] R.B. Smith, and M.Z. Bazant, *Multiphase porous electrode theory*, Journal of the Electrochemical Society, 164 (11), E3291-E3310, 2017.
- [27] J. Vazquez-Arenas, L.E. Gimenez, M. Fowler, T. Han, and S. Chen, A rapid estimation and sensitivity analysis of parameters describing the behavior of commercial li-ion batteries including thermal analysis, Energy Conversion and Management, 87, 472-482, 2014.
- [28] T. Danner, M. Singh, S. Hein, J. Kaiser, H. Hahn, and A. Latz, *Thick electrodes for li-ion batteries: A model based analysis*, Journal of Power Sources, 334, 191-201, 2016.

- [29] J. Smekens, J. Paulsen, W. Yang, N. Omar, J. Deconinck, A. Hubin, and J. Van Mierlo, A modified multiphysics model for lithium-ion batteries with a Li<sub>x</sub>Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> electrode, Electrochimica Acta, 174, 615-624, 2015.
- [30] V.R. Subramanian, V. Boovaragavan, V. Ramadesigan, and M. Arabandi, Mathematical Model reformulation for lithium-ion battery simulations: Galvanostatic boundary conditions, Journal of the Electrochemical Society, 156 (4), A260-A271, 2009.
- [31] F. Ciucci and W. Lai, Derivation of micro/macro lithium battery models from homogenization, Transport in Porous Media, 88, 249-270, 2011.
- [32] S. Golmon, K. Maute, and M.L. Dunn, Multiscale design optimization of lithium ion batteries using adjoint sensitivity analysis, International Journal for Numerical Methods in Engineering, 92, 475-494, 2012.
- [33] V. Taralova, O. Iliev, and Y. Efendiev, Derivation and numerical validation of a homogenized isothermal li-ion battery model, J. Eng. Math., 101, 1-27, 2015. DOI 10.1007/s10665-015-9842-6.
- [34] H. Arunachalam, S. Onori, and I. Battiato, On veracity of macroscopic lithiumion battery models, Journal of the Electrochemical Society, 162 (10), A1940-A1951, 2015.
- [35] P.M. Biesheuvel, Y. Fu, and M.Z. Bazant, *Diffuse charge and Faradaic reactions* in porous electrodes, Physical Review E, 83, 061507, 2011.
- [36] A. Salvadori, D. Grazioli, and M.G.D. Geers, Governing equations for a two-scale analysis of li-ion battery cells, International Journal of Solids and Structures, 59, 90-109, 2015.
- [37] G.G. Botte, V.R. Subramanian, and R.E. White, Mathematical modeling of secondary lithium batteries, Electrochimica Acta, 45, 2595-2609, 2000.
- [38] A.G. Kashkooli, S. Farhad, D.U. Lee, K. Feng, S. Litster, S.K. Babu, L. Zhu, and Z. Chen, Multiscale modeling of lithium-ion battery electrodes based on nano-scale X-ray computed tomography, Journal of power Sources, 307, 496-509, 2006.
- [39] D.E. Stephenson, E.M. Hartman, J.N. Harb, and D.R. Wheeler, Modeling of particle-particle interactions in porous cathodes for lithium-ion batteries, Journal of the Electrochemical Society, 154 (12), A1146-A1155, 2007.
- [40] V. Srinivasan, and J. Newman, *Discharge model for the lithium iron-phosphate electrode*, Journal of the Electrochemical Society, 151 (10), A1517-A1529, 2004.
- [41] R. García-García and R.E. García, *Microstructural Effects on the average properties in porous battery electrodes*, Journal of Power Sources, 309, 11-16, 2016.
- [42] W. Lai and F. Ciucci, Mathematical modeling of porous battery electrodes Revisit of Newman's model, Electrochimica Acta, 56, 4369-4377, 2011.
- [43] W. Lai, Electrochemical modeling of single particle intercalation battery materials with different thermodynamics, Journal of Power Sources, 196, 6534-6553, 2011.

- [44] W. Lai and F. Ciucci, Thermodynamics and kinetics of phase transformation in intercalation battery electrodes - phenomenological modeling, Electrochimica Acta, 56, 531-542, 2010.
- [45] Cioranescu, D. and Donato P., An introduction to homogenization, 1st Edition, New York: Oxford University Press, 1999.
- [46] S. Whitaker, The method of volume averaging, Springer, Netherlands, 1999.
- [47] U. Hornung, Homogenization and porous media, Springer, New York, 1997.
- [48] M. A. Peter, Coupled reaction-diffusion processes inducing an evolution of the microstructure: Analysis and homogenization, Nonlinear Anal. Theory Methods Appl., 70 (2), 806, 2009.
- [49] J. H. Cushman, L. S. Bennethum, and B. X. Hu, A primer on upscaling tools for porous media, Adv. Water Resour., 25 (8-12), 1043, 2002.
- [50] J.W. Cahn, *Phase separation by spinodal decomposition in isotropic systems*, The Journal of Chemical Physics, 42 (1), 93-99, 1964.
- [51] R.E. García, C.M. Bishop, and W.C. Carter, Thermodynamically consistent variational principles with applications to electrically and magnetically active systems, Acta Materialia, 52, 11-21, 2004.
- [52] J.E. Guyer, w.J. Boettinger, J.A. Warren, and G.B. McFadden, *Phase field modeling of electrochemistry*. I. Equilibrium, Phys. Rev. E 69, 021603, 2004.
- [53] A. Ven der Ven, K. Garikipati, S. Kim, and M. Wagemaker, The Role of Coherency Strains on Phase Stability in Li<sub>x</sub>FePO<sub>4</sub> Journal of the Electrochemical Society, 156 (11), A949–A957, 2009.
- [54] M. Z. Bazant, Theory of chemical kinetics and charge transfer based on nonequilibrium thermodynamics, Accounts Chem. Res., 46, 1144–1160, 2013.
- [55] D.A. Cogswell, and W.C. Carter, *Thermodynamic phase-field model for microstructure with multiple components and phases: the possibility of metastable phases*, Phys. Rev. E 83, 061602, 2011.
- [56] D.A. Cogswell, and M.Z. Bazant, *Theory of coherent nucleation in phase-separating nanoparticles*, NanoLetters, 13, 3036-3041, 2013.
- [57] G.K. Singh, G. Ceder, and M.Z. Bazant, Intercalation dynamics in rechargeable battery materials: General theory and phase-transformation waves in LiFePO<sub>4</sub>, Electrochimica Acta, 53, 7599-7613, 2008.
- [58] I.M. Gelfand, and S.V. Fomin, *Calculus of variations*, Englewood Cliffs (NJ): Prentice-Hall; 1963.
- [59] W.C. Carter, J.E. Taylor, and J.W. Cahn, Variational methods of microstructureevolution theories, Journal of Materials, 49, 30–36, 1997.
- [60] Y.M. Chiang, D. Birnie III, and W.D. Kingery, *Physical ceramics: principles for ceramic science and engineering*, New York, Wiley, 1997.

- [61] H. Yamada, and P.R. Bandaru, *Electrochemical kinetics and dimensional con*siderations at the nanoscale, AIP ADVANCES 6, 065325, 2016.
- [62] P. Bai, D.A. Cogswell, and M.Z. Bazant, Suppression of phase separation in LiFePO<sub>4</sub> nanoparticles during battery discharge, Nano Letters, 11, 4890-4896, 2011.
- [63] Y. Zeng, R.B. Smith, P. Bai, and M.Z. Bazant, Simple formula for Marcus-Hush-Chidsey kinetics, Journal of Electroanalytical Chemistry, 735, 77-83, 2014.
- [64] A. Jana, and R.E. García, Lithium dendrite growth mechanisms in liquid electrolytes, Nano Energy, 41, 552-565, 2017.
- [65] C. Monroe, and J. Newman, *The effect of interfacial deformation on electrodeposition kinetics*, Journal of the Electrochemical Society, 151, A880–A886, 2004.
- [66] C. Monroe, and J. Newman, The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces, Journal of the Electrochemical Society, 152, A396–A404, 2005.
- [67] C. Monroe, and J. Newman, *Dendrite growth in lithium/polymer systems*, Journal of the Electrochemical Society, 150, A1377–A1384, 2003.
- [68] W. Wu, X. Xiao, M. Wang, and X. Huang, A microstructural resolved model for the stress analysis of lithium-Ion Batteries, Journal of the Electrochemical Society, 161 (5), A803–A813, 2014.
- [69] W.H. Woodford, Y.-M. Chiang, and W.C. Carter, "Electrochemical shock" of intercalation electrodes: a fracture mechanics analysis, Journal of the Electrochemical Society, 157, A1052-A1059, 2010.
- [70] W.H. Woodford, W.C. Carter, and Y.-M. Chiang, Design criteria for electrochemical shock resistant battery electrodes, Energy Environ. Sci, 5, 8014-8024, 2012.
- [71] R.E. García, Y.M. Chiang, W.C. Carter, P. Limthongkul, and C.M. Bishop, *Microstructural modeling and design of rechargeable lithium-ion batteries*, Journal of the Electrochemical Society, 152 (1), A255-A263, 2005.
- [72] S. J. Moura, N. A. Chaturvedi, and M. Krstic, Adaptive partial differential equation observer for battery state-of-charge/state-of-health estimation via an electrochemical model, J. Dyn. Sys., Meas., Control, 136 (1), 2013.
- [73] Q. Sun, Q. Wang, X. Zhao, J. Sun, and Z. Lin, Numerical study on lithium titanate battery thermal response under adiabatic condition, Energy Convers. Manage., 92, 184, 2015.
- [74] Wolfram Research, Inc., Mathematica, Version 10.4.0.0, Champaign, IL (2020)
- [75] S. Basu, R.S. Patil, S.Ramachandran, K.S. Hariharan, S.M. Kolake, T. Song, D. Oh, T. Yeo, and S.Doo, Non-isothermal electrochemical model for lithium-ion cells with composite cathodes, Journal of Power Sources, 283, 132-150, 2015.

- [76] W. Wu, X. Xiao, and X. Huang, The effect of battery design parameters on heat generation and utilization in a Li-ion cell, Electrochimica Acta, 83, 227-240, 2012.
- [77] M. Xu, Z. Zhang, X. Wang, L. Jia, and L.Yang, A pseudo three-dimensional electrochemical-thermal model of a prismatic LiFePO<sub>4</sub> battery during discharge process, Energy, 80, 303-317, 2015.
- [78] Y. Dai, and V. Srinivasan On graded electrode porosity as a design tool for improving the energy density of batteries, Journal of the Electrochemical Society, 163 (3), A406-A416, 2016.
- [79] P. Albertus, J. Christensen, and J. Newman, Experiments on and modeling of positive electrodes with multiple active materials for lithium-ion batteries, Journal of the Electrochemical Society, 156 (7), A606-A618, 2009.
- [80] A.G. Kashkooli, G. Liu, S. Farhad, D.U. Lee, K. Feng, A. Yu, and Z. Chen, Nano-particle size effect on the performance of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> spinel, Electrochimica Acta, 196, 36-40, 2016.
- [81] X. Yang, W. Tang, H. Kanoh, and K. Ooi, Synthesis of lithium manganese oxide in different lithium-containing fluxes, Journal of Materials Chemistry, 9, 2683-2690, 1999.
- [82] Y. Yu, J. Wang, P. Zhang, and J. Zhao, A detailed thermal study of usual LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiFePO<sub>4</sub> cathode materials for lithium ion batteries, Journal of Energy Storage, 12, 37-44, 2017.
- [83] J. Christensen, V. Srinivasan, and J. Newman, Optimization of lithium titanate electrodes for high-power cells, Journal of Electrochemical Society, 153 (3), A560, 2006.
- [84] A. Donev, I. Cisse, D. Sachs, E.A. Variano, F. H. Stillinger, R. Connelly, S. Torquato, and P.M. Chaikin, *Improving the density of jammed disordered packings using ellipsoids*, Science, 303, 990-993, 2004.
- [85] N. Nitta, F. wu, J.T. Lee, and G. Yushin, *Li-ion battery materias: present and future*, Materials Today, 18 (5), 252-264, 2015.
- [86] A. Baczynska, W. Niewiadomski, A. Goncalvez, P. Almeida, and R. Luis, Li-NMC batteries model evaluation with experimental data for electric vehicle application, Batteries, 4 (11), 1-16, 2018.
- [87] S.U. Kim, P. Albertus, D. Cook, C.W. Monroe, and J. Christensen, Thermoelectrochemical simulations of performance and abuse in 50-Ah automotive cells, Journal of Power Sources, 268, 625-635, 2014.
- [88] D.W. Dees, D.P. Abraham, w. Lu, K.G. Gallagher, M. Bettge, and A.N. Jansen, Electrochemical Modeling and Performance of a lithium-and manganese-rich layered transition-metal oxide positive electrode, Journal of the Electrochemical Society, 162 (4), A559-A572, 2015.
- [89] J.Y. Ko, M. Varini, M. Klett, H. Ekstrom, and G. Lindbergh, Porous electrode model with particle stress effects for Li(Ni<sub>1</sub>/3Co<sub>1</sub>/3Mn<sub>1</sub>/3)O<sub>2</sub>, Journal of the Electrochemical Society, 166 (13), A2939-A2949, 2019.

- [90] P. Liu, R. Xu, Y. Liu, F. Lin, and K. Zhao, Computational modeling of heterogeneity of stress, charge and cyclic damage in composite electrodes of Li-ion Batteries, Journal of the Electrochemical Society, 167, 040527, 2020.
- [91] J.A. Campos, A. Deva, and R.E. García, μueκ: Microstructural electrochemomechanical kinetics, 2020.
- [92] J.E. Guyer, D. Wheeler, and J.A. Warren, "FiPy: Partial differential equations with Python", Computing in Science & Engineering, 11 (3) pp. 6—15, 2009 doi:10.1109/MCSE.2009.52, http://www.ctcms.nist.gov/fipy
- [93] M. Sala, W. Spotz, and M. Heroux, PyTrilinos: High-performance distributedmemory solvers for Python, ACM Transactions on Mathematical Software (TOMS), 34 (2), 2008.
- [94] Yabuuchi, N., Makimura, Y. and Ohzuku, T., Solid-state chemistry and electrochemistry of LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> for advanced Lithium-ion batteries III. Rechargeable capacity and cycleability, Journal of the Electrochemical Society, 154 (4), A314–A321, 2007.
- [95] M. Safari, and C. Delacourt, *Modeling of a commercial graphite/LiFePO*<sub>4</sub> cell, Journal of the Electrochemical Society, 158 (5), A562-A567, 2011.
- [96] L.O. Valøen, and J.N. Reimers, *Transport properties in LiPF*<sub>6</sub>-based Li-ion battery electrolytes, Journal of the Electrochemical Society, 152 (5), A882-A891, 2005.
- [97] R. Xu, H. Sun, L.S. de Vasconcelos, and K. Zhao, Mechanical and structural degradation of LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub> cathode in li-ion batteries: An experimental study, Journal of the Electrochemical Society, 164 (13), A3333-A3341, 2017
- [98] J. Cannarella, X. Liu, C.Z. Leng, P.D. Sinko, G.Y. Gor, and C.B. Arnold, Mechanical properties of a battery separator under compression and tension, Journal of the Electrochemical Society, 161 (11), F3117-F3122, 2014.
- [99] W. H. Woodford, Electrochemical shock mechanical degradation of Ionintercalation materials, PhD dissertation, Massachusetts Institute of Technology, 2013.
- [100] S. Torquato, Random heterogeneous materials: Microstructure and macroscopic properties, Interdisciplinary Applied Mathematics v. 16, Springer Science & Business Media, 2013.
- [101] N. Chawla, B.V. Patel, M. Koopman, K.K. Chawla, R. Saha, B.R. Patterson, E.R. Fuller, and S.A. Langer, *Microstructure-based simulation of thermomechanical behavior of composite materials by object-oriented finite element analysis*, Materials Characterization, 49, 395-407, 2003.

VITA

Juan Alfonso Campos was born in Zacatecas, México. Alfonso received his Bachelor of Science in Engineering Physics in 2000, and his Master of Science in Energy Engineering in 2002, from Tecnológico de Monterrey. Alfonso worked as Manufacturing Engineer in Samsung SDI Co., in Tijuana México from 2003 to 2006. Later, Alfonso joined General Electric Co. in Querétaro México and worked as Thermodynamics Application Engineer from 2006 to 2012 in the Energy Division, and from 2012 to 2014 as Aero-thermal System Modeling Engineer in the Aviation Division. In spring 2016, Alfonso joined the Ph.D. program in Materials Engineering at Purdue University. At Purdue, Alfonso developed homogenized phase field models for Lithium-ion rechargeable Batteries.