A MULTIPHYSICS MODEL FOR THE STRESS ANALYSIS OF THE SEPARATOR IN A LITHIUM-ION BATTERY

By

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ABSTRACT

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The separator is a critical component to the durability and safety of lithium-ion (Liion) batteries. It prevents the physical contact between the positive and negative electrodes while enabling ionic transport. The integrity of the separator is vital to the performance and reliability of a battery.

In a Li-ion battery, stresses arise as the results of mechanical loading and constraints, intercalation-induced deformation in the active materials in the electrodes, and thermal expansion mismatch between the battery components. Currently, there are no methods available to evaluate the in - situ stresses of the separator.

This work appertains to the development of a modeling tool for the evaluation of stresses in the separator in a Li-ion battery. Towards this end, a multiphysics model for a basic Li-ion battery cell had been developed and implemented in the multiphysics finite element package $\text{COMSOL}^{\textcircled{R}}$. The model considered charge/species transport through diffusion and migration, charge balance, electrochemical reaction kinetics, heat generation and heat transfer, as well as the stress and deformation due to mechanical loading, Li intercalation and temperature variation in the battery.

The multiphysics model was based on a validated one-dimensional (1D) battery model developed by Newman's group and its implementation in $\text{COMSOL}^{\textcircled{R}}$ for a $\text{Li}_{x}\text{C}_{6}|\text{LiPF}_{6}|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell. For stress analysis, a 1D "Thermal" sub-model and a 2D meso-scale representative volume element (RVE) "Stress" sub-model were subsequently added. These sub-models were fully coupled with each other. The temperature dependence of the transport properties and reaction rate parameters was also included. The separator was modeled with a linear viscoelastic model based on experimental data. Its temperature dependence was established through the time-temperature superposition principle.

The model was used to investigate the stress in the separator with battery cycles. The simulation results revealed that the stress in the separator varies in phase with the battery cycles. The effects of Li interaction and temperature rise in the battery could not be superimposed, requiring both to be considered concurrently. The stress state and magnitude depended upon the mechanical properties of separator, active particle size and packing. Besides addressing separator stresses, the model was also used to evaluate the influence of the active particle size and component thickness on the heat generation rate and battery performance. The simulations revealed the evolution of the rate limiting mechanisms with charge/discharge rates and a set of complex relationships between the battery design parameters and battery utilization.

The 1D battery model was limited by the assumption that the electrodes were constructed with uniformly distributed spherical particles of equal size. To consider the influence of real microstrucutural effects, a 2D microstructure resolved model has also been developed. This model was used to investigate the stresses in the active particles and conductive binder.

This work presents a feasible approach to understanding the relationships among different physical phenomena in a Li-ion battery, evaluating the stress state and magnitude in battery components such as the separator, and battery design optimization.

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KEY TO SYMBOLS AND ABBREVIATIONS

ion number across section area of the battery (cm^2) A_{cell} Li concentration (mol m^{-3}) cspecific heat capacity $(J (kg K)^{-1})$ C_p diffusion coefficient of Li^+ in the solid electrode particles (m² s⁻¹) D_1 electrolyte salt diffusivity (m² s⁻¹) D_2 f_{\pm} average molar activity coefficient EYoung's modulus (MPa) the activation energies associated with $D_1 ~(\text{KJ mol}^{-1})$ $E_{a,D}$ the activation energies associated with $k_0 ~(\text{KJ mol}^{-1})$ $E_{a,R}$ Faradays constant, 96487 (C mol $^{-1}$) FGstress relaxation modulus (Pa) lumped heat transfer coefficient (W m⁻² K⁻¹) hpartial molar enthalpy $(J \text{ mol}^{-1})$ \bar{H}_{ij} enthalpy change in the chemical reaction p $(J \text{ mol}^{-1})$ ΔH_p current density (A m $^{-2}$) iexchange current density (A m^{-2}) j_0 local current density (A m $^{-2}$) jn instantaneous compliance (N m $^{-2}$) J_0 compliance (N m⁻²) Jreaction rate constant (A $m^{2.5} mol^{-1.5}$) k_0 solid phase electronic conductivity (S m^{-1}) k_1

k_2	liquid phase ionic electrocity (S m $^{-1}$)
K_{therm}	thermal conductivity (W (m K) ^{-1})
$l_{i,j}$	constants
L	thickness of each battery component i (μm)
n	charge number
M	mobility of solute $(m^2 (V s)^{-1})$
N_0	Li^+ flux (mol m ⁻² s ⁻¹)
p	the exponent in empirical relation for effective transport properties
p_{C}	constant
q	heat generation rate (W L^{-1})
r	radial distance from the center of electrode active particle (μm)
R	electrode active particle radius (μm)
R_{C}	gas constant, 8.314 (J (mol K) $^{-1}$)
R_{col}	electronic resistivity of current collector (Ω m)
S_a	specific surface area (m^{-1})
S_t	maximum tensile stress (Pa)
t	time (s)
t_+	transport number of Li^+
t_{-}	transport number of anion
Т	absolute temperature (K)
U	open circuit potential of the electrode (V)
v	the product of thermodynamic factor and the anion transference number
v_0	solvent velocity (m s ^{-1})

V cell potential (V)

z charge number

Greek letters

 α reaction coefficient

- α_{ij} thermal expansion coefficient (K⁻¹)
- α_T horizontal time-temperature shift factor
- γp reaction rate of a side chemical reaction p (mol m⁻¹ s⁻¹)
- Γ_i active particle/electrolyte interface
- Γ_n negative electrode/current collector interface
- Γ_p positive electrode/current collector interface
- δ_{ij} Dirac delta function
- ΔS_i entropy change (J (mol K)⁻¹)
- ε porosity of the battery electrode

 ε_{ij} strain component

- η local surface overpotential (V)
- μ chemical potential (V)
- ν Poissons ratio
- Π interface heat generation due to the entropy change in the electrode (W L⁻¹)
- ρ material density (kg m⁻³)

 σ stress (Pa)

 σ_b battery domain

 σ_e electrolyte domain

 σ_h hydrostatic component of stress (Pa)

- σ_s solid, active particle domain
- σ_V yield stress (Pa)
- τ retardation time (s)
- τ_t tortuosity
- ϕ electrical potential (V)

Subscripts and superscripts

- 1 solid phase or first principal
- 2 liquid phase or second principal
- 3 third principal
- c current collector
- *i* cell component or constant
- *n* negative electrode or reaction charge number
- p positive electrode
- s separator
- ave average value
- eff effective value
- ei, T eigen strain due to thermal expansion
- ei, c eigen strain due to intercalation
- *ini* initial value
- *max* maximum value
- me mechanical
- ref reference value
- surf surface value

- VM Von Mises
- ∞ infinity
- + positive
- negative

Chapter 1

Introduction

After the first commercial product of lithium-ion(Li-ion) batteries by Sony Corporation in 1991, the market has grown rapidly. Currently, Li-ion batteries are widely used in consumer electronics such as laptops, digital cameras, and cell phones. The applications for Li-ion batteries have recently expanded to include electric or hybrid-electric vehicles by automakers as well as aerospace missions conducted by NASA [1]. Compared to other battery systems, the Li-ion battery offers numerous advantages such as light weight, high energy density and ease of manufacture.

1.1 Lithium-Ion Battery

A basic Li-ion battery cell comprises a current collector, a negative electrode (anode), a separator, a positive electrode (cathode), and another current collector, as depicted in Figure 1.1 [1]. The material and microstructures of electrodes and separators vary widely. Figure 1.1 presents the materials used in today's Li-ion batteries: a graphite negative electrode, a $Li_yMn_2O_4$ positive electrode, and a polymeric separator. The entire battery is immersed in the electrolyte.

The electrodes are made of active particles and conductive additives. They are mixed with the polymeric binders to form a paste and coated onto a metal foil (current collector). The function of the binder is to maintain physical integrity and to help maintain an electrical pathway between active material particles and the current collector. The size of active particles (red and green balls), with which Li^+ ions react and into which lithium inserts, ranges from the submicrometer level to 10 μ m.



Figure 1.1: Schematic of a Li-ion battery being charged [1]. The lower pictures in the figure are scanning electron microscope (SEM) images of different battery component materials. From left to right, they are a current collector, which is a metal foil to collect current from outside circuit, a negative electrode using graphite as active particle materials [1], a polymeric separator (Celgard) [2], the positive particles using $\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ active particles [3]. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.

For current Li-ion batteries, graphite is one of the most common anode material, because

of its relatively high specific capacity, small irreversible capacity, and good cycle ability. Various kinds of carbonaceous materials, from crystalline to strongly disordered carbon, have been examined as anodes in Li-ion battery [5]. Besides graphite, amorphous carbon, silicon, nitrides, tin oxides and tin-based alloys have also been investigated as the anode material [4]. The common cathode material in Li-ion battery could be spinel Li_yMn₂O₄, and other layered oxides such as LiNi_{1-y}CoyO₂, LiMnO₂, LiNi_{1-y}Mn_yO₂, LiNi_{1-y-z}Mn_yCo_zO₂ and Li_{1+x}M_{1-x}O₂ [6]. The crystal structures of these cathode materials are similar to the α -NaFeO₂ type structure. Because of the compact crystal lattice, the α -NaFeO₂ type of structure has an inherent advantage in energy stored per unit volume.

An electrolyte contains ions and releases cations and anions by electrolysis. The electrolyte acts as a good ionic conductor. The cations and anions move towards cathode and anode respectively thus conducting current. Generally, there are two types of electrolyte in Li-ion batteries: non-aqueous liquid electrolyte, which is a mixture of lithium salt and organic solvent; and gel-type polymer electrolyte, which is composed of polymer matrices and organic solvents or plasticizers [7].

The electrochemical process in a Li-ion battery depends on a Li intercalation reaction. The active material in the positive electrode is a compound in which Li is thermodynamically stable. It may be any material that can store Li but at a lower thermodynamic potential than the negative electrode material. The movement of ions is driven by the thermodynamic force. When an external electrical potential is imposed, Li⁺ is forced to move from the positive electrode to the negative electrode. At the surface of the negative electrode, Li⁺ reacts with an electron and either reduces to Li or forms an ion-electron pair, which then moves into the electrode material by diffusion. When the external power supply is removed, the reverse reaction takes place. A charge balance is maintained in the battery through the

movement of ions and electrons. At the graphite negative electrode, the reaction is

$$LiC_6 \xleftarrow{discharge}{charge} xLi^+ + Li_{1-x}C_6 + e^-$$
 (1.1)

At the $\rm Li_xMn_2O_4$ positive electrode, the reaction is

$$xLi^{+} + xe^{-} + Li_{1-x}Mn_2O_4 \xrightarrow{discharge}_{charge} LiMn_2O_4 \tag{1.2}$$

For a $\rm Li_xC_6|Polyproplyene(PP)|Li_{1-x}Mn_2O_4$ cell, the reaction is

$$LiC_6 + Mn_2O_4 \xleftarrow{discharge} Li_xC_6 + Li_{(1-x)}Mn_2O_4$$
(1.3)

To distinguish Li⁺ in the active particles from that in the electrolyte, it is designated as Li in the following text.

1.2 Separator

The separator is a porous membrane that prevents physical contact between the positive and negative electrodes while enabling ionic transport [2, 8, 9]. Three common types of separators are polymeric membranes, nonwoven mats, and ceramic enhanced membranes. Currently, polymeric membranes are used predominantly due to their low cost and relative thinness. A thin separator facilitates the ionic transport and provide higher energy and power densities [2]. The commercial PP membranes, such as Celgard series, with several dozen micrometer thickness and 30-50% porosity are typical separator materials. The integrity of the separator is vital to the performance and stability of Li-ion batteries. A short circuit due to separator failure can lead to a thermal event [10, 11]. One of the major remaining challenges for large-scale Li-ion batteries used in high energy applications, such as electric or hybrid-electric vehicles is to further improve the performance of the separator.

It is well recognized that stress can have a significant impact on the performance of the separator. Currently, there is no method to evaluate the stress inside a battery. Consequently, there are no clear guidelines for the mechanical property requirements for the separators. To improve the performance of battery separators, the stress in the separator must be known. This includes the origin of the stress, its state, amplitude, and evolution. This investigation is crucial to future separator development for improved battery abuse tolerance and durability. It will contribute to the establishment of the relationships between the stress and other physical phenomena involved in Li-ion batteries. This knowledge is needed for the optimization of the separator materials, battery design, and charge-discharge strategies for enhanced battery durability.

1.3 Problem Definition

In addition to the mechanical stress, two types of non-mechanical stresses can arise in a Li-ion battery. The first type is the intercalation stress, a unique problem for rechargeable Li-ion batteries [12–15]. The second type of non-mechanical stresses is the thermal stress due to self-heating of the battery during its operation or due to environmental temperature variation. The electrochemical process in a rechargeable Li-ion battery depends on a Li intercalation and deintercalation reaction. One of the consequences of the reaction is the volume expansion and contraction of the electrode materials. The intercalation stress arises due to the Li concentration gradient inside an active electrode particle, which is the same as the diffusion induced stress referred to in physics [16]. In the literature, the studies on intercalation stress often focus on the stresses inside an electrode particle and the fracture of the particle itself [12–15, 17–19]. In a battery, the effect of intercalation stress is not limited to the individual particles. Due to the constraint of the surrounding components, the expanding/contracting particle will induce stresses in the surrounding materials.

When subjected to a temperature change, thermal stress arises in structures composed of constituents with different coefficients of thermal expansion. A battery consists of a wide variety of materials including metals, ceramics, and polymers. These components are stacked up and packed into a given volume under pressure. Thermal stress is inevitable in such structures. In the literature, the sources of heat generation [20, 22–24] and heat transfer [21, 25–30] have been investigated for Li-ion batteries. However, there are no published results concerning thermal stress.

In a Li-ion battery, a membrane separator is sandwiched between two electrodes. During the charge and discharge cycles, the active particles expand in one electrode and contract in another. To evaluate the stress in a separator in a battery during operation, both electrodes must be considered.

At the present time, besides measuring the response of a battery pack in its through thickness direction, there is no method to evaluate the stress in a separator inside a battery with ongoing electrochemical reactions. Furthermore, the stress measured on a battery pack provides an average global stress in the through thickness direction. At the local level, the stress state and its amplitude are unknown. The electrodes used in state-of-theart Li-ion batteries are composites of discrete particles, binders, and other additives. The surfaces of the electrodes are rough at the microscopic scale. Thus, the local stresses may depart significantly from the global stress measured at the surface. A rechargeable battery is expected to last for a designated number of discharge-charge cycles. Thus the stress in the separator may be cyclic. What its amplitude is and how to predict its fatigue life are open questions.

Because the separator is a polymeric material, the temperature dependence of the separator's mechanical properties is of great concern. A temperature variation of 20-30 °C is not uncommon for a battery during operation. For a polymer, this temperature variation may cause a significant acceleration in stress relaxation which in turn will influence the stress in the material. Without the knowledge of the thermal history of the battery, it is difficult to estimate this influence.

1.4 Literature Review

In literature, some aspects of the above mentioned problems have been investigated. This section provides an overview on current understandings relevant to this problem.

1.4.1 Mathematical Modeling of the Electrochemical Phenomenon

The most well-established model describing the electrochemical phenomenon in the porous electrode was developed by Newman's group [31, 32]. This model adopted much of the theory developed previously from other battery systems, such as lead acid, nickel hydride or molten salt LiAl-FeS [33]. Both the porous electrode theory and the concentrated solution theory

were employed in Newman's model. The porous electrode theory treated the electrode homogeneously at the macro level without going into the exact geometric microstructure detail. Most electrolyte solutions in Li-ion batteries exhibit the concentrated solution behavior as a non-ideal solution. Therefore the concentrated solution theory was used to describe the Li⁺ transport in the liquid electrolyte. It includes all species present in the solution.

Comparisons of the simulation and experimental results [31, 32, 40, 41] indicated that Newman's model is sufficient to describe the electrochemical phenomenon in Li-ion batteries. Thus various researchers incorporated this model in their work to investigate electrochemicalthermal [34, 39, 40] and electrochemical-mechanical [13–15, 35] phenomena.

Recently, volume averaging of generalized Poisson-Nernst-Planck equations on a de Levie straight pore model was performed to simulate the electrochemical phenomenon of porous electrodes by Lai et al.[38]. Compared to Newman's model, these equations are more thermodynamically consistent, as they consider the innate correlation between the thermodynamic and kinetic material properties. For example, the chemical diffusivity in Lai's work is dependent on the other thermodynamic and kinetic properties of the battery. While it is treated as a constant in Newman's work.

1.4.2 Stress in a Li-Ion Battery

Non-mechanical stress arises in different battery systems during the battery operation process. In a lead-acid battery system, the internal stress originates from two issues: volume change due to the formation of sulfate and thermal expansion [42] due to battery self-heating. In nickel-metal hydride batteries [43, 44], the non-mechanical stress generates by the lattice expansion and contraction by hydrogen intercalation and deintercalation. Furthermore, the numerical model including reaction kinetics, heat generation and mechanical analysis addressed there are another two types of non-mechanical stress: the chemical stress induced by the oxygen potential gradient [45, 46] and the thermal stress induced by the mismatch of thermal expansion of different cell components [47]. Overall, the non-mechanical stress generated in battery systems is from two aspects: material volume change by specific battery electrochemical mechanism and thermal mismatch by battery temperature variation.

In a Li-ion battery, Li ions are in motion during charge and discharge. The ions either intercalate into or deintercalate from the active electrode particles. This creates a Li concentration gradient from the center of the particle to its surface and therefore a non-uniform strain field in the particle. Similarly as the diffusion-induced stress referred to in physics [16], intercalation stress arises in a particle with the Li concentration gradient.

The analysis of the intercalation stress requires the knowledge of the Li concentration field in the particles which is determined by battery kinetics. Christensen and Newman [13, 14] presented a mathematical framework for the intercalation stress inside a spherical particle. The diffusion in a spherical particle is one-dimensional (1D). The stress, diffusion and battery kinetics were described by a set of 20 equations. These coupled equations were solved by the finite difference method. For a more general shape, this approach becomes unmanageable.

Another approach to this problem is the multiscale method. A common treatment is to divide the differential equations into two sets. The first set consists of the equations associated with the electrochemical kinetics of the battery; these include the expressions for Li⁺ transport and migration in the electrolyte (ionic charge balance, mass conservation), Ohm's law, and the interface reaction kinetic equation. The second set consists of the diffusion equation and constitutive equations between stress and strain with the inclusion of eigenstrain (non-mechanical strain). This approach allows different physical phenomena to be

represented by models at different scales. Based on the porous electrode and concentrated solution theories [48], a 1D macroscopic model has been well established for the electrochemical kinetics of Li-ion batteries [31, 32]. Utilizing this 1D battery model significantly reduces the complexity of the multiphysics problem. The Li⁺ flux from the 1D model was mapped to a three-dimensional (3D) model of a particle in a deformable matrix according to its depth in the electrode. The stresses in the composite electrode were then evaluated using a micromechanics model [49] based on the Mori-Tanaka effective-field theory [50].

Alternatively, the analysis of intercalation stress in particles can also be conducted by applying a prescribed Li⁺ flux at the particle boundary without a battery model [12, 15, 18, 51– 53]. Zhang et al. [15] investigated the intercalation stress for a single active particle using a detailed 3D finite element (FE) model using this approach. The study focused on the stress in a particle with a fixed boundary condition. Cheng et al. investigated 1D analytical solutions for intercalation stress under galvanostatic and potentiostatic conditions for spherical particles [18] and cylinder nanowire electrodes [52]. These 1D analytical solutions in nano-sized particles with the consideration of surface tension and surface modulus were also provided [12]. Furthermore, these solutions for nano-sized particles were applied to investigate the cyclic stress inside a particle under a predefined periodic potential boundary condition [51]. On the other hand, Golmon et al. [53] investigated the intercalation stress in a silicon spherical particle by applying the linear decrease overpotential to the particle surface.

Two dimensional (2D) and 3D battery models have also been developed [19, 36]. Garcia et al. [19] developed a 2D battery model for a $\text{Li}_{x}\text{C}_{6}$ — $\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell and implemented it in the object-oriented finite element program. This model considered the intercalation stress in the composite cathode consisting of $\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ particles in a matrix of an electrolyte.

The electrolyte was assumed to be a compliant gel with negligible resistance to deformation. With a low volume fraction of active particles in the model, this treatment limited the effect of intercalation stress to individual particles. Wang and Sastry [36] developed a 3D mesoscale battery model for the prediction of the electrochemical performance of the Li-ion battery utilizing the Nernst-Planck equation in $\text{COMSOL}^{\textcircled{R}}$, a multi-physics FE package. The stress analysis was not included in the mesoscale model.

So far, the analysis of intercalation stress has only been considered within individual particles.

An experimental investigation of the intercalation stress in the thin battery electrode film was developed. A common technique is the laser beam deflection method (LBDM), initially suggested by Stoney [54]. The stress in a thin film deposited on a thick plate substrate will cause the bilayer to bend. Stoney derived an equation relating the stress to the curvature of the film.

In Li-ion batteries, the curvature change of the electrode film during battery charge and discharge can be monitored by the LBDM method [55–58]. Using Stoney's equation, the in - situ stress of the electrode film was calculated by the experimental value of film curvature. Several groups adopted this method [57] or a modified form such as the multibeam optical sensor(MOS) technique [59, 60] to study the stress in a large volume change electrode material such as Si or Sn.

In open literature, there are no reports about the thermal stress in a Li-ion battery.

1.4.3 Thermal Analysis

The temperature variation during the battery working process not only causes the thermal stress in the Li-ion battery, but also significantly affects the viscoelastic mechanical property of polymeric separator. Therefore, understanding the heat generation is a necessary step in assessing the stress within the separators of Li-ion batteries.

Newman and co-workers developed a number of heat generation models [20, 22, 23] based on a framework derived by Bernardi et al. [20] from the view of energy balance in the battery system. For Li-ion batteries, four heat generation sources were identified, namely: irreversible resistance heating, reversible entropy heating, heat of mixing and heat of phase change. The irreversible resistance heating includes joule heating and the energy dissipated due to electrode overpotential. The reversible entropy heating is related to the change of the Gibbs function of the cell contents. During electrochemical reactions, the composition of individual species in each phase departs from their initial composition and hence the total entropy of the cell varies. The heat of mixing represents the heat associated with the generation or relaxation of concentration profiles. Thomas and Newman [23] found that for a battery well designed to mitigate concentration overpotential, the heat of mixing was negligible. Zhang et al. [24] implemented the heat generation model by Thomas and Newman [23] into $\text{COMSOL}^{(\widehat{\mathbb{R}})}$ and examined the heat generation in a single $\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ particle using a detailed 3D model. Their results confirmed that the heat of mixing was negligible compared to the irreversible resistance heating and reversible heating. Without considering the side chemical reactions within a Li-ion battery, there is only one reaction happening in each electrode, and no phase change occurs. Therefore, heat of phase change was negligible [20, 61].

The heat generation expression proposed by Bernardi et al. [20] in its simplified form is cited in the global heat generation model [25, 26, 29, 30, 62, 63]. The global model has been applied in thermal analysis of a single cell [29] and cell stacks [30]. In this model, the electrode potential is obtained based on the average composition.
Inside a battery cell, the local current and potential vary from point to point. To consider this effect, Rao and Newman [22] derived a local heat generation model in the subsequent study. The heat associated with electrochemical reactions was considered at each electrochemical interface, which includes the irreversible resistance heat due to local overpotential and reversible entropy contributions. The remaining irreversible resistance heat was further divided into electronic and ionic types in which the electronic ohmic heat occurs in all solid phases and the ionic ohmic heat occurs in the electrolyte phase. The local heat generation model has been incorporated into the electrochemical model to investigate the thermalelectrochemical behavior of a $\text{Li}_{x}\text{C}_{6}|\text{LiPF}_{6}|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ [34, 39] and a $\text{Li}_{x}\text{C}_{6}|\text{LiPF}_{6}|\text{Li}_{y}\text{CoO}_{2}$ cell [40, 64].

On the other hand, the heat generation rate of Li-ion batteries was also measured by several groups by three primary experimental methods: accelerated-rate calorimetry [65–67], isothermal heat conduction calorimetry [68–78, 103] and radiative calorimeter [80]. Most of the experiments were focused on discharge or charge rates lower than 1C during discharge [65–78, 80, 103] or charge [66–68, 70–77, 80, 103]. Due to the variations in battery materials and the uncertainties in battery geometries [61], the reported volumetric heat generation rate had a wide range. The peak values changed from 0.31 W L⁻¹ [71] to 84.5 W L⁻¹ [69] under 1C discharge rate. Furthermore, the reversible entropy heating can be relatively large under low rates [61, 68, 70, 77], and the consideration of this heat source is essential.

1.5 Objective of Research

The objective of this research is to develop a modeling tool for the evaluation of stresses in the separator in a Li-ion battery. In addition to the mechanical stress, the model must consider the intercalation stress and thermal stress as well as the physics associated with these two stresses. Overall, the model should include the battery kinetics, mass transport, thermal behavior, and stress analysis at the level of a basic cell with all battery components. Such models have not been reported in open literature thus far.

To accomplish this goal within the time frame of a Ph.D thesis, the model will be built upon a validated 1D battery model that has been implemented in the multiphysics code $COMSOL^{\textcircled{R}}$ [32, 83]. It has two sub-models, "Battery" and "Electrode". To consider the stress, two additional sub-models, "Thermal" and "Stress", will be developed. All coupling relationships among different sub-models will be considered. This will create a multiphysics, multiscale model that allows one to assess the stress in the separator of a Li-ion battery.

The model development consists of the following tasks:

- "Stress" sub-model
- "Thermal" sub-model
- Coupling among the "Thermal", "Battery", and "Electrode" sub-models
- Coupling between the "Stress" and "Battery" sub-models
- Coupling between the "Thermal" and "Stress" sub-models

the physical phenomena considered in each sub-model and the coupling relationship between them are depicted in Figure 1.2.

Based on this multiphysics model, parameter studies will be conducted to investigate the possibility of optimization of battery design parameters such as the thickness of the



Figure 1.2: The fully coupled multiphysics model consists of four sub-models. The schematic shows the physical phenomena in each sub-model and the coupling relationships among four sub-models.

components and the size of the active particles on the battery heat generation, as well as the performance of the battery.

Several contributions to the field of a Li-ion battery research are expected to be achieved through this model:

- Improvement of the fundamental understanding of the stress in the separator;
- Enabling of the investigation of interrelated mechanisms and provide insights into the interactions between different physical phenomena in a Li-ion battery;
- Enabling of battery design optimization for better performance and longer cycle life;
- Estiblishment of useful information in the evaluations of battery control strategies.

1.6 Scope of the Thesis

The purpose of this work is developing a multiphysics model to investigate the stress in the separator of a Li-ion Battery.

Chapter 1 provides the background information about this research, describes the objective and scope of the work, and presents the organization of this thesis.

Chapter 2 introduces the main phenomena occurring inside the Li-ion battery, and provides the corresponding governing equations and coupling relationships among various physical phenomena.

Chapter 3 describes the multiphysics model developed in this research and provides a summary of the input parameters in the models.

Chapter 4 presents the simulation results of heat generation and temperature rise in a battery. The temperature rise not only causes the thermal stress in the separator, but also affects the viscoelastic behavior of the polymeric separator. The relationship between the temperature and electrochemical reaction as well as cell utilization are discussed.

Chapter 5 presents the simulation results for the stress and strain in the separator. The thermal effect on the stress in the separator is examined. The effect of discharge rate on the stress in the separator is also involved in this chapter.

Chapter 6 describes the microstructure resolved model as the extension of the multiphysics model. The stress in the active particles and binders was examined based on the realistic electrode microstructure geometry.

Chapter 7 summarizes the major findings in this work and suggests possible directions for the future work.

Chapter 2

Multiphysics Phenomena

In order to evaluate the stress in the separator during the working process of the battery, the electrochemical, thermal and mechanical phenomena in the battery must be considered. The specific description of each phenomenon and the relationships among multiphysics phenomena are introduced in this chapter.

2.1 Electrochemical Phenomenon

In this work, Newman's model [31, 32] is employed to describe the electrochemical phenomenon in a Li-ion battery. The porous electrode theory and the concentrated solution theory are adopted in Newman's model. The model considers an electrochemical system consisting of two porous electrodes and a separator saturated with the electrolyte. The porous solid together with the electrolyte is modeled as a homogenized composite medium. The volume fraction of the electrolyte equals the porosity. On the other hand, the concentrated solution theory is used to describe the mass transport in the electrolyte. The electrochemical reaction that occurs at the active material surfaces is represented by the Bulter-Volmer equation. The solid phase is denoted as phase 1 and the electrolyte phase is denoted as phase 2. The variables and parameters that appear in both phases are distinguished by a subscript 1 or 2.

2.1.1 Ionic Transport

In the electrolyte phase, Li⁺ is transported through two mechanisms: diffusion and migration. Based on the concentrated solution theory, the governing equation for material conservation is:

$$\varepsilon_2 \frac{dc_2}{dt} = \nabla \cdot \left(D_2^{eff} \nabla c_2 \right) - \frac{1}{F} \mathbf{i_2} \cdot \nabla t_+ + \frac{S_a j_n}{F} (1 - t_+)$$

in
$$\Omega_{\rm e}$$
, the electrolyte domain (2.1)

where c_2 is the Li⁺ concentration, t is the time, D_2^{eff} is the effective diffusion coefficient in the electrolyte, ε_2 is the porosity (volume fraction of the electrolyte), F is Faraday's constant, t_+ is the cation transport number representing the percentage of the current in the electrolyte carried by Li⁺, the vector \mathbf{i}_2 is the current density in the electrolyte, j_n is the charge transfer current density at the interface, and S_a is the specific surface area of the electrode, which is defined as the surface area of the active materials per unit volume of the total electrode. For the spherical particle, S_a is expressed as:

$$S_a = \frac{3\varepsilon_1}{R} \tag{2.2}$$

where ε_1 is the volume fraction of the active materials, and R is the active particle radius.

The relationship between \mathbf{i}_2 and j_n obeys the following equation:

$$\nabla \cdot \mathbf{i_2} - S_a j_n = 0 \tag{2.3}$$

Equation 2.1 states that the change in Li^+ concentration is the net result of Li^+ diffusion (first term), Li^+ migration in an electrical field (second term), and the concentration change induced by the Li^+ that leaves or enters the electrolyte through the interface with the active particles (third term). The third term vanishes for a volume that is not adjacent to an active particle.

2.1.2 Ionic Charge Balance

For ionic charge balance in the electrolyte phase, the governing equation is given as

$$\nabla \cdot \left[-k_2^{eff} \nabla \phi_2 + \frac{2R_c T k_2^{eff}}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_2} \right) \left(1 - t_{\pm} \right) \nabla (\ln c_2) \right] = S_a j_n$$

in
$$\Omega_{\rm e}$$
, the electrolyte domain (2.4)

Here R_c denotes the gas constant, T denotes the temperature, kk_2^{eff} is the effective ionic conductivity, ϕ_2 is the ionic potential, and f_{\pm} is the mean molar activity coefficient. Equation 2.4 is derived for an electrolyte of a binary salt using concentrated solution theory. It can be considered as a modified Ohm's law. The first term in the bracket is equivalent to the expression describing the electron movement in a solid conductor. The second term accounts for the effect of Li^+ concentration on the ionic current [48].

In order to consider the effect of material porosity and tortuosity on the ionic diffusion coefficient and conductivity, the effective values of these parameters are used in equation 2.4. Both the ionic diffusion coefficient and conductivity depending on the porosity and tortuosity follow the relationship:

$$D_2^{eff} = \varepsilon_2^{\ p} D_2 = \frac{\varepsilon_2 D_2}{\tau_t} \tag{2.5}$$

$$k_2^{eff} = \varepsilon_2^p k_2 = \frac{\varepsilon_2 k_2}{\tau_t} \tag{2.6}$$

where D_2 and k_2 are the ionic diffusion coefficient and conductivity measured from the pure electrolyte, p is a constant, which is the exponent in the above empirical relations for effective transport properties, and τ_t is the tortuosity of the battery material.

For a system made of a continuous conductive phase, for example the dilute solution with the porosity near zero, the value of p is 1.5 based on the asymmetrical Bruggeman effective model [38, 48]. This value sometimes is used as a default value in battery models. However, the porosity of the normal porous battery material is around 0.4 or even higher. Thus the default value 1.5 is unable to correctly predict the mass transport resistance [38, 48, 84, 85].

One way to obtain the value of the tortuosity or exponent p of the electrode or separator is using discharge curves to fit as the adjustable value [32, 41, 88, 89, 133]. The mathematical model of porous networks in relation to battery electrodes and separators is another way to get the value [85]. Recently, the experimental measurement of the tortuosity of the porous electrode and separators was developed [89, 90]. All of three methods depict that the value of p is higher than the default value 1.5.

2.1.3 Mass Transport

The active materials in the electrodes are considered to be spherical particles. The Li diffusion in the active particles follows Fick's second law with the spherical coordinate:

$$\frac{\partial c_1}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(-r^2 D_1 \frac{\partial c_1}{\partial r} \right) = 0$$

in
$$\Omega_{\rm S}$$
, the solid, active particle domain (2.7)

where c_1 is the Li concentration, D_1 is the solid phase diffusion coefficient, and r is the radial position in the spherical particle.

At the particle surface, the Li⁺ flux is related to the local current density by:

$$N_0 = -j_n/F \tag{2.8}$$

where N_0 is the Li⁺ flux at the particle surface.

2.1.4 Electronic Charge Balance

The charge balance in the solid phase of the electrode obeys Ohm's law:

$$\nabla \cdot (-k_1 \nabla \phi_1) = \mathbf{i_1}$$

in
$$\Omega_{\rm S}$$
, the solid, active particle domain (2.9)

where ϕ_1 is the electronic potential of the solid phase and k_1 denotes the electronic conductivity of the porous electrode. It is found by measuring the resistance to the passage of current through the porous electrode. The vector $\mathbf{i_1}$ is the current density in the solid phase and

$$\nabla \cdot \mathbf{i_1} + S_a j_n = 0 \tag{2.10}$$

2.1.5 Reaction Kinetics

The electrochemical reactions occur at the active particle surface. The reaction kinetics is described by Butler-Volmer equation:

$$j_n = j_0 \left[\exp\left(\frac{\eta \alpha_n F}{RT}\right) - \exp\left(\frac{(-\eta)\alpha_p F}{RT}\right) \right]$$

on $\Gamma_{\rm i}$, the active particle/electrolyte interface (2.11)

where α_n and α_p are the transfer coefficient of electrochemical reaction in the negative and positive electrode respectively. η is the local surface overpotential for the electrode, which is defined as

$$\eta = \phi_1 - \phi_2 - U_i(c_{1,surf}) \tag{2.12}$$

and j_0 denotes the exchange current density. This is determined by

$$j_0 = k_0 \sqrt{c_2 (c_{1,max} - c_{1,surf}) c_{1,surf}}$$
(2.13)

In equations 2.12 and 2.13, k_0 is the reaction rate constant, $c_{1,surf}$ is the Li concentration at the surface of the particle, $c_{1,max}$ is the maximum achievable Li concentration in the particle, and U_i is the electrode's open circuit potential (OCP) or equilibrium potential, which is the potential that no current flows. The OCP can be treated as a function of the intrinsic nature of the species and is influenced by concentration or temperature.

2.2 Thermal Phenomenon

The heat transfer in a 1D isotropic material is described by:

$$\rho C_p \frac{\partial T}{\partial t} = K_{therm} \nabla^2 T + q$$

in
$$\Omega_{\rm b}$$
, the battery domain (2.14)

where K_{therm} is the thermal conductivity, ρ is the density, C_p is the specific heat capacity of the material, and q is the heat generation rate.

The heat generation accompanying the electrochemical phenomenon is the critical part of the thermal phenomenon in a Li-ion battery. Currently, both the global model and the local model are used to simulate the heat generation in a Li-ion battery [61].

2.2.1 Heat Generation: Global Model

The general heat generation expression for Li-ion batteries was first derived by Bernardi et al. [20] from the energy balance of the battery system. The general expression for the heat generation rate is [20]

$$q = I(V - U) + IT\frac{dU}{dT} + \sum_{p} \Delta H_{p}^{ave} \gamma_{p} + \int \sum_{j} \sum_{i} (\bar{H}_{ij} - \bar{H}_{ij}^{ave}) \frac{\partial c_{ij}}{\partial t} dv \qquad (2.15)$$

where U is the OCP of the full Li-ion cell, I is the cell current, V is the cell potential, \bar{H}_{ij} is the partial molar enthalpy of species *i* in phase *j*, γ_p is the reaction rate of a side chemical reaction p and ΔH_p^{ave} is the average enthalpy change in the chemical reaction p. In Equation 2.15, the four terms correspond to the heat generation by irreversible resistance heating, reversible entropy heating, heat of phase change from side chemical reactions, and heat of mixing, respectively.

The global heat generation model has been applied in thermal analysis of a single cell [29] and cell stacks [25–27, 30, 62]. Due to the lack of data, the heat of mixing and phase change were neglected in these studies and Equation 2.15 is further reduced to

$$q = I(V - U) + IT\frac{dU}{dT}$$
(2.16)

2.2.2 Heat Generation: Local Model

In order to consider the local current and potential variation from point to point in a Li-ion battery, Rao and Newman [22] derived a local heat generation model. The local model is adopted in this work.

In the local model, the total heat generation is obtained by adding up the contributions at electrochemical interfaces and in bulk phases of the cell [22], thus

$$q = q_p + q_s + q_n \tag{2.17}$$

where subscripts p, s and n correspond to the positive electrode, the separator, and the negative electrode, respectively.

For a porous electrode, the heat generation at an electrochemical interface includes a reversible part due to the entropy change in the electrode, Π , and an irreversible part due to the local surface overpotential, η , which is expressed by Equation 2.12 for both negative and positive electrodes. The reversible part Π is described as:

$$\prod_{i} = T \frac{\Delta S_i}{F} \tag{2.18}$$

$$\frac{\Delta S_i}{F}$$
 is proportional to $\frac{\partial U_i}{\partial T}$ [48, 64], such that

$$\frac{\Delta S_i}{nF} = \frac{dU_i}{dT} \tag{2.19}$$

where n is the charge number contributing to the reaction. For a Li-ion battery, n=1 and, therefore,

$$\prod_{i} = T \frac{\Delta S_i}{F} = \frac{dU_i}{dT} \tag{2.20}$$

where ΔS_i is the electrode entropy change (i=p or n). It is typically measured in the reduction reaction in the working electrode, which is the discharge reaction for a cathode in a half cell, where the anode typically is Li metal foil. Considering the convention, the sign of heat generation can be either negative or positive for the exothermic reaction. When the heat generation for the exothermic reaction is positive, the anodic current is positive, and the cathodic current is negative. In this work, the positive sign for heat generation in an exothermic reaction is adopted.

The heat generation of a porous electrode in a local area is given by

$$q_i = S_{ai}i_n(\eta_i + \Pi_i) + i_1 \cdot \nabla \phi_1 + i_2 \cdot \nabla \phi_2 \tag{2.21}$$

where i_1 and i_2 are the current densities in the solid phase and the electrolyte phase, respectively.

In the separator, the current is conducted through ion transport. The heat generation due to the ionic ohmic heat in the porous separator is given by

$$q_s = i_2 \cdot \nabla \phi_2 \tag{2.22}$$

The heat generation in each current collector is calculated by

$$q_c = i_{col}^2 R_{col} \tag{2.23}$$

where i_{col} is the current density in the current collector and R_{col} is the resistivity of the current collector.

Thomas and Newman [23] have developed a heat generation model which considered the heat of mixing and compared the simulation results with measured heat of mixing for a Li|LiPF₆(EC/DMC)|LiAl_{0.2}Mn_{1.8}O_{4- δ}F_{0.2} cell. It suggests that the heat of mixing during high rate pulses may be negligible considering that the concentration relaxation is relatively small at these rates. Therefore, the heat of mixing is not considered in this work. In addition, the heat from the side reaction is also not considered.

2.3 Mechanical Phenomenon

Besides mechanical stress, the intercalation stress and thermal stress arise during the working process of the battery.

The diffusion-induced eigenstrain $\varepsilon_{ij}^{ei,c}$ (non-mechanical strain) in an isotropic electrode material is considered through a diffusion/thermal analogy such that [12, 16]:

$$\varepsilon_{ij}^{ei,c} = \frac{1}{3} \Delta c_1 \Omega \delta_{ij} \tag{2.24}$$

where Δc_1 is the change in the concentration of the diffusion species, Ω is the partial molar volume of the solute in the host material, and δ_{ij} is the Dirac delta function.

The partial molar volume can be calculated using the following Equation [15]

$$\Omega = \frac{3\varepsilon_{ij}^{ei,c}}{\Delta y c_{s,max}} \tag{2.25}$$

where $\varepsilon_{ij}^{ei,c}$ is the strain caused by intercalation expansion along the major axis of the material, Δy refers to the change in the number of lithium atoms that occurs during the charge and discharge cycles, and $c_{s,max}$ is the stoichiometric maximum concentration in the electrode.

On the other hand, stress will affect the diffusion process. The effect of stress on diffusion has been considered through the chemical potential of a solute in a solid solution [91] as:

$$\mu = \mu_0 + RT \ln c_1 - \sigma_h \Omega \tag{2.26}$$

where μ_0 is the chemical potential at the reference condition, and σ_h is the hydrostatic component of the stress, which is defined as:

$$\sigma_h = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3} \tag{2.27}$$

where σ_{xx} , σ_{yy} and σ_{zz} are the normal stresses along x, y, and z directions respectively.

The driving force for diffusion is a gradient in chemical potential. In this sense, the diffusion flux is expressed by the following equation:

$$\mathbf{N_0} = -Mc_1 \nabla \mu = Mc_1 \left(RT \frac{\nabla c_1}{c_1} - \Omega \nabla \sigma_h \right)$$
(2.28)

where M is the mobility of the solute. Noting that the diffusion coefficient $D_1 = MRT$, Equation 2.28 changes to:

$$\mathbf{N_0} = -D_1 \left(\nabla c_1 - \frac{\Omega c_1}{RT} \nabla \sigma_h \right) \tag{2.29}$$

The law of mass conservation is:

$$\nabla \cdot \mathbf{N_0} = -\frac{\partial c_1}{\partial t} \tag{2.30}$$

Substituting Equation 2.29 into Equation 2.30, the diffusion equation with stress effects is derived as

$$D_1\left(\nabla^2 c_1 - \frac{\Omega}{RT}\nabla c_1 \cdot \nabla \sigma_h - \frac{\Omega c_1}{RT}\nabla^2 \sigma_h\right) = \frac{\partial c_1}{\partial t}$$
(2.31)

In Equation 2.31, D_1 is assumed to be independent of stress.

The mechanical property evolution as a function of Li concentration is a very active research topic [92–94]. The first-principles density functional theory is employed to reveal the concentration dependence of Young's modulus of electrode materials such as graphite or silicon [92, 94]. However, at the present time, there is no one generally accepted model. In this study, the Li concentration dependence of the mechanical property is not considered.

The other eigenstrain $\varepsilon_{ij}^{ei,T}$ caused by thermal expansion or shrinkage is calculated by:

$$\varepsilon_{ij}^{ei,T} = \alpha_{ij} \Delta T \delta_{ij} \tag{2.32}$$

where α_{ij} is the coefficient of thermal expansion.

For an isotropic elastic material, the constitutive relationship for the mechanical strain ε_{ij}^{me} due to the mechanical stress is given as [95]

$$\varepsilon_{ij}^{me} = \frac{1}{E} \left[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij} \right]$$
(2.33)

where E is Young's modulus and ν is Poisson's ratio of the material. In this work, E and ν were treated as constants. The variation of the elastic constants with temperature and Li concentration was not considered.

The total strain is the summation of two types of eigenstrains and the mechanical strain in the elastic battery material as:

$$\varepsilon_{ij} = \varepsilon_{ij}^{me} + \varepsilon_{ij}^{ei,T} + \varepsilon_{ij}^{ei,c}$$

$$= \frac{1}{E} \left[(1+\nu)\sigma_{ij} - \nu\sigma_{kk}\delta_{ij} \right] + \alpha_{ij}\Delta T\delta_{ij} + \frac{1}{3}\Delta c\Omega\delta_{ij}$$
(2.34)

2.4 Multiphysics Coupling

The electrochemical, thermal, and mechanical phenomena contemporarily exist in the battery when it is in the operation process. They are highly related with one another, which is clearly demonstrated in Figure 2.1.



Figure 2.1: The coupling relationships among thermal, electrochemical and mechanical phenomena.

According to the description of the thermal phenomenon in Section 2.2, the electric and ionic transport in the bulk materials and the interface reaction at the active particle surfaces induce the heat generation in the Li-ion battery.

On the other hand, mass transport and reaction rate strongly depend on temperature. The influence of temperature on the mass transport and reaction rate is considered for six variables. They are the solid phase diffusion coefficient D_1 , reaction rate constant k_0 , OCP, electrolyte ionic conductivity k_2 , electrolyte diffusion coefficient D_2 , and the product of the thermodynamic factor and the anion transference number v. D_1 , OCP, and k_0 are related to the electrodes; k_2 , D_2 and v are related to the Li⁺ transport in the electrolyte system.

The concentration gradient causes intercalation stress in the active electrode particles in a Li-ion battery. In addition, the temperature variation due to the heat generation causes the thermal stress in a Li-ion battery.

The influence of temperature on the viscoelastic behavior of the polymeric separator is considered by using the time-temperature superposition principle [96]. A thermo-viscoelastic model based on the experimental data will be implemented to the multiphysics model.

The influence of Li concentration on the elastic properties of the active particles as well as the effect of stress on Li diffusion in solid particle will not be considered in the current work.

Chapter 3

Multiphysics Model

A multiphysics model for the stress analysis of a basic Li-ion battery cell has been developed. In this model, the multi-physics equations were solved concurrently using four sub-models at different scales. The battery electrochemical kinetics, current balance, ionic transport and mass transport were solved by a 1D macroscopic "Battery" sub-model and a pseudo 2C "Electrode" sub-model based on an existing 1D battery model in COMSOL[®]. The thermal behavior was considered by the 1D "Thermal" sub-model. The stress analysis at the level of a battery cell was conducted with a meso-scale representative volume element (RVE) "Stress" sub-model of the battery cell. Based on this approach, a multi-scale model with the inclusion of intercalation stress was developed for a $\text{Li}_{x}\text{C}_{6}|\text{PP}|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell, with the electrolyte of 1M LiPF₆ in a solvent of ethylene carbonate (EC)/dimethylene carbonate (DMC) (2:1 by volume).

3.1 Model depiction

A major difficulty in modeling the stress due to Li intercalation at the battery cell level is the multi-scale, multi-physics nature of the problem. A separator is sandwiched between two electrodes in a basic cell. In the thickness direction, a basic cell ranges from 150 to 300 μ m. The intercalation stress occurs at the level of individual active particles which have an average size of 5-20 μ m. On the other hand, in a planer (pouch) cells used in large-scale battery, the in-plane dimension of a single cell is in the range of 20-30 cm. The aspect ratio for a single planer cell is at the order of 10^3 .

To overcome the difficulty of the large aspect ratio of a planer cell, a RVE approach was employed together with a multi-scale approach. RVE by definition is the smallest material volume element of a heterogeneous material for which the effective constitutive representation is a sufficiently accurate model to represent the mean constitutive response of the material [97]. In this work, the concept of RVE is applied in a slightly different sense. RVE is the smallest volume of a battery cell that represents the mechanical and physical response at the center region of a planar cell. Ideally, a RVE model should be sufficient to reveal the response of individual components in a battery. The RVE used in this work is illustrated in Figure 3.1. The deformation of the RVE is restricted in the plane of the pouch cell and hence may be considered under a plane strain condition and analyzed with a 2D RVE.

Figure 3.2 presents the schematics of the individual sub-model implemented in COMSOL[®]. In this model, the equations of the multi-physics problem are divided into four sets and solved by four sub-models at three different scales. The battery electrochemical kinetics is solved by a 1D macroscopic "Battery" sub-model based on that of Doyle et al. [31, 32]. The Li diffusion in the active particles and the interaction between the particle diffusion and battery kinetics is solved using a microscopic "Electrode" sub-model for spherical particles in the electrode. The thermal behavior is solved by the 1D macroscopic "Thermal" sub-model. The stress analysis was carried out at the level of a basic battery cell using a RVE. Compared to the other sub-models, the RVE "Stress" sub-model is at a meso-scale. It allows the investigation of mechanical responses of individual components in a battery environment. The first two sub-models have been reported in literature [32] and available in COMSOL[®] for Li_xC₆|PP|Li_yMn₂O₄ battery cell. The current multiphysics model is built upon the 1D



Figure 3.1: The meso-scale representative volume element (RVE) represents the stress state at the center of the battery cell.

battery model in COMSOL[®]. A description of the first two sub-models and their coupling are provided in the following text, in addition to the discussion of "Thermal" sub-model and "Stress" sub-model.

3.1.1 1D Battery Model

The Newman's 1D Battery model, including the 1D "Battery" sub-model and pseudo 2D "Electrode" sub-model, was used to describe the electrochemical phenomenon in the Li-ion battery.



Figure 3.2: $\text{COMSOL}^{(\mathbb{R})}$ implementation of the fully coupled thermal-electrochemical-stress model. The electrochemical performance of the battery is evaluated with an existing 1D Li-ion battery model in $\text{COMSOL}^{(\mathbb{R})}$ which consists of two sub-models; (a) "Battery" and (b) "Electrode". The thermal analysis is performed using (c) "Thermal" sub-model. The stress analysis for the components in a cell is performed concurrently using (d) a meso-scale RVE "Stress" sub-model.

3.1.1.1 "Battery"Sub-Model

The ionic charge transport, charge balance, and reaction kinetics in the negative electrode, separator and positive electrode were described in the 1D "Battery" sub-model. The current collectors were not involved. The two ends of the 1D geometry in the "Battery" sub-model as shown in Figure 3.2(a) represented the electrode/current collector boundaries.

Substituting Equation 2.3 into Equation 2.1, the ionic charge transport in the electrolyte was derived as:

$$\varepsilon_{2} \frac{dc_{2}}{dt} = \nabla \cdot \left(D_{2}^{\text{eff}} \nabla c_{2} \right) - \frac{1}{F} \mathbf{i}_{2} \cdot \nabla t_{+} + \frac{\nabla \cdot \mathbf{i}_{2}}{F} (1 - t_{+})$$

$$= \nabla \cdot \left\{ \left(D_{2}^{\text{eff}} \nabla c_{2} \right) + \frac{\mathbf{i}_{2}}{F} (1 - t_{+}) \right\}$$

$$(3.1)$$

The dimensionless length method was adopted in the 1D "Battery" sub-model. Consequently, Equation 3.1 was changed to:

$$L_i \varepsilon_2 \frac{dc_2}{dt} - \nabla \cdot \left\{ \left(\frac{D_2^{\text{eff}}}{L_i} \nabla c_2 \right) \right\} = \frac{L_i \nabla \cdot \mathbf{i_2}}{F} (1 - t_+) = \frac{L_i S_a j_n}{F} (1 - t_+)$$
(3.2)

In the same manner, Equations 2.4 and 2.9, which describe the ionic balance in the electrolyte and electronic balance in the solid phase, respectively, were changed to:

$$\nabla \cdot \left\{ \frac{k_2^{eff}}{L_i} \left[-\nabla \phi_2 + \frac{2RT}{F} (1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_2})(1 - t_{\pm}) \nabla (\ln c_2) \right] \right\} = L_i S_a j_n \tag{3.3}$$

and:

$$L_i \nabla \cdot \left(-\frac{k_1^{eff}}{L_i^2} \nabla \phi_1 \right) = -L_i S_a j_n \tag{3.4}$$

Here, the local charge transfer current density j_n was described by the Bulti-Volmer equation, as shown in Equation 2.11.

3.1.1.2 "Electrode" Sub-Model

In the pseudo 2D "Electrode" sub-model as shown in Figure 3.2(b), the dimensionless radius y, y = r/R, where R was the particle radius, was introduced to Li solid state diffusion. Equation 2.7 was rearranged as:

$$y^{2}R\frac{\partial c_{1}}{\partial t} + \frac{\partial}{\partial y}\left(-y^{2}\frac{D_{1}}{R}\frac{\partial c_{1}}{\partial y}\right) = 0$$
(3.5)

In Figure 3.2(b), there are two squares in the pseudo 2D "Electrode" sub-model representing negative and positive electrodes, respectively. The x-axis (horizontal-axis) corresponds to the position along the width of the electrodes and the y-axis (vertical-axis) represents the particle radius. The Li concentration at the surface of the active particles, y = 1, was coupled to the 1D "Battery" sub-model for the battery kinetics calculation.

The Li diffusion was considered within the individual spherical particles in this model.

The mass transport among different spherical particles was neglected. Therefore, the anisotropic diffusion is employed in the pseduo 2D "Electrode" model. The negligible diffusion coefficient was applied in the x-axis direction, while a scaled diffusion coefficient $(\frac{D_1}{r_p})$ was applied in the y-axis direction.

3.1.1.3 Boundary Conditions

The model was constructed by a galvanostatic charge/discharge battery operation mode. By the electronic balance, the applied current density i_{app} was specified at the positive electrode/current collector boundary (a2 in Figure 3.2(a)). It is:

$$i_1 = i_{app}$$

on
$$\Gamma_{\rm D} = 3$$
, the positive electrode/current collector interface (3.6)

The cell voltage was calculated relative to the negative electrode. Therefore, the electronic potential of the solid phase at the interface of the negative electrode and current collector (a1 in Figure 3.2(a)) is set to zero:

$$\phi_1 = \mathbf{0}$$

on $\Gamma_{\rm n} = 0$, the negative electrode/current collector interface (3.7)

For the ionic charge balance in the electrolyte, the electrode/current collector boundaries were insulating:

$$\mathbf{i_2} = \mathbf{0}$$

on $\Gamma_{\mathrm{n}} = 0$, $\Gamma_{\mathrm{p}} = 3$ (3.8)

For the ionic transport, ions do not diffuse to the current collectors. Therefore, the insulating condition was applied at the electrode/current collector boundaries:

$$\nabla c_2 = 0$$
 on $\Gamma_n = 0$, $\Gamma_p = 3$ (3.9)

The lithium ion flux N₀ calculated from the 1D "Battery" sub-model was mapped to the surface of the particles, which is the boundary of y = 1 in the "Electrode" sub-model (see Figure 3.2(b)). All the other boundaries for the pseudo 2D model were insulated.

3.1.1.4 Model Implementation

For the 1D "Battery" sub-model, the Equations 3.3 and 3.4 describing ionic balance in the electrolyte and electronic balance in the solid phase were implemented into PDE Interfaces mode. The ionic transport in the electrolyte was modeled using Diffusion and Convection Application mode in $\text{COMSOL}^{\textcircled{R}}$. This mode is also used to describe the mass transport in active particles in the pseudo 2D "Electrode" sub-model.

3.1.2 "Thermal" Sub-Model

The 1D "Thermal" sub-model considered the heat generation and thermal analysis of a basic Li-ion battery consisting of a negative electrode, a separator, a positive electrode and two current collectors. The heat generation was considered by the local heat generation model as described in Section 2.2.2. As the same as the 1D "Battery" sub-model, The electrodes and the separator are considered as composites consisting of solid and liquid phases. The current collectors contribute to the thermal energy balance only.

The 1D "Thermal" sub-model has a symmetric boundary condition (insulated) at the end of Cu current collector(b1 in Figure 3.2(c)) and a lumped heat transfer coefficient of h=0.2 W m⁻²K⁻¹ assigned at the end of Al current collector (b2 in Figure 3.2(c)). The lumped heat transfer coefficient represented the combined effect of heat conduction, convection heat transfer and radiative heat transfer.

The "Thermal" was implemented into the Heat Transfer mode in $\text{COMSOL}^{\textcircled{R}}$.

3.1.3 "Stress"Sub-Model

To carry out the stress and deformation analysis, the model should be at least in 2D. The "Stress" sub-model presented in Figure 3.2(d) was a prototype quarter-sized 2D model. From left to right, the components included were current collector, negative electrode, separator, positive electrode, and current collector. The circles in the electrodes represent the active particles. In its thickness direction, the electrode in the quarter-sized sub-model had a dimension that was equivalent to a quarter of the original electrode thickness.

The multi-physics phenomena considered in the "Stress" sub-model included the diffusion of Li inside the electrode particles and the stress due to Li intercalation and thermal expansion, as well as mechanical loading. To reduce the modeling effort and allow active particles of different sizes and shapes to be considered, the diffusion process in the "Stress" sub-model had one-way coupling with the 1D "Battery" sub-model. The Li flux in the 1D "Battery" submodel was mapped to the active particle surface in the "Stress" sub-model. In this way, even if the volume fraction of the active particles of a certain shape and packing pattern cannot be realized accurately in the "Stress" sub-model, it would not affect the battery kinetics in the 1D "Battery" sub-model. The temperature rise obtained from the "Thermal" sub-model was also mapped to the "Stress" sub-model. The deformation from the mechanical stress, volume changes due to Li intercalation and thermal expansion, as shown in Equation 2.34, are considered in this analysis. At this stage, the effects of the stress on the Li diffusion as expressed by Equation 2.31 is not considered.

The boundary condition of the stress analysis is presented in Figure 3.3. A periodical boundary was assigned at the lower and upper boundaries in the in-plane direction. A fixedfree boundary condition was prescribed in the through-thickness direction where the left end was fixed while the right end was subjected to a pressure normal to the boundary. The pressure level investigated in this work was 10 psi.

The Li solid state diffusion and stress analysis was implemented into the Diffusion and Convection Application mode and the Solid Mechanics (plane strain) mode in $\text{COMSOL}^{\textcircled{R}}$, respectively.



Figure 3.3: The boundary conditions for stress analysis.

3.2 Material Properties and Simulation Condition

The battery considered in this work is a $\text{Li}_{x}\text{C}_{6}|\text{LiPF}_{6}(\text{EC/DMC})|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell. The electrolyte is the solution electrolyte of $1M(1000 \text{ mol m}^{-3})$ LiPF₆ dissolved in a mixture of EC and DMC with a volume ratio of 2:1.

3.2.1 Temperature Dependent Variables

The temperature dependence is considered for six sets of physical properties. These are (1) k_0 , the reaction rate constant; (2) D_1 , the diffusion coefficient of Li in the solid active particles; (3) OCP of the electrodes; (4) D_2 , the diffusion coefficient of Li⁺ in the electrolyte; (5) k_2 , the electrolyte ionic conductivity; and (6) $v = \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_2}\right) (1-t_+)$, the product of the thermodynamic factor and the anion transference number. Table 3.1 provides a summary for the expressions used to describe their temperature dependency, Equations 3.10 through 3.15. The decoupled model is the referred as the model that the temperature dependence of the physical properties is not considered.

Physical Property	Expressions	Equation	Ref.
Active material			
(1) Li Ddiffusion coefficient	$D_1 = D_{1,ref} \exp[\frac{Ea_D}{R}(\frac{1}{T_{ref}} - \frac{1}{T})]$	3.10	[64]
(2) Reaction rate constant	$k_{0} = k_{0,ref} \exp[\frac{Ea_{R}}{R}(\frac{1}{T_{ref}} - \frac{1}{T})]$	3.11	[64]
(3) Open circuit potentials	$U = U(SOC_{surf}, T_{ref}) + \frac{\partial U_i}{\partial T} \Big _{SOC_{surf}, T_{ref}} (T - T_{ref})$	3.12	[64]
	$= \frac{\Delta S_i}{nF} \Big _{SOC_{surf}, T_{ref}} (T - T_{ref})$		
Electrolyte			
(4) Ionic conductivity	$\sqrt{\frac{k_2(c_2,T)}{c_2}} = \sum_{i=0}^m \sum_{j=0}^n l_{i,j} c_2^i T^j$	3.13	[106]
(5) Li diffusion coefficient	$\log_{10}D_2 = -4.43 - \frac{54}{T - (229 + 5c_2)} - 0.22c_2$	3.14	[106]
(6) $v = \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_2}\right) \left(1 - t_{+}\right)$	$v = \frac{1 - 0.363}{1 - 0.399} \left(0.601 - 0.24c_2^{0.5} - 0.982 \left[1 - 0.0052(T - 294) \right] c_2^{1.5} \right)$	3.15	[32, 106]

Table 3.1: Temperature dependency of six sets of physical properties.

3.2.1.1 Variables Related to the Electrodes

The variables related to the electrodes include k_0 , D_1 and OCP. For Li in graphite and $Li_yMn_2O_4$, the temperature dependences of these variables has been reported in open literature [32, 39, 64, 99–105].

Solid state diffusion coefficient D_1 and the reaction rate constant k_0

The temperature dependences of D_1 and k_0 follow the Arrhenius relationship [64], as shown in Equations 3.10 and 3.11. The constants at $T_{ref} = 25$ °C for the battery system considered in this work are listed in Table 3.2. Figures 3.4(a) and (b) present D_1 and k_0 as a function of temperature, respectively. The state of charge (SOC) dependence of D_1 and k_0 was not considered at this stage of the work due to lack of data.

D (Negative electrode	Positive electrode	
Property	$(\mathrm{Li}_x\mathrm{C}_6)$	$(\mathrm{Li}_{y}\mathrm{Mn}_{2}\mathrm{O}_{4})$	
Solid phase diffusion coefficient at 25 $^{\circ}C$	1/	1×10^{-13} [32]	
$D_{1,ref} (m^2 s^{-1})$	$3.9 \times 10^{-14} [32]$		
Diffusion coefficient activation energy		20 [39]	
$Ea_D (\mathrm{KJ \ s}^{-1})$	35[99]		
Reaction rate constant at 25 $^{\circ}C$		$2 \times 10^{-6} [32]$	
$k_{0,ref} (A m^{2.5} mol^{-1.5})$	$2 \times 10^{-6} [32]$		
Reaction activation energy	[]	53.07 [101]	
$Ea_R $ (KJ mol ⁻¹)	20 [100]		

Table 3.2: Solid phase diffusion coefficient D_1 and reaction rate constant k_0


Figure 3.4: Temperature dependence of (a) the diffusion coefficient D_1 and (b) reaction rate constant k_0 for Li in the negative (graphite) and positive (Li_yMn₂O₄) electrodes. The values of D_1 at 25 °C are 3.9×10^{-14} m² s⁻¹ for graphite and 1×10^{-13} m² s⁻¹ for Li_yMn₂O₄. The value of k_0 at 25 °C is 2×10^{-6} A m^{2.5} mol^{-1.5} for both electrodes.

The temperature dependence of the OCP can be expressed with a Taylors expansion [64], Equation 3.12. As shown, the OCP is a function of the local SOC at the surface of the active particle, the entropy change ΔS , and temperature. For graphite and Li_yMn₂O₄ electrodes, these two functions at 25 °C have been obtained by experiments [32, 103–105]. Figures 3.5(a) and (b) represent the SOC dependent ΔS at 25 °C for the two electrodes. Figures 3.6(a) and (b) represent OCP as a function of SOC and temperature calculated by Equation 3.12 for graphite and Li_yMn₂O₄, respectively. As shown, the effect of temperature is negligible on OCP.

3.2.1.2 Variables Related to the Li⁺ Transport in the Electrolyte

Due to the lack of experimental data, the temperature dependence of Li^+ transport in LiPF_6 in EC/DMC (2:1 by volume) was assumed to follow the trends of similar electrolyte systems.



Figure 3.5: The entropy change as a function of SOC at 25 $^{\circ}$ C for (a) graphite [104] and (b) LiyMn₂O₄ [105].



Figure 3.6: OCP of (a) graphite and (b) $\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ vs. lithium metal as a function of SOC and temperature. The curves at the reference temperature 25 °C were determined by experiments [32, 104].

Ionic conductivity k_2

The ionic conductivity k_2 for LiPF₆ in PC/EC/DMC (10:27:63 by volume) has been investigated experimentally [106]. The concentration and temperature dependence of k_2 was found to follow an empirical relationship given by Equation 3.13 and the PC/EC/DMC system (10:27:63 by volume) exhibited a trend such that $k_2 \rightarrow 0$ as $c_2 \rightarrow \infty$. Combining the parameters for LiPF₆ in EC/DMC (2:1 by volume) at 25 °C [32] with the trend of the temperature dependence for the PC/EC/DMC system [106], for m=n=2, the following expression was obtained:

$$\sqrt{\frac{k_2(c_2,T)}{c_2}} = 1.12 \times (-8.2488 + 0.053248T - 0.000029871T^2 + 0.26235c_2)$$

$$-0.0093063c_2T + 0.000008069c_2T^2 + 0.22002c_2^2 - 0.0001765c_2^2T)$$

$$(3.16)$$

where the unit of c_2 is mol L⁻¹, the unit of T is Kelvin, and the unit of k_2 is mS cm⁻¹. Figure 3.7 plots k_2 as a function of Li⁺ concentration at temperatures from -20 to 60 °C. The value of k_2 used in the decoupled model is from Ref. [32].

Diffusion coefficient D_2

The diffusion coefficient D_2 in LiPF₆ in PC/EC/DMC (10:27:63 by volume) was studied in [106]. The experimental results of the temperature and concentration dependence of D_2 were fitted to Equation 3.14. The magnitude of D_2 given in Ref. [106] is similar to what was reported for LiPF₆ in EC/EMC for a set of volume ratios [107] and LiN(CF₃SO₂)₂ in EC/DEC (2:3 by volume) with a copolymer PVdF-HFP as a host [108]. The above results indicate that the transport property of LiPF₆ in carbonate solvents is strong functions of c_2 and T but a much weak function of the formulation of the carbonate mixture. Based on



Figure 3.7: The ionic conductivity k_2 as a function of the salt concentration and temperature in 1M LiPF₆ in EC/DMC (2:1 by volume), calculated with Equation 3.16.

this observation, Equation 3.14 was employed to describe the temperature and concentration dependence of D_2 in the current work, even though the solvent mixture was different.

Figure 3.8 presents D_2 as a function of the salt concentration at different temperatures. As seen, using a constant D_2 can lead to significant errors when the local environment deviates from the standard condition of 1M concentration and 25 °C.

$\label{eq:product} \textit{Product of the thermodynamic factor and the anion transference number } v$

Product of the thermodynamic factor and the anion transference number is given as $v = \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_2}\right) (1-t_+)$ where t_+ represents the measured conductivity associated with Li⁺ mobility. For LiPF₆ in PC/EC/DMC (10:27:63 by volume), it was found that $t_+=0.399$ and this value appeared to be independent of Li⁺ concentration [106]. For LiPF₆ in EC/DMC (2:1 by volume), the reported value was $t_+ = 0.363$ [32]. Combining the em-



Figure 3.8: The Li⁺ diffusion coefficient D_2 as a function of the salt concentration and temperature in LiPF₆ in EC/DMC (2:1 by volume), calculated with Equation 3.14.

pirical result of the concentration and temperature dependence of from Ref. [106] and $t_{+} = 0.363$ for LiPF₆ in EC/DMC, Equation 3.15 was derived.

Figure 3.9 presents v as a function of Li⁺ concentration under different temperatures. As shown, v increases with the salt concentration but decreases with the temperature. Among the two factors, the salt concentration has a much stronger effect on v.

3.2.2 Viscoelastic Property of Separator

The viscoelastic behavior reflects the combined viscous and elastic response of the materials under mechanical stress [96]. The stress-strain relation of a viscoelastic material is time and temperature dependent. As a polymeric membrane, the separator exhibits the viscoelastic property. The stress relaxation and thermal softening of the polymeric separator are consid-



Figure 3.9: The product of the thermodynamic factor and the anion transference number v as a function of the salt concentration and temperature in LiPF₆ in EC/DMC (2:1 by volume), calculated with Equation 3.15.

ered in this work. At this stage, the linear viscoelastic material model is adopted to describe the viscoelastic behavior of separator.

The polymeric separator has the anisotropic microstructure. Figure 3.10 presents a typical image of Celgard 2400 observed under SEM. As seen, the membrane has two distinct material directions, which are commonly referred as machine direction (MD) and transcerse direction (TD). In this work, the viscoelastic behavior of the separator was tested along MD.

3.2.2.1 Time Dependent Viscoelastic Behavior

The viscoelastic property of the polymeric separator can be characterized by the creep compliance and stress relaxation function. A creep test measures the strain with time under a constant load. There was a series of tensile creep tests performed with a commercially avail-



Figure 3.10: SEM image of the surface of a single layer Celgard 2400 separator [9]. The arrow indicates the transverse direction (TD).

able PP membrane, Celgard 2400, in the electrolyte solution of $1.1M \text{ LiPF}_6$ in EC/DMC(1:1 by volume) using a dynamic mechanical analyzer (DMA)[110]. The creep tests was applied along machine direction (MD).

The measured creep compliance in the linear viscoelastic range was fitted by a model with Kelvin-Voigt elements by Sheidaei et al [110]. The Kelvin-Voigt model can be described mathematically by a Prony series [118]

$$J(t) = J_0 + \sum_{i=1}^n J_i e^{-\frac{t}{\tau_i}}$$
(3.17)

where J_0 is the instantaneous compliance, J_i is the creep constant and τ_i is the retardation

times associated with Kelvin-Voigt element i.

The stress relaxation function E(t) is related to the creep compliance function, J(t), in the Laplace domain by the following relation [112, 117, 118, 118]:

$$E(s)J(s) = \frac{1}{s^2}$$
 (3.18)

Therefore, the Prony series for stress relaxation function is:

$$E(t) = E_{\infty} + \sum_{i=1}^{n} E_i e^{-\frac{t}{\tau}}$$
(3.19)

The measured creep compliance was fitted to Prony series using a non-linear least-square subroutine in Matlab 2006, which was presented in Appendix A. The parameters in the stress relaxation function expressed in Prony series were obtained by Laplace transformation using Mathematica 8, which was presented in Appendix B. The results were presented in Table 3.3 and Figure 3.11. As the samples were tested under the tensile mode, the data represented Young's modulus. The stress relaxation function was implemented into the multiphysics model.

3.2.2.2 Temperature Effect

The temperature dependence of the separator's mechanical properties is of great concern. The time-temperature dependence of viscoelastic solids is modeled based on the framework



Figure 3.11: The stress relaxation function for the separator Celgard 2400 in 1.1 M LiPF_6 in EC/DMC (1:1 by volume) [110].

Table 3.3: Prony series parameters for the stress relaxation modulus in 1.1M ${\rm LiPF_6}$ in EC/DMC (1:1 by volume).

i	Stress relaxation constant (Pa)	Relaxation time (s)
	$E_{\infty} = 1.23 \times 10^8$	
1	$E_1 = 1.69 \times 10^8$	$\tau = 66.33$
2	$E_2 = 1.22 \times 10^7$	$\tau = 968.07$
3	$E_3 = 1.92 \times 10^8$	$\tau = 3860.3$
4	$E_4 = 2.81 \times 10^5$	$\tau = 99756$

of the time-temperature superposition principle (TTSP) of the linear viscoelasticity theory [112, 118]. TTSP states that the relaxation or deformation behavior of a linear viscoelastic material at an elevated temperature over a time period is equivalent to that occurs at a lower temperature over a longer period time. Accordingly, the effect of temperature can be represented in a viscoelastic function through the use of a master curve and a reduced time $t' = t/\alpha_T$ where α_T is the so-called horizontal time-temperature shift factor. α_T is obtained through constructing a master curve at a reference temperature from a set of curves measured under an isothermal condition over a range of temperatures. Considering time-temperature superposition, the Prony series is adjusted as [114]:

$$E(t) = E_{\infty} + \sum_{i=1}^{4} E_i e^{-\frac{t}{a_T \tau}}$$
(3.20)

This dependence was measured for Celgard 2400 separator by conducting creep test at different temperatures in air [115]. It was then assumed that the temperature dependence obtained in air is equivalent to that in electrolyte solutions. Electrolytes tend to evaporate. During room temperature tests, the amount of electrolyte can be monitored and hence maintained. This option is not possible for testing at elevated temperatures.

The Celgard 2400 in this test had a nominal thickness of 25 μ m. The clamp had a gage length fixed at 15 mm. The samples in the form of long strips were cut from the separator film by a razor blade. The sample width varied from 4.88 mm to 5.20 mm.

The creep tests were carried out under a tensile mode using a DMA Q800 with a film clamp as shown in Figure 3.12(a). The isothermal tests were established by accommodating



Figure 3.12: The images depicting the sample installation and isothermal test establishment. (a) sample installation; (b) & (c) the establishment of the isothermal test by closing the furnace.

the clamp and film in a closed furnace as shown in Figure 3.12(b) and (c). The creep experiments were carried out at 25 $^{\circ}$ C, 40 $^{\circ}$ C, 45 $^{\circ}$ C, 50 $^{\circ}$ C, 55 $^{\circ}$ C and 60 $^{\circ}$ C.

The temperature range from 25 °C to 60 °C was the common range for a battery in the working situation [116]. The heat generated from the electrical board below clamp would dissipate into the furnace. The temperature in the furnace would gradually increase if external cooling by connecting liquid nitrogen tank to the furnace was not provided.

The creep test was conducted by three steps. At the beginning, the temperature was increased from the room temperature (23.5 °C to 25 °C) to the specified temperature by the ramp rate 4C min¹. A preload force 0.001N was applied to maintain the sample at straight and tight status. Then the sample was hold at the isothermal state for 5 min. At the last step, a series of creep test were performed with samples in MD at different load levels. A new sample was used in each creep test. The samples were subjected to a constant load for



Figure 3.13: The creep compliance of Celgard 2400 at different stress levels.

 $20\ {\rm minutes}.$

For a linear viscoelastic material, the creep compliance is independent of the stress level [110]. At the frist step, the stress range of the linear creep response needs to be determined. Figure 3.13 presents the creep compliances measured at 1, 1.5, 1.75 and 2 MPa at 60 $^{\circ}$ C. As shown, the creep compliances at the 1 and 1.5 MPa were close to each other while the creep compliances at the higher stress levels were obviously higher. The results indicate that the creep response is linear at least up to 1.5 MPa. At 1.75 and 2 MPa, the creep response is nonlinear. In further investigation, the creep tests were conducted under 1.5 MPa at different temperatures.

Figure 3.14 plots the creep compliance under 1.5 MPa at different temperatures. The creep compliance curves were converted to the stress relaxation curves by Laplace transformation [117, 118] and plotted versus logarithmic time in Figure 3.15.



Figure 3.14: The creep compliance of Celgard 2400 at different temperatures: 25 °C, 40 °C, 45 °C, 50 °C, 55 °C and 60 °C. The stress level is 1.5 MPa.



Figure 3.15: Construction of a master curve for PP using shear stress relaxation experimental data. The stress plots are at 25 $^{\circ}$ C, 40 $^{\circ}$ C, 45 $^{\circ}$ C, 50 $^{\circ}$ C, 55 $^{\circ}$ C and 60 $^{\circ}$ C. The above stress relaxation plots are obtained from creep compliance measured curves at the corresponding temperatures by Laplace transformation.



Figure 3.16: The relationships of a_T and temperature for PP.

The process of constructing a master curve is illustrated in Figure 3.15. First, a reference temperature T_{ref} has to be chosen. For the current case, $T_{ref} = 25$ °C. Next, the curves measured at other temperatures are shifted horizontally to join the reference curve in order to form a composite curve, or the so-called master curve. The amount of horizontal shift required for these curves to form the master curve yields the α_T function, as shown in Figure 3.16. When plotted versus 1/T, a_T is found to follow a Williams-Landel-Ferry (WLF) relation for amorphous polymers, and Arrhenius relation for semi-crystalline polymers [117]. In Figure 3.16, in the range of 25 to 60 °C, the a_T function displayed a bilinear shape, i.e. Arrhenius type of response. A change in slope corresponds to a change in the activation mechanism [113].

By fitting shift factors at different temperatures in Figure 3.16, the temperature dependent a_T can be expressed as:

25 °C - 50 °C:

$$Loga_T = 14230(\frac{1}{T}) - 47.76 \tag{3.21}$$

50 °C - 60 °C:

$$Loga_T = 7526.9(\frac{1}{T}) - 27 \tag{3.22}$$

3.2.3 Battery Parameters and Other Properties

Table 3.4 provides a summary of the battery parameters used in this work, which include the battery design parameters and the electrochemical related variables. The cross-section of the cell is 24 cm² and the total volume of the battery cell is 0.830 cm³. The thickness of each collector is 20 μ m.

The effect of the tortuosity of the composite electrode and the separator on the ionic conductivity and diffusion coefficient in the electrolyte was considered using the Bruggeman relation by Equations 2.5 and 2.6, respectively. For the composite electrodes investigated in this study, p = 3.3 [32]. For the separator, p = 3.3 is estimated with $\tau_t = \varepsilon^{p-1}$ based on the measured tortuosity value of $\tau_t = 6.0$ [84, 86] and a porosity of $\varepsilon = 0.46$ [133].

The physical properties of the battery component materials used in the local heat generation model are listed in Table 3.5. The property parameters of the negative electrode, the positive electrode, the separator, the Cu foil and the Al foil are transposed from Ref.

Quantity	Negative electrode	Positive electrode	Separator	Electrolyte	Cu foil	Al foil
$\begin{array}{c} \text{Thickness} \\ L \ (\mu \mathrm{m}) \end{array}$	100^a	174^{a}	52^a	/	10^{b}	10^{b}
Particle radius $R \ (\mu m)$	12.5^{a}	8.5^{a}	/	/	/	/
Initial concentration $c_{ini} \pmod{\mathrm{m}^{-3}}$	$\begin{array}{c} 23751^{b} \\ (\text{SOC}=0.9) \end{array}$	$\begin{array}{c} 4572^b \\ (\text{SOC}=0.2) \end{array}$	/ 1000 ^b		/	/
Maximum concentration $c_{max} \pmod{\mathrm{m}^{-3}}$	26390 ^a	22860 ^a	/	/	/	/
Volume fraction of solid phase ε_1	0.471^{a}	0.362^{b}	/	/	/	/
Volume fraction of liquid phase ε_2	0.357^{a}	0.444^{a}	0.46^{C}	/	/	/
Electronic conductivity of solid phase k_1 (S m ⁻¹)	100^{a}	3.8^{a}	/	/	/	/
Exponent p in Bruggeman relation	3.3^a	3.3^a	3.3^{a}	/	/	/
Cross sectional area $A_{cell} \ (\mathrm{cm}^2)$	24^a	24^a	24^a	/	24^a	24^a

Table 3.4: Critical battery parameters used in the battery model.

a: Ref. [32]

b: estimated or assumed value.

c: Ref. [133]

Materials	Density ρ kg m ⁻³	Heat capacity C_p (J (kg K) ⁻¹)	Thermal conductivity K_{therm} (w (m K) ⁻¹)	Electrical resistivity $r_c \times 10^{-8}$ (Ω m)
Negative electrode	2223	641	6.5	/
Positive electrode	4202	672	6.2	/
Separator	900	1883	2.16	/
Electrolyte	1210	1518	0.099	/
Cu foil	8700	396	398	1.7
Al foil	2700	897	237	1.8
Electrolyte filled negative electrode	1861	845	4.21	/
Electrolyte filled positive electrode	2874	830.2	3.49	/
Electrolyte filled separator	1043	1688	1.21	/

Table 3.5: Physical properties of the battery components in "Thermal" sub-model.

[119], with the exception of the electrolyte heat capacity. Both the experimental data and calculated result of the heat capacity of EC and DMC were reported in Ref. [120]. Therefore the electrolyte heat capacity in this work was calculated by the data from Ref. [121] based on the rule of mixtures. The porous electrode can be treated as a composite of active particles embedded in a matrix of the electrolyte [121, 122]. The densities, thermal conductivities, and heat capacities of the two electrodes and separator with filled electrolyte were calculated based on the rule of mixtures for composites as described in Ref. [121].

The mechanical properties of the different battery components are listed in Table 3.6 and

Descrite	Negative	Vegative Positive Cu A		Al	C	
Parameter	electrode	electrode	foil	foil	Separator	
Thermal expansion						
coefficient	4.06^{a}	8.62^{b}	17^{b}	23.6^{b}	130^{b}	
$\alpha \times 10^{-6} (\mathrm{K}^{-1})$	1.00	0.02		20.0		
Partial molar						
volume	3.5^{c}	4.17^{c}	/	/	/	
$\Omega \times 10^{-6} \; (\mathrm{m^3 \; mol^{-1}})$	0.0			/	/	
Young's modulus	1.00	100	1170	700		
E (GPa)	12	10	117	70*	section 3.2.2	
Poisson's ratio	0.20	0.20	0.250	0.240		
ν	0.5	0.5	0.55	0.34°		

Table 3.6: Mechanical properties of different battery components used in the "Stress" submodel.

a: Ref. [123]

b: Ref. [124]

c: Ref. [125]

Table 3.7 .

The elastic modulus of LiyC_6 calculated in theoretical studies is in the range of 28-108 GPa [92, 126]. These values are high as compared with those reported in the data sheet of graphite particles, which are in the range of 9-15 GPa [127]. This discrepancy is due to the imperfection and porosity in commercial grade graphite particles. The present work concerned a battery with commercially available graphite particles. A value of 12 GPa was therefore selected.

The value of the Young's modulus of graphite particles was reported in the range of 9-15 MPa [127]. Concerning a battery with the commercially available graphite particles, the value of 12 GPa was selected in this work.

The partial molar volume for $\text{Li}_{x}\text{C}_{6}$ was calculated using Equation 2.25. The stoichiometric maximum concentration for $\text{Li}_{x}\text{C}_{6}$ was given as 2.64×10^{4} mol m⁻¹ [32] and 3.06×10^{4}

Parameter	Value
Thermal expansion coefficient $\alpha 10 \times ^{-6} (\mathrm{K}^{-1})$	1000
Bulk modulus K (MPa)	4
Shear modulus G (MPa)	0.3
Branch $G_i(i=1)$ (MPa)	0.1 (300s)

Table 3.7: Mechanical properties of electrolyte ${\rm LiPF}_6$ in EC/DMC (1:1 by volume)

mol m⁻¹ [128]. From C to $\text{Li}_{x}C_{6}$, $\Delta y = 1$. Assuming a maximum volume change of 11% and the stoichiometric maximum concentration of 2.64×10^{4} mol m⁻³, the partial molar volume of $\text{Li}_{x}C_{6}$ was estimated as:

$$\Omega = \frac{3\varepsilon_{ij}^{e_i,c}}{\Delta y c_{s,\max}} \approx \frac{3 \times 0.11^{1/3}}{1 \times 2.64 \times 10^4} = 4.17 \times 10^{-6} \text{m}^3 \text{mol}^{-1}$$
(3.23)

The partial volume of $Li_yMn_2O_4$ was already estimated using the same method in Ref. [15].

The viscoelastic behavior of the electrolyte was represented using the Prony series [118] with an instantaneous shear modulus of 0.2 MPa. To avoid the convergence problem, the value used in this work is about an order higher than that reported for the compliant gels [129]. The assumed value of 0.2 MPa was more than two orders lower than the modulus of the separator and, therefore, was judged as acceptable.

3.3 Simulation Condition

The multiphysics models for the lithium ion battery were constructed and analyzed using software $\text{COMSOL}^{\textcircled{R}}$ 3.5a. The sub-models of "Battery" and "Electrode" had a dimension of a unit length whereas the "Thermal" and "Stress" sub-models had a real dimension. The type, number and the maximum size of the elements in each sub-model is summarized in Table 3.8.

	Type of element	Dimensionless	Number of element	Max. size
Battery	1D linear	\checkmark	140	0.048
Electrode	2D triangle	\checkmark	11776	0.025
Thermal	1D linear	Х	64	$6.5 \mu m$
Stress	2D triangle	X	180522	$1 \mu m$

Table 3.8: Element information in four sub-models of the multiphysics model.

The displacement field across different components was assumed to be continuous and modeled with a continuous mesh. It should be noted that in a battery, the active particles are in contact with, instead of bonded to, the separator. The relative movement between the separator and electrodes may happen at a local area at microscopic level. To take into consideration of this effect requires a contact definition between the particles and separator.



Figure 3.17: Finite element meshes for (a) the "Battery"; (b) the "Electrode"; (c) the "Thermal" and (d) RVE "Stress" sub-models.

It was possible to establish a contact relationship between the particles and separator in a stand alone model. When incorporating the RVE "Stress" sub-models with contact definition in the multi-scale model, convergence problems arose. The problem became worsen when a compliant electrolyte phase was added. A continuous mesh, therefore, was adopted in the RVE sub-models in this work. The stress revealed by this model, at best, may represent the condition in the separator where the particle roughness created a nonslip condition in the local area.

The models were solved using the "Direct (UMFPACK)" time dependent solver. The relative tolerance was set as 0.0001 and the absolute tolerance was set as 0.001. UMPACK is a robust, highly efficient linear solver for non-symmetric systems. The average solution times was within 2 hours using a single CPU.

Chapter 4

Heat Generation in a Li-Ion Battery

The preceding chapters have described the development of a multiphysics model to simulate a basic $\text{Li}_{x}\text{C}_{6}|\text{LiPF}_{6}(\text{EC/DMC})|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell. The "Thermal" sub-model is capable of simulating the heat generation and temperature rise in a Li-ion battery. Understanding the heat generation is a necessary step in assessing the thermal stress in a battery cell. Additionally, since the separator is a polymeric material, the temperature dependence of the separator's mechanical properties is of great concern. In this chapter, the "Thermal" submodel was validated against literature data. The predicted heat generation rates were within the range of available experimental results. The model was used to evaluate the influence of active particle size and component thickness on the heat generation rate and battery performance.

4.1 Model Validation

The "Thermal" sub-model is validated by the comparison of the simulated data with the experimental data from the similar battery system. Ye et al. [41] measured the temperature rise of a $\text{Li}_{x}\text{C}_{6}|1.2\text{M}$ LiPF₆ (PC/EC/DMC)|Li_yMn₂O₄ prismatic battery using a thermocouple at the surface of the battery under a thermally insulated condition. The lumped heat transfer coefficient determined under this condition was h=0.38 W m⁻² K⁻¹. Experiments were performed under galvanostatic charge and discharges at 0.2C, 1C and 2C rates.

Ye's experiments were simulated using the current model with the same geometrical battery parameters for a similar $\text{Li}_{x}\text{C}_{6}|1.2\text{M LiPF}_{6}$ (EC/DMC)| $\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell. Simulations were performed considering the lumped heat transfer coefficient at the surface of both two current collectors. With h=0.38 W m⁻² K⁻¹, the predicted temperature rises were lower than Ye et al. [41]. Nevertheless, good agreements were obtained at all three rates with h=0.2 W m⁻² K⁻¹, as shown in Figure 4.1. This result provided a certain justification for the current model approach. It should be noted that the battery system investigated here is not exactly the same as in Ye et al. [41]. Furthermore, the parameters in the current model were based on literature data or selected from similar systems as described in section 3.2.3. There was no additional adjustment or fitting as the model in Ref. [41]. Under this condition, the agreement between the model predictions and the experimental results is rather good. Therefore, in the following text, h=0.2 W m⁻² K⁻¹ was applied at the surface of both two current collectors.

4.2 Thermal Analysis

The validated model was used in the investigation of the influence of individual physical and battery design parameters in the heat generation of the battery. In simulations, the thermal analysis was performed with an initial temperature of 25 °C. The battery was operated under galvanostatic conditions. The applied current for a 1C rate was 28 A m⁻². The discharge cut-off voltage was 3.0 V. The discharge was stopped when the battery cell voltage reached the cut-off voltage or when the reaction stopped because of the shortage of Li⁺ supply at the reaction interface [32].

Because the heat is generated in all battery components and the thin thickness of the



Figure 4.1: Comparison of predicted temperature rises with the experimental results of Ye et al. [41].

cell, the temperature distribution is uniform through the thickness of a basic cell. This was observed even at the highest charge rate. Thus only the temporal variation of the temperature will be discussed.

4.3 The Effect of Temperature Dependence of Physical Properties

The influence of temperature dependence of individual properties on battery performance was investigated by keeping one property as temperature independent at a time. Figure 4.2 presents the influence of each property on the predicted temperature rise under three discharge rates: 1C, 4C and 8C. The results were compared with those from coupled and decoupled models, when all six sets of properties were with or without temperature dependence, respectively.

At the same depths of discharge (DOD) level, the decoupled model predicted a higher temperature rise than the other models. At 4C and 8C, the decoupled model also predicted much lower achievable DOD. At 1C, only the temperature dependence of the Li⁺ diffusion coefficient D_2 in electrolyte and reaction rate constant k_0 for the positive electrode had a noticeable effect on the temperature rise. At 4C, the influence of the ionic conductivity k_2 , and the Li diffusion coefficient D_1 and reaction rate constant k_0 of the negative electrode also became distinguishable. The influence of OCP was omitted in Figure 4.2 since its effect was negligible.

Kumaresan et al. [88] investigated the effects of the temperature dependence of D_2 , k_2 , and ν for the electrolyte and D_1 for the negative electrode on the cell capacity for a Li_xC₆|LiPF₆ (PC/EC/DMC) |Li_yCoO₂ cell at 1C. Judging by the discharge profiles, their results indicated that, with a starting temperature of 25 °C, the effect of temperature dependence of k_2 was negligible. These are in agreement with our results at 1C. However, the current study indicated that the influences of temperature dependence of k_2 became important with increasing rates. The same was true for some other properties. For properties with a temperature dependence described by the Arrhenius equation, the one with a larger value of activation energy exhibited a stronger influence, such as the k_0 for the positive electrode and D_1 of the negative electrode.

The difference between the decoupled and coupled models under different discharge rates was then investigated. Figures 4.3(a) and 4.3(b) present the temperature rise and cell utilization at the end of discharge obtained for rates from 0.1C to 4C. The cell utilization is defined as the ratio of the actual achieved capacity to the maximum capacity. As shown, the



(c) 1C, positive electrode

Figure 4.2: Influence of the temperature dependent parameters on the predicted temperature rises during a galvanostatic discharge at 1C (a-c), 4C (d-f) and 8C (g-i). Simulations were performed with one temperature dependent parameter at a time. The corresponding temperature rises from coupled and decoupled model were also plotted in each figure.

Figure 4.2: (cont'd)



(f) 4C, positive electrode





(i) 8C, positive electrode



Figure 4.3: (a) The temperature rise and (b) cell utilization as a function of discharge rate. The cut off voltage is 3.0 V.

decoupled model predicted a much lower utilization at higher rates. The lower temperature rise predicted by the decoupled model at rates greater than 4C was due to earlier termination of the discharge process. In reality, a moderate temperature rise improves the ion transport and reduces concentration polarization which leads to a better cell utilization. To consider these effects, it is necessary to use coupled thermal-electrochemical battery models. The results presented thereafter are produced with the coupled model.

4.4 Heat Generation

In numerical simulations, the contributions of individual heat generation mechanisms can be computed separately. Figure 4.4 plots the heat generation rates vs. DOD under 1C discharge rate by individual mechanisms as well as their summation. The values from overpotential and ohmic heats were all positive and among which the overpotential heat at the electrochemical



Figure 4.4: Partial heats due to different sources contributing to the total heat during 1C discharge.

interface and the ohmic heat in the electrolyte phase appear to be dominant. The amplitude of the entropic heat was high, but it exhibited an S shape with DOD. Its shape resembles a mirror image of the entropy change versus SOC curve of the Li_yMn₂O₄ cathode in Figure 3.5(b). Due to the entropic heat, the total heat generation rate also exhibited an S shape. Sshaped heat generation curves have been observed in experimental measurements [23, 61, 68– 71] and reported in model predictions [23, 61, 68, 69, 71] of Li-ion batteries with different electrode materials.

Figure 4.5 plots the total heat generation rate vs. DOD as a function of the discharge rate. Both the magnitude of the heat generation rate and its undulation increased with the discharge rate. At 6C, the heat generation rate had a range from 227 W L⁻¹ to 400 W L⁻¹. For example, at 6C, the maximum achievable DOD was about 20%. The battery

performance at higher rates will be further discussed in section .

Several groups have measured the heat generation rates for Li-ion batteries [9,16-30]. As discussed in the review paper of Bandhauer et al. [61], due to the difficulty in measuring transient high rate heat generation, most of the experiments were conducted at lower rates (1C) during discharge [16-28] or charge [16,18,19,21-30].

Table 4.1 compares the predicted minimum and maximum generation rates with the available experimental data in the literature under discharge rates of 0.1C, 0.5C, and 1C. The same comparison is provided in Figure 4.6. Because of the variations in battery materials and uncertainties in battery geometries [61], the reported values varied widely. The purpose of comparison in Table 4.1 and Figure 4.6 is to examine whether the prediction of this study is within the same order of magnitude as the literature data. The results show that both the maximum and the minimum heat generation rates at all three rates determined in this work were within the range of the literature data. The predicted maximum heat generation rates were within the range but appeared to be high compared to most of the experimental data point. This might be caused by the range of DOD in the experiments. Figure 4.4 shows that the maximum heat generation occurs at the end of discharge. Therefore, experiments with a smaller DOD will yield a lower maximum heat generation rate.

4.5 Effects of Battery Design Parameters

The battery cells with different design parameters were designated as the following. The baseline model with the set of parameters listed in Table 3.4 was referred to as 1R/1L, where R and L stand for the active particle size and component thickness, respectively. In other models, the radii of the positive and negative particles and/or the thicknesses of the



Figure 4.5: Heat generation rate versus DOD for discharge rates from 0.1C to 6C: (a) 0.1C-2C; (b) 0.1C-6C.

Heat Generation Rate	Discharge Rate				
$q (W L^{-1})$	0.1C	$0.5\mathrm{C}$	1C		
Minimum values from the experimental data	-0.45 to 0.79	-0.32 to 4.12	-0.05 to 13.3		
Predicted minimum value	-0.4	1.273	8.67		
Maximum values from the experimental data	0.03 to 11	1.77 to 44	0.31 to 84.5		
Predicted maximum value 1.79		13.9	37.0		
References	[68-73, 78]	[65, 66, 69, 70, 80]	[65, 66, 68-71, 73, 76]		

Table 4.1: Comparison of the predicted minimum and maximum heat generation rates with the available experimental data in literature.



Figure 4.6: Comparison of the predicted heat generation rates with the upper and lower bounds of experimental data in literature (a) the maximum heat generation rate; (b) the minimum heat generation rate.

battery components were changed proportionally while the porosity and thickness of the current collectors remained the same. A list of the models with different particle size and component thickness used in the design parameter study is given in Table 4.2.

Madal	Negative		Positive		Company	Cu	Al
Model	electrode		electrode		Separator	foil	foil
D (L	R	L	R	L	L	L
Parameter	(μm)						
0.1R/1L	100	1.25	174	0.85	52	10	10
$1\mathrm{R}/1\mathrm{L}$	100	12.5	174	8.5	52	10	10
$1.5\mathrm{R}/1\mathrm{L}$	100	18.75	174	12.75	52	10	10
1R/0.5L	50	12.5	87	8.5	26	10	10
0.1 R / 0.5 L	50	1.25	87	0.85	26	10	10

Table 4.2: Models with different particle sizes R and component thicknesses L investigated in the design parameter study

4.5.1 Particle Size

Lu et al. [131] reported that reducing the particle size of the $\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ positive electrode improved the battery capacity. Botte et al. [132] used a mathematical model to investigate the effect of particle size in the negative electrode on temperature rise in a $\text{Li}_{x}\text{C}_{6}|\text{LiPF}_{6}$ (EC/DMC)|Li_yNiO₂ cell. The effect of particle size has been recognized in the intercalation



Figure 4.7: (a) The cell temperature rise and (b) utilization at the end of the discharge in the 0.1R/1L, 1R/1L and 1.5R/1L models.

stress model [12].

The effect of the electrode particle size was investigated with the 0.1R/1L, 1R/1L, and 1.5R/1L models. Figure 4.7(a) presents the temperature rise at the end of discharge as a function of the discharge rate. As shown, the influence of particle size on temperature rise was small at discharge rates below 2C. Above 2C, the temperature rise apparently decreased with reducing particle size. A further inspection revealed that the lower temperature rise was related to the low battery utilization. As shown in Figure 4.7(b), the 0.1R/1L model exhibited the highest utilization at the lower and higher rates. In the range of 2C to 4C, however, the trend reversed. In other words, while a smaller particle size in general reduced the temperature rise and improved the cell utilization, the trend was not monotonic across the rates.

To understand this phenomenon, the concentration profiles of different particle sizes were examined. Figures 4.8(a) through 4.8(e) present the concentration profiles in the electrolyte
and at the surface of the active particles at three discharge rates: 1C, 3C and 5C. The comparison was made for DOD=0.91 (1C), DOD=0.55 (3C), and DOD=0.24 (5C) respectively, when the cell voltage of the model with the lowest value reached the cut-off value of 3.0 V.

At 1C, the rate limiting mechanism was Li diffusion in the negative particles. As shown in Figure 4.8(b), with a large particle size of 1.5R, Li at the surface of the particles was depleted across the negative electrode. With the same volume fraction, reducing the particle size increases the surface area and reduces the local current density [48]. A smaller particle size also reduces the distance of Li diffusion from the particle interior to the surface and sustains the supply of Li at the surface.

At 3C, the rate limiting mechanism switched to Li^+ transport in the electrolyte. As shown in Figure 4.8(c), Li^+ depletion in the electrolyte in the positive electrode started from the end next to the current collector. Because of a greater concentration gradient earlier in the 0.1R/1L cell, Li^+ depletion occurred earlier in this cell.

At 5C, Li⁺ transport in the electrolyte remained to be the rate limiting mechanism, Figure 4.8(e). However, Li⁺ depletion occurred first in the 1.5R/1L cell at DOD=0.24. At this DOD level, 1.5R/1L exhibited the highest Li⁺ concentration gradient in the electrolyte.

Apparently, the effect of particle size on Li^+ concentration gradient varied during the discharge. This phenomenon was further investigated. Figure 4.9 compares the development of the Li^+ concentration profile during a discharge at 1C between the 1R/1L and 0.1R/1L models at four DOD levels: 0.026, 0.28, 0.53, and 0.91. As shown, at the two lower DOD levels, 0.1R/1L model had a lower Li^+ gradient. The trend changed with increasing DOD. At the two higher DOD levels, 0.1R/1L model had a greater Li^+ gradient. This explains the non-monotonic effect of the particle size. The maximum DOD that a cell can reach decreases with the discharge rate. At lower discharge rates, the cell can reach a higher maximum DOD



Figure 4.8: Comparison of the Li^+ concentration profiles in the 0.1R/1L, 1R/1L and 1.5R/1L models under three discharge rates. (a, b) at DOD=0.91, 1C; (c, d) at DOD=0.55, 3C; (e, f) 5C; when one of the cells reached the cut-off voltage. (a, c, e) Li⁺ concentration in the electrolyte, (b, d, f) Li concentration at the surface of the active particles.



Figure 4.9: The evolution of Li^+ concentration profiles in electrolyte in the 0.1R/1L and 1R/1L models at 1C discharge rate; (a) at DOD=0.026 (100 s), (b) DOD=0.28 (1000 s), (c) DOD=0.53 (2000 s), (d) DOD=0.91 (3400 s).

when cells with a smaller particle size exhibit a greater Li^+ gradient. At higher discharge rates, the maximum DOD of the cell is much lower. The cells with a smaller particle size have a smaller Li^+ gradient at lower DODs and hence exhibit a higher utilization than the cells with a larger particle size.

4.5.2 Component Thickness

The effect of the component thickness was examined using the 0.1R/0.5L, 0.1R/1L, 1R/0.5L and 1R/1L models. Figure 4.10 compares the temperature rises and utilizations of these four cells. With the same particle size, cells with thinner components resulted in a much lower temperature rise. Reducing the component thickness reduced the concentration polarization. The apparently higher temperature rise of 0.1R/0.5L and 1R/0.5L cells at discharge rates greater than 4C was due to their much higher utilization rate.

It should be noted that the result presented here is at the cell level. At the battery level, for the same total power, a battery constructed with thinner basic cells would require more cells. The added weight and volume of the additional current collector layers must be considered for the overall optimization of the battery.

4.5.3 Component Thickness and Particle Size Effects

As discussed in Section 4.5.2, the influence of particle size on battery utilization is not monotonic across the rates. The same trend was observed in models with a thin component. Figures 4.11(a) and 4.11(b) compare the temperature rise and cell utilization for 0.1R/0.5L and 1R/0.5L models up to a discharge rate of 18C. The 0.1R/0.5L model had a higher utilization up to a discharge rate of 8C. It was overtaken by 1R/0.5L in the range of 8C to 15C. The trend was reversed back at above 15C.

Figures 4.12(a) through 4.12(c) compare the discharge profiles of 0.1R/0.5L, 0.1R/1L, 1R/0.5L and 1R/1L cells at 1C, 4C and 10C. The results clearly indicated that, with the same particle size, reducing the component thickness is a rather efficient method to improve the cell utilization. On the other hand, the effect of particle size is not monotonic.



Figure 4.10: The temperature rise and cell utilization at the end of the discharge. (a) temperature rise, 1R/0.5L and 1R/1L cells; (b) temperature rise, 0.1R/0.5L and 0.1R/1L cells; (c) cell utilization, 1R/0.5L and 1R/1L cells; (d) cell utilization, 0.1R/0.5L and 0.1R/1L cells.



Figure 4.11: The temperature rise and cell utilization at the end of the discharge of 0.1 R/0.5L and 1 R/0.5L. (a) temperature rise; (b) cell utilization.

4.5.4 Tortuosity

The tortuosity of a porous material may be affected by material design and manufacturing processes [9, 135]. To investigate the effect of tortuosity, batteries with Bruggeman's exponents of p=3.3 and p=2 were compared. Table 4.3 presents the effective ionic conductivities and diffusion coefficients in all porous components in these two batteries. The porosity of each component was the same as in Table 3.4.

The effect of active particle size on temperature rise and cell utilization was examined in Figure 4.13 for the batteries with p=3.3 and p=2. The impact of tortuosity was much more significant as compared to that of the particle size. Reducing tortuosity reduced the temperature rise and improved the cell utilization. With p=2, the temperature rises at 2C discharge rate were about 51% and 33% of those for p=3.3 batteries for the 1R/1L and 0.1R/1L models, respectively. The cell utilization was about 91% at 6C even for the 1R/1L model when p=2.



Figure 4.12: Comparison of the discharge profiles between cells with a thickness of 0.5L and 1L. Discharge rate: (a) 1C, (b) 4C, and (c) 10C.

	Exponent p	Tortuosity $ au_t$	Effective ionic conductivity k_{eff}	Effective Li ⁺ diffusion coefficient in electrolyte D_{eff}
Battery I	3.3	$10.7 \\ 6.0 \\ 6.5$	$\begin{array}{c} 0.033 k_2({\rm Li_xC_6}) \\ 0.077 k_2({\rm PP}) \\ 0.069 k_2({\rm Li_yMn_2O_4}) \end{array}$	$\begin{array}{c} 0.033 D_2({\rm Li_xC_6}) \\ 0.077 D_2({\rm PP}) \\ 0.069 D_2({\rm Li_yMn_2O_4}) \end{array}$
Battery II	2	2.8 2.2 2.3	$\begin{array}{c} 0.13k_2(\text{Li}_{x}\text{C}_{6}) \\ 0.21k_2(\text{PP}) \\ 0.2k_2(\text{Li}_{y}\text{Mn}_2\text{O}_{4}) \end{array}$	$\begin{array}{c} 0.13D_2({\rm Li_xC_6}) \\ 0.21D_2({\rm PP}) \\ 0.2D_2({\rm Li_yMn_2O_4}) \end{array}$

Table 4.3: The description of exponent p, tortuosity τ_t and effective electrolyte transport properties for battery I and battery II respectively.



Figure 4.13: The temperature rise and cell utilization at the end of the discharge from the battery models with different particle size: (a) temperature rise; (b) cell utilization. The models are simulated with p values 3.3 and 2, respectively.



Figure 4.14: The temperature rise and cell utilization from the battery models with two battery thicknesses: (a) temperature rise; (b) cell utilization. The models are simulated with a Bruggeman exponent of p=3.3 and p=2.

Figure 4.14 compares the effect of the component thickness. With p=2, the battery with 1L thickness actually had a better utilization at high discharge rates compared to the 0.5L battery. The improved utilization of p=2 batteries is attributed to reduced concentration polarization, as shown in Figure 4.15. The gradient of Li⁺ in electrolyte in Figure 4.15(c) was much smaller as compared to that in the p=3.3 battery in Figure 4.15(a). The rate limiting factor for p=2 batteries was the Li depletion at the surface of the negative particles, as opposed to the Li⁺ depletion at the positive electrode/current collector interface for p=3.3 batteries.

The above case studies demonstrate the complexity in battery design. There are competing rate limiting mechanisms. Due to the close couplings among thermal, transport, and electrochemical processes, the controlling mechanism can switch from one to another depending upon the battery operating condition and battery design. The influence of one de-



Figure 4.15: Comparison of the Li⁺ concentration profiles of the 1R/0.5L and 1R/1L cells under a discharge rate of 3C for the p=2 battery and the p=3.3 battery respectively. (a) Li+ concentration in the electrolyte for the p=3.3 battery; (b) Li concentration at the surface of the active particles for the p=3.3 battery; (c) Li⁺ concentration in the electrolyte for the p=2 battery; (d) Li concentration at the surface of the active particles for the p=2 battery. (a) and (b) were made at DOD=0.706, when 1R/1L firstly reaches the cut-off voltage 3V; and (c) and (d) were made at DOD=0.908, when 1R/0.5L firstly reaches the cut-off voltage 3.0 V.

sign parameter, therefore, may be opposite under different conditions. This presents a great challenge to an experiment based design optimization. In this sense, mathematical and numerical models are advantageous. They are much more efficient in examining a wide variety of conditions and combinations and in identifying the underlying relationships and mechanisms. In Chapter 5, the "Thermal" sub-model was incorporated with the "Stress" sub-model [125] to form a framework for the stress investigation in the separator.

4.6 Summary

The "Thermal" sub-model in the multiphysics model computes the heat generation and temperature rise for a $\text{Li}_x\text{C}_6|\text{LiPF}_6(\text{EC/DMC})|\text{Li}_y\text{Mn}_2\text{O}_4$ cell. The model prediction on temperature rise was in good agreement with experimental results of a similar battery at 1C and 2C. The predicted heat generation rates were in good agreements with the experimental data available in literature in the range of 0.1 to 1C.

The influence of the temperature dependence of the variables on temperature rises varied with rates. Their importance was given in the following sequence: Li^+ diffusion coefficient in electrolyte, reaction rate constant in the positive particles, Li diffusion coefficient in the negative particles, ionic conductivity, reaction rate constant in the negative particles.

Among various heating sources, the overpotential at the electrochemical interface and the ohmic heat in electrolyte were the dominant sources. The magnitude of the heat generation rate and its undulation increased with the discharge rate. At discharge 6C, the heat generation rate had a range from 227 W L⁻¹ to 400 W L⁻¹.

The primary rate limiting mechanism was Li⁺ transport in the electrolyte. The thickness of battery components had a great impact on concentration polarization. The batteries with a thin component thickness had a lower temperature rise and better battery utilization. The second rate limiting mechanism was Li diffusion in the negative particles. Reducing the active particle size was most efficient in improving the cell utilization when this mechanism became dominant. The relationship between the particle size and cell utilization was not monotonic across the discharge rates. The cell with a smaller particle size in general exhibited a higher utilization but the cells with larger particle sizes had better utilization at certain intermedium rates. This behavior was related to the evolution of the Li⁺ concentration gradient with DOD.

Chapter 5

Stress in the Separator

In Li-ion batteries, stresses in the separator arise as the results of mechanical loading and constrains, intercalation induced deformation in the active materials in the electrodes, and thermal expansion mismatch between the battery components. This chapter focuses on the simulation results about the stress and strain in the separator by the multiphysics model including all three types of deformation. The Li-ion battery with the parameter 1R/0.5L was chosen to investigate. The simulation results revealed that the stress in the separator varied in phase with the battery cycles. Its state and magnitude depended upon the mechanical property of the separator, electrode particle size and packing of the cell. Moreover, in the separator, the thermal stress was comparable with the stress caused by intercalation deformation of the electrode particle. Considering thermal effect modified the stress curves in the separator but the results remained in the same order.

5.1 Numerical Experiments

To begin with, the prototype quarter-sized and half-sized 2D RVE "Stress" sub-models were built for the 1D battery $\text{LiC}_6|\text{PP}|\text{Li}_{y}\text{Mn}_2\text{O}_4$ battery in $\text{COMSOL}^{\textcircled{R}}[32]$. The original particle size and the component thickness are listed in Table 3.4. In its thickness direction, the electrode in the quarter-sized sub-model had a dimension that was equivalent to a quarter of the original electrode thickness. The thickness of the separator was about a half of that in Table 3.4. Keeping the same particle size, the resulted quarter-sized "Stress" sub-model had one layer of particles in the negative electrode and three layers of particles in the positive electrode. The construction of the half-sized RVE followed the same rule.

In the multi-scale model, some of the parameters in the 1D battery sub-models need to be modified with the change in battery dimension. Table 5.1 presents the battery component thickness of the multi-scale model with a quarter-sized and a half-sized 2D RVE "Stress" submodels. The initial DOD in the negative electrode and positive electrode is 0.75 and 0.2, respectively. All other parameters in the multi-scale model were kept the same as in Table 3.4 unless otherwise specified in the following text.

Parameter	Unit	"Stress" sub-model		
		Quarter-sized	Half-sized	
Negative active particle radius	μm	12.5	12.5	
Positive active particle radius	μm	8.5	8.5	
Negative electrode thickness	μm	25	50	
Positive electrode thickness	μm	51	85	
Separator thickness	μm	26	26	
Applied current density (2C rate)	Δm^{-2}	11.7	23.4	
(20 Iate)	лш			

Table 5.1: Parameters in the 1D "Battery" sub-model with the original battery size and in the multi-scale model with a quarter-sized or a half-sized 1D RVE "Stress" sub-model.

The numerical experiments for the stress in separator were conducted with a dischargecharge cycle with a discharge rate 2C. The cycle consists of a discharge (0 s - 1000 s), open circuit (1000 s - 1500 s), charge(1500 s - 2500 s), and another open circuit period (2500 s - 3000 s). Figure 5.1(a) plots the current density history for a 2C discharge-charge cycle for a half-sized cell. The history of cell voltage obtained by simulations using the 1D "Battery" sub-model is presented in Figure 5.1(b).



Figure 5.1: (a) A battery cycle for a 1R/0.5L unit cell at a 2C discharge and charge rate. The cycle consists of discharge (0 s-1000 s), open circuit period (1000 s-1500 s), charge(1500 s-2500 s), and open circuit period(2500 s-3000 s). (b) The cell voltage history for the discharge charge cycle.

5.2 Numerical Investigations

5.2.1 The Effect of Particle Packing

The initial numerical investigations were conducted with a prototype quarter-sized RVE sub-model. The particles in this RVE had two packing patterns. As shown in Figure 5.2, particles 2 and 4 are in contact with their neighbors. This packing pattern is referred as a close packed pattern thereafter. On the other hand, particles 1, 3 and 5 are separated from their neighbors by a space filled with electrolyte, which is referred as a loose-packed pattern in the following text.



Figure 5.2: The predicted through thickness strain distribution at the end of discharge (1000 s) under a fixed-free (10 psi) boundary condition using a quarter-sized 2D "Stress" sub-model. The areas with a void like appearance have a strain value beyond the range and hence are removed from the display. Particles 2 and 4 have a close-packed pattern whereas particles 1, 3 and 5 have a loose-packed pattern. The maximum strain in the separator is found near a loose-packed particle of larger diameter.

Numerical simulations revealed that the stress and strain fields in the separator were not uniform and varied in-phase with the discharge-charge cycle. For the discharge-charge cycle studied in this work, a stress and strain maxima occurred at the end of the discharge period at the surface in contact with the negative particles. At the side in contact with the positive particles, it happened at the end of charge. When other conditions were equal, the maximum strains and stresses were found near particles with a larger diameter.

Figure 5.2 displays the distribution of strain component along thickness direction at the end of discharge. In the "Stress" sub-model, the strain in the electrolyte phase was much higher as compared to that in other components. To ease the analysis of strain in the separator, in Figure 5.2, the range of the display scale is set to ± 0.05 and therefore, the areas with a higher strain have a void like appearance.

Figure 5.2 reveals that the strain in the separator is higher in the area adjacent to a particle with a loose-packed pattern. This is evident by comparing the strain distribution in the vicinity of particle 1 with that of particle 2. The same trend was observed for strain along in plane direction. It was suspected that this high stress might be due to the limitation of the prototype RVE model that a continuous mesh is employed, instead of a contact definition, between the particles and the separator.

FE models with a continuous mesh between components may be employed to study the stress behavior of a "Stress" sub-model with close-packed particles. With a sufficient number of particles, the central area of the "Stress" sub-model may reveal information about the stress and strain history in a battery cell. For this purpose, half-sized 2D "Stress" sub-models were investigated. The final "Stress" sub-model consisted of a total 76 particles, comprised of 16 negative particles and 60 positive particles. Further investigations were carried out with this RVE "Stress" sub-model.

The multiphysics model including the half sized 2D RVE "Stress" sub-model was employed to do further investigation. In order to compare the importance of intercalation stress with thermal stress in the separator, another two half-sized models, one considering the intercalation stress alone (labeled as intercalation only) and one considering the thermal stress alone (labeled as thermal only), were also involved in this work. All the material properties and boundary conditions were kept the same unless otherwise specified in the following text.

5.2.2 Concentration Change and Temperature Rise

In order to consider the strain caused by Li insertion/removal in a Li-ion battery, the Li concentration distribution in the electrode is calculated in the "Stress" sub-model. Figure 5.3 depicts the Li concentration distribution in the electrode particles. As shown, Li concentration varied along the through thickness direction in the electrodes. The regions near separator behaved larger concentration changes than those far away from the separator. It demonstrates that the reaction rate is initially highest at this location, as the solid phase electronic conductivity is higher than that of the electrolyte [48, 133]. In addition, there was larger concentration gradient in the negative electrode than in the positive electrode, as diffusion coefficient D_1 of the negative electrode is lower than that of the positive electrode.

Table 5.2 compares the Li concentration range from "Stress" and "Electrode" sub-models at different times. It demonstrated that the recalculated Li concentration from "Stress" submodel is at a similar level of that in "Electrode" sub-model. This recalculation is capable to obtain the actual Li concentration distribution in the active particles under the current 2C discharge-charge cycle.

The temperature rise in the Li-ion battery under the discharge-charge cycle was examined by the "Thermal" sub-model. The temperature rise in the cell during the discharge-charge



Figure 5.3: The Li concentration distribution in the negative and positive electrode at different times during discharge-charge cycle: (a) 0 s, (b) 500 s, (c) 1000 s, (d) 1500 s, (e) 2000 s, and (f) 2500 s.

	Electrode (mol m^{-3})	Stress (mol m^{-3})
$\rm Li_xC_6$ at 1000 s	5659-13628	4540-14029
$Li_yMn_2O_4$ at 1000 s	4540-13757	9440-14045
$\rm Li_{x}C_{6}$ at 2500 s	16957-23610	16364-25354
$Li_yMn_2O_4$ at 2500 s	4244-5526	3759-5912

Table 5.2: The comparison of Li concentration range in "Electrode" and "Stress" sub-models at the end of discharge (1000 s) and the end of charge (2500 s)

cycle at 2C is plotted in Figure 5.4. As shown, the temperature rise during discharge is about 8 °C and during charge is about 7 °C. The temperature rise decreased during the open circuit periods (1000 s-1500 s and 2500 s-3000 s), as there was no heat generated. For the entire discharge-charge cycle, the temperature rise is about 13 °C. This temperature profile obtained from the "Thermsl "sub-model was mapped to the "Stress"sub-model to calculate the thermal stress in the Li-ion battery.

5.2.3 Thickness Variation

The dimensional change in the thickness direction of the battery is a measurable parameter. To validate the model, the displacement in the thickness direction was investigated.

5.2.3.1 Particle Indentation

It was observed, upon applying a surface pressure, there was an immediate reduction in the cell thickness. This dimensional change was absorbed by the deformation of the separator.



Figure 5.4: The temperature rise history in the Li-ion battery during discharge-charge cycle: discharge (0 s-1000 s), open circuit period (1000 s-1500 s), charge(1500 s-2500 s), and open circuit period(2500 s-3000 s).

The amount of deformation depended upon the elastic modulus of the separator and the pressure at the surface of the cell. Figure 5.5 presents the displacement field of the RVE "Stress" sub-model at t = 0 s. The simulation was conducted with a separator under a pressures of 10 psi. At t = 0 s, the volume of the active particles remained the same. The deformation was, therefore, entirely due to the pressure. As seen in Figure 5.5, at the microscopic level, the deformation was not uniform in the separator. The areas in contact with the particles exhibited a larger deformation. Further evidence is provided by the displacement profiles obtained at the surfaces of the separator, as displayed in Figure 5.6.

The Li intercalation/deintercalation in the active particles and battery temperature rise result in the dimensional change of the battery cell and its components. By numerical



Figure 5.5: The through thickness displacement field at t = 0 s predicted by a half-sized 2D RVE "Stress" sub-model with close-packed particles. The black lines in the separator represent the position where the through thickness direction at the end of discharge was checked in Figure 5.6.

simulations, the information on displacement, stress and strain components for individual battery components at a specific location can be examined. This provides additional insights into the fundamental mechanisms of stress in the separator in a Li-ion battery.

Figure 5.6(a), (b) and (c) present the through thickness displacement in the separator at the end of discharge. The curves were plotted along a line which is in close proximity and parallel to the interface with the negative electrode and positive electrode, respectively. This clearly showed the indentation of particles into the separator. The periodical pattern in displacement curve corresponded to the periodical packing pattern of the electrode particles. The maximum displacement value appeared at the point where the particle is in contact with the separator.

In the separator, as there was no active particles for Li diffusion, the value of the displacement caused by Li intercalation from the place near negative electrode and positive electrode were similar in Figure 5.6(b). However, as shown in Figure 5.6(c), the value of the displacement caused by thermal expansion near the positive electrode was 0.04 μ m higher than that near the negative electrode, because the thermal expansion coefficient of the separator was 130 K⁻¹, which was much higher than the value of the other battery components. As a result, the difference of the displacement involving two factors near negative electrode and that near positive electrode, as shown in Figure 5.6(a), was mainly caused by thermal expansion of the separator.

The local indentation of particles at the surface of the separator had further implications. The particles in the current model have a spherical shape. If irregular shaped particles are employed, they may be pressed into the separator. Similar situations are when an irregular shaped foreign particle is landed at the surface of the separator during manufacturing or a dendrite forms at a particle surface near the separator. In these cases, a non-slipping



Figure 5.6: The indentations into the separators made by negative and positive electrode particles. (a) caused by both Li intercalation and thermal expansion; (b) caused by Li intercalation; (c) caused by thermal expansion.

interface may be created and a local tensile stress may arise.

5.2.3.2 Cell Thickness Variation

The variation of the cell thickness during the discharge-charge cycle was measured by the through thickness displacement at the midpoint of the right side of the cell. As shown, for the simulated case, the deformations due to intercalation only or thermal (thermal expansion) only were in the same order. As in the previous investigation [125], the intercalation induced deformation was cyclic. The maximum value of the deformation due to intercalation only was about 0.04 μ m in this work, about an order lower as compared to the previous results [125] of 0.4 μ m obtained under 1C rate. The deformation due to thermal expansion had the same shape as the temperature history curve. The total maximum deformation was 0.1 μ m over a cell thickness of 181 μ m.

The smaller thickness variation in the current simulation may be due to the viscoelastic relaxation of the separator and/or a higher particle volume fraction (lower porosity) in the positive electrode in the current simulation. To examine this effect, batteries with two different volume fractions in the positive electrode were compared. Table 5.3 lists the electrode porosity of two batteries. Battery 1 has the original electrode porosity as shown in Table 5.1, while Battery 2 presents higher porosity in positive electrode. The other material property and battery geometry were kept the same in both batteries. The results in Figure 5.8 showed that the difference between the two batteries was relatively small in the thermal deformation but large in the interaction deformation. An increase in particle volume fraction from 0.301 to 0.362 resulted in around 0.21 μ m thickness variation increment.

A further inspection revealed that the greater thickness change is from the positive electrode thickness change. Figure 5.9(a), (c) and (e) present the through thickness change at



Figure 5.7: The displacement-history plots at the right hand end of the cell. Battery 1 ($\varepsilon_{1,pos} = 0.362$) and Battery 2 ($\varepsilon_{1,pos} = 0.301$) were investigated.

Table 5.3: The volume fractions of active materials and liquid phase in Battery 1 and 2.

Matarial mean anta	Negative electrode		Positive electrode	
Material property	Battery 1	Battery 2	Battery 1	Battery 2
volume fraction of active materials ε_1	0.471	0.471	0.362	0.301
volume fraction of liquid phase (porosity) ε_2	0.357	0.357	0.444	0.505



Figure 5.8: The displacement-history plots at the right hand end of the cell. (a) the thickness caused by thermal expansion (b) the thickness caused by Li intercalation.

different times. The difference of thickness change in the positive electrode between Battery 1 and 2 increased with discharge time. The difference between the two batteries was negligible in the negative electrode.

The corresponding Li concentrations at the surface of the active particles at different times were also plotted in Figure 5.9(b), (d) and (f). In the Battery 2, the value at the positive electrode was higher than that of Battery 1. This concentration difference was increased with time. The higher surface concentration in the positive electrode would represent higher average Li concentration for the electrode with same properties and active particle size. As a result, the Li concentration difference Δc_1 in Battery 2 was larger than that in Battery 1. According to Equation 2.24, the large Li concentration difference induced the large strain caused by Li intercalation, and finally caused the large thickness change in the positive electrode of Battery 2.

The predicted maximum thickness variations for Battery 1 and Battery 2 was about



Figure 5.9: The through thickness displacement and corresponding Li particle surface concentration at different discharge times: (a) through thickness displacement, 360 s; (b) Li concentration, 360 s; (c) through thickness displacement, 720 s; (d) Li concentration, 720 s; (e) through thickness displacement, 1000 s; (f) Li concentration, 1000 s. The data was from the simulation that intercalation stress is considered alone.

0.060% and 0.18%, respectively. This value seems to be low as compared to the values obtained in an experimental study on $\text{LiC}_6|\text{LiPF}_6|\text{LiCoO}_2$ battery [81]. The reported thickness variation was 7.69 μ m when averaged for a cell using natural graphite and 2.29 μ m for using mesophase carbon micro beads (MCMB). The cell thickness was 171 μ m. This translates into a linear strain of 4.49% for nature graphite and 1.34% for MCMB respectively.

It should be noted that the thickness variation predicted by the current model is due to Li insertion/removal and thermal expansion. The volume expansion due to gas generation in the Li-ion batteries [82] will also result in volume change. The volume variation due to Li insertion/removal in cyclic, and that due to thermal expansion is mimic to the battery temperature rise curve; whereas the volume expansion due to gas generation increases gradually over time.

The smaller dimensional change of the battery cell in the present study can also be partially attributed to a better cell design. The maximum expansion of $LiCoO_2$ positive electrode is in the range of 1% [81] whereas the maximum volume change of $Li_yMn_2O_4$ positive electrode is 6.5%. Because the volume variation of the two electrodes is opposite in sign, it is the difference in volume change between the two electrodes, instead of the absolute expansion of one electrode, determines the volume variation of the battery cell. From this perspective, a $LiC_6|Li_yMn_2O_4$ battery would have a smaller net volume variation as compared to a $LiC_6|LiCoO_2$ battery. Furthermore, in the present "Stress" sub-model, Battery 1 with low porosity demonstrated a much lower thickness change than Battery 2. This result suggests that the dimensional change of the battery may be reduced by optimizing the electrode porosity in accordance with their volume expansion ratio. The stress analysis in the following text was based on Battery 1.

5.2.4 Strain and Stress in the Separator

The stress state and its magnitude were found to vary greatly across the cell in both temporal and spatial senses. As an example, Figure 5.10 presents the profiles of stress and strain in the thickness direction at the end of discharge (t = 1000 s) across the cell thickness alone a line here the separator is in contact with electrode particles at both side. As seen, there are periodical hills and valleys in the profiles corresponding to the periodical location of the particles. At 1000 s, the discharge had just stopped, and a Li concentration gradient still existed in the particles. For the negative particles, the surface Li concentration was lower than at the center. This resulted in a strain gradient in the particle. The stress gradient was opposite in sign with the strain gradient. A maximum compressive intercalation stress of 44 MPa was found at the center of the negative particles. The trend was opposite in the positive particles. The center of the positive particle had a lower Li concentration than its surface and the intercalation stress was therefore intensive.

The value of the strain and stress caused by Li diffusion and that caused by thermal extension in different battery components was also examined in Figure 5.10. In the electrode particles, both the stress and strain caused by Li diffusion were about two orders higher than the stress or strain caused by thermal extension. However, in the separator, the two kinds of stress were comparable. They were around several mega pascals. The strain caused by thermal extension was around 0.2%, which was higher than that caused by Li diffusion.

Figure 5.11 presents the distributions of the normal stresses and the shear stress in the separator at t = 1000 s under a pressure of 10 psi. High compressive stresses can be seen in the area in contact with the particles. The stress was higher at the side with larger diameter of particles. As above-mentioned, due to difficulty with the contact modeling, a continuous



Figure 5.10: The through thickness stress and strain across the RVE "Stress" sub-model at the end of discharge.

mesh has been used between the particles and separator. The results only represent the condition where the particle roughness created a nonslip condition in the local area.

When subjected to load, a material may yield due to shear stress or rupture due to high tensile stress depending upon the stress state in the material, the available deformation mechanisms in the material and other factors. Under 3D stress, the commonly used criteria are the maximum distortion energy theory (i.e. Von Mises theory, Equation 5.1) and the maximum principal stress theory (i.e. the theory of maximum tensile stress, Equation 5.2, the Mohr and modified Mohrs theories etc.), respectively [134].

$$\sigma_{VM} = \sqrt{\frac{(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2)}{2}} = \sigma_Y \tag{5.1}$$



Figure 5.11: Stress components in the separator in the cell at the end of discharge. (a) σ_x ; (b) σ_y ; (c) σ_{xy} .

$$\operatorname{Maximum}(\sigma_1, \sigma_2, \sigma_3) = S_t \tag{5.2}$$

where σ_1 , σ_2 , σ_3 represent first, second and third principal stress, respectively; σ_{VM} is the Von Mises stress; σ_Y is the yield stress; and S_t is the maximum tensile stress.

The variation of the stress during the discharge-charge cycles at a location of high stress near a negative active particle and a positive active particle was inspected. Figure 5.12 presents a summary of stress history plots for the principal stresses and the Von Mises stress. The left and right columns in Figure 5.12 present the stresses from the place near the negative electrode particles ans positive electrode particles, respectively. Figure 5.12 shows that the three principal stresses in the separator were in the negative range, i.e. under compression, regardless it was near a negative or a positive particle. This result is consistent with previous study [125]. The maximum Von Mises was 3.6 MPa, found at the side of positive electrode. This value was lower than the measured strength of a value greater than 10 MPa for the separator at 25 $^{\circ}$ C with the presence of electrolyte solutions [110]. The above results indicate that under a normal operation condition with a closely packed particle bed, the stress level in the separator is far from in danger of immediately yield or rupture in the center of the cell.

Figure 5.12 also compares the stresses computed with intercalation only, thermal only, and when both factors were in effect. Unlike the cell thickness variation where the two effects were cumulative (Figure 5.7), the effect of two factors on stress was not a simple summation of the two individual cases. Considering thermal effect modified the previously observed interaction induced stress but the results remain in the same order.

The results in Figure 5.12 were obtained with the consideration of thermal-viscoelastic relaxation of the separator. Neglecting this effect, the estimated stress would be much higher [125]. The effect of the constitutive relationship on the stress was investigated in Figure 5.13. Simulations were carried out with three types of constitutive behaviors for the separator: linear elastic(E(const), Young's modulus of E = 496 MPa, which is the stress relaxation modulus at the beginning time), viscoelastic without temperature dependence (E(t), Figure 3.11), and thermal-viscoelastic (E(t, T), Equations 3.21 and 3.22). The thermal effect was considered in all three cases in the other three sub-models. It was found that the stress values were at least twice higher when the separator was modeled as linear elastic as compared to the two viscoelastic cases. Moreover, the thermal effect on the stress relaxation barely reduced



Figure 5.12: The history plots of the principal stresses and the Von Mises stress in the separator near the negative and positive electrode particles. (a) (c) (e) and (g): near negative electrode; (b) (d) (f) and (h): near positive electrode.



Figure 5.12: (cont'd)

the amplitude of the cyclic stress.

5.2.5 The Effect of Discharge Rate

For individual particles, increasing the charge/discharge rate would result in a greater Li concentration gradient in the particle and therefore higher stresses. The effect of charge rate on stresses in the separator is not as unambiguous. The stress in the separator in a Li-ion battery cell is the results of mechanical loading and constrains, intercalation induced deformation in the active materials in the electrodes, and thermal expansion mismatch between the battery components. The value also depends upon the viscoelastic relaxation of the separator itself.

Table 5.4: The range of Li concentration in sub-models at DOD = 0.3 at different discharge rates.

Discharge Rate	Electrode (mol m^{-3})	Stress (mol m^{-3})
2C	7710 - 17721	6604 - 18134
4C	5903 - 19084	2142 - 19325
$6\mathrm{C}$	4636 - 19568	0 - 19683

To investigate the effect of charge/discharge rate on stress in the separator, simulations were carried out for discharge at 4C and 6C rates. As mentioned before, the Li concentration


Figure 5.13: The history plots of the principal stresses and the Von Mises stress in the separator near the negative and positive electrode particles. (a) 1st principal stress; (b) 2nd principal stress; (c) 3rd principal stress; (d) Von Mises stress. Three different mechanical properties of separator are considered: constant linear elasticity (E(const)); time dependent viscoelasticity (E(t)); and time and temperature dependent viscoelasticity (E(t,T)).

distribution in the active particles in "Stress" sub-model should be at a similar level of that in the "Electrode" sub-model. However, it was observed that the discrepancy between the two sub-models increased at higher rates. An example is shown for the depth of discharge (DOD) = 0.3 in Table 5.4. The "Stress" sub-model tends to have a large concentration gradient as compared to that in the "Electrode" sub-model. Moreover, the discrepancy also increased with the DOD under the discharge/charge rate. This is caused by the difference in the volume fraction of the active particles in the two sub-models. To have a consistent representation of the micro structure in "Stress" sub-model requires a micro-structural resolved model, which was described in Chapter 6. A qualitative discussion is given at here based on the observation of the trend with the results of 2C and 4C from DOD = 0 to DOD = 0.7. When DOD was higher than 0.7, the concentration in "Stress" sub-model was not at the same level of that in "Electrode" sub-model.

Figures 5.14 and 5.15 compare the temperature rise and the cell thickness variation for discharge at 2C and 4C. A higher discharge rate resulted in a higher temperature rise in the cell. At DOD = 0.7, the temperature rise was 9.6 °C and 18 °C for 2C and 4C, respectively. The higher cell temperature resulted in a larger change in the cell thickness. As shown in Figure 5.15, the value increased about 50% at the rate of 4C.

The changes in stress values, however, were relatively small as shown in Figure 5.16. This may be attributed to the combined effect of a higher rate. At one hand, it reduces the time for relaxation. On the other hand, a higher temperature rise at higher rates accelerates the relaxation process. In summary, a higher discharge rate did not lead to a substantial increase in stress in the separator.

The stress in the separator with the different cell voltage range was also examined by Figure 5.17. When DOD = 0.7, the cell voltage decreased to 3.64 V and 3.54 V under



Figure 5.14: The temperature rise Vs. DOD under discharge rate 2C and 4C. The DOD range is 0 to 0.7.



Figure 5.15: The comparison of the thickness variations for the half-sized cell under discharge rate 2C and 4C. The DOD range is 0 to 0.7.



Figure 5.16: The evolution of the stress components in the separator near the negative particles under different discharge rate: 2C and 4C: (a) the first principal stress; (b) second principal stress; (a) third principal stress and (d): Von Mises stress. The DOD range is from 0 to 0.7.

discharge rate 2C and 4C, respectively, as shown in Figure 5.17. There was no obvious stress value change shown in Figure 5.17 when the cell voltage boundary was decreased to 3.54V under 4C.



Figure 5.17: The cell voltage for the half-sized cell under discharge rate 2C and 4C. The DOD range is 0 to 0.7.

5.2.6 Anisotropy

The polymeric separator Celgard 2400 considered in this work has anisotropic mechanical properties. A typical SEM image of Celgard 2400 is presented at Figure 3.10 in Chapter 3 [9]. The material displays a higher stiffness and strength along MD than TD. The separator in the "Stress" sub-model is in a plane consisting of MD and the through thickness direction. Limited by the isotropic viscoelastic material model in $\text{COMSOL}^{\textcircled{R}}$ the separator was modeled in this work as an isotropic material with properties measured with MD specimens tested in DMC.

When tested in air, separator exhibits strong anisotropy between MD and TD. Nevertheless, the difference in mechanical properties between the two directions diminishes when tested in electrolyte solution [110]. The ratio of the elastic modulus between TD and MD in 1.1M LiPF6 EC/DMC is about 0.88. The ratio is 0.51 when tested in air. The mechanical properties in the through thickness direction is not available currently. A close inspection of Celgard 2400 suggests that the microstructure in through thickness direction has some similarity as in TD. Therefore, it is reasonable to assume Celgard 2400 as a transverse isotropic solid, i.e., the property in the through thickness is the same as TD. Based on the above information, the error induced by using an isotropic model is limited.

5.3 Summary

A multi-scale modeling approach for the stress analysis of the separator in a basic Li-ion battery cell has been proposed. The stress analysis at the level of a battery cell was conducted with a meso-scale RVE "Stress" sub-model of a basic cell. Currently, the model parameters are available for a $Li_xC_6|LiPF_6|Li_yMn_2O_4$ cell. It is applicable for other insertion batteries.

The Simulation results provided new insights into the deformation of battery components caused by Li insertion/removal in a charge and discharge cycle. It was observed that the net cyclic dimensional variation of the battery cell was determined by the difference of the volume change of the two electrodes and this amount may be regulated by optimizing the porosity of the two electrodes. For the $\text{LiC}_6|\text{LiPF}_6|\text{Li}_{y}\text{Mn}_2\text{O}_4$ battery cell analyzed, the maximum thickness variation caused by Li insertion/removal with different electrode porosities was about 0.2% and 0.05% respectively under a pressure of 10 psi.

The multiphysics model was used to analyze the stress in the separator. Simulations were also conducted to investigate the influences of interaction and thermal phenomena and their coupling, and the types of constitutive relationship of the separators on the stress. The results showed that effects of interaction and thermal are not simple summation and hence must be considered concurrently. With an elastic behavior for the separator, the stresses in the separator were about twice of those with a viscoelastic constitutive behavior.

The results indicate that under normal operation conditions the stress level in the separator is far from in danger of immediately yield or rupture in the center of the cell. It should be noted that due to the difficulty in solving contact problems in $\text{COMSOL}^{\textcircled{R}}$, a continuous mesh has been used between the particles and the separator. The results only represented the condition where the particle roughness had created a nonslip condition in the local area in a battery with a closely packed particle bed.

Chapter 6

Model Extension

The multiphysics model described in previous chapters is based on a 1D battery model. It is sufficient when the effect of the microstructure of the electrodes on the battery performance is negligible. To consider the influence of microstructure, and particularly its evolution with battery cycles, a 2D microstructure resolved model is desired. This chapter presents the development and validation of a 2D microstructure resolved multiphysic model for a Li-ion battery cell. The model is then used in the investigation of stresses in the active particles and binders.

6.1 The Needs of a Microstructural Resolved Model

In the previous chapters, a multiphysics model for a Li-ion battery cell has been developed. The model considered species and charge transport in electrodes, battery kinetics, heat generation and heat transfer, intercalation and thermal induced stress as well as mechanical stress. These phenomena were described with four sub-models that were coupled together. The species and charge transport, battery kinetics, and Li diffusion in active particles were described using the 1D battery model developed by Newman's group [32, 48, 137], which considers an averaged active particle size and porosity in the electrode. The intercalation, thermal and mechanical stresses within and between battery components were analyzed using a 2D RVE model with idealized microstructure. Within a certain range, the Li concentration profiles were similar between the 1D "Battery" sub-model and "Stress" sub-model. However, it was difficult to maintain the consistency between the two sub-models. Furthermore, the model cannot consider the effect of real microstructure and their evolution during battery cycle on the battery performance.

Figure 6.1 shows the cross-section of a graphite electrode of a commercial battery. As illustrated, the microstructure of the electrodes is far from uniform. Particles are different shapes and sizes, as are the pores. The variation in local microstructures will influence the species transport and therefore the local current density. The volume change of the active particles with charge and discharge may also result in a change in local tortuosity. This effect would be substantial in electrodes with high capacity materials. To consider the influence of microstructure, particularly its evolution with battery cycles, it is desirable to have a microstructural resolved model.

The need for a microstructure resolved model has been discussed by different groups. Wang and Sastry [36] have developed the 3D microstructure resolved model constructed on the porous cathode in Li $|PEO_2 - LiClO_4|LiMn_2O_4$ half cell. The modified Nernst-Planck equation [48, 139] was involved to describe the mass transfer and ionic charge balance in the electrolyte. Simulations with regular and random particle arrays and different particle size revealed that the electrode microstructure was critical to battery performance. Graham et al. [140] employed the 3D particle resolved model of Li-ion batteries with regular particle arrays to evaluate the approximations and to assist in the estimation of empirical Bruggeman exponents in Newman's 1D model. However, in the above works, the active materials were treated as spherical particles. The irregular particle geometry was ignored.

In order to consider a more realistic electrode geometry, the 2D microstructure resolved model developed by Smith et al. [37] was constructed based on the cross-section SEM image



Figure 6.1: (a) The cross-section image of a typical LiC_6 -LiCoO₂ rechargeable Li-ion battery [37]. The upper, middle and bottom layer correspond to the graphite negative electrode, polymeric separator and LiCoO_2 positive electrode, respectively. (b) An individual slice from a 3D X-ray tomography of graphite electrode [138].

of $\text{LiC}_6|\text{LiCoO}_2$. The investigation revealed that the Li diffusion in the active particles is affected by particle size, morphology, packing and surface roughness. Moreover, Less et al. [141] built the 3D microstructure resolved model based on the FIB-SEM micrography of the electrode. The result showed the battery performance can be optimized by varying the geometric parameters of the electrodes.

To date, the microstructure resolved model has been employed to investigate the effect of microstructure on the battery performance. However, the microstructure effect on the stress in battery components has not been examined. The stress state and magnitude at the local level may change largely depending on the electrode microstructure. In this work, the 2D microstructure resolved model was developed to study the mechanical phenomenon of the active particles and binders in the electrodes of a basic $\text{Li}_x \text{C}_6 |\text{PP}| \text{Li}_y \text{Mn}_2 \text{O}_4$ cell. This model was constructed based on the realistic electrode geometry. By using this model, the effect of complex electrode geometry on the mechanical phenomenon of the battery was investigated.

6.2 Model Depiction

In this work, a 2D microstructure resolved model is built within the framework $COMSOL^{\textcircled{R}}$ multiphysics. Figure 6.2 depicts the structure of the model. The entire microstructure resolved model consists of two sub-models: a "Electrochemical" sub-model and a "Stress" sub-model. The "Electrochemical" sub-model computes the spices and charge transport, as well as electrochemical reaction. The "Stress" sub-model computes the intercalation induced strain, the mechanical strain and the stress. At this stage, the heat generation and thermal effect is not considered.

6.2.1 "Electrochemical" Sub-model

The battery kinetics, mass transfer and electronic balance are described in the "Electrochemcial" sub-model. Figures 6.3 and 6.4 illustrate the governing equations and boundary conditions, respectively.

6.2.1.1 Active Electrode Particles

The governing equations for Li diffusion and charge balance in the active particles in the "Electrochemical" sub-model are the same as those used in Newman's 1D "Battery "model. The Li diffusion in the solid particles follows Fick's second law. The charge balance in the



Figure 6.2: The schematic of the 2D microstructure resolved model.



Figure 6.3: A schematic diagram of part of the Li-ion battery (one current collector, one electrode and the separator) with the governing equations.



Figure 6.4: The boundary equations for the Electrochemical sub-model.

solid particles obeys Ohm's law, as shown in Equation 2.9.

The Li ion flux N_0 and local current density j_n are applied at the particle boundary. The Bulter-Volmer equation is used to describe the relationship among the local electrochemical reaction, concentration, and potential:

$$j_n = k_0 \sqrt{c_2 \left(c_{1,\max} - c_{1,surf} \right) c_{1,surf}} \left[\exp\left(\frac{\eta \alpha_n F}{RT}\right) - \exp\left(\frac{(-\eta)\alpha_p F}{RT}\right) \right]$$
(6.1)

The Li ion flux has a linear relationship with the local current density j_n , as shown in Equation 2.8.

6.2.1.2 Electrolyte

The Nernst-Planck equations are used to describe the Li⁺ diffusion and charge balance in the liquid phase[36, 137].

Based on the concentrated solution theory [137], the flux of binary ionic species is described by:

$$N_{+} = \left[-\left(1 - \frac{d\ln c_{0}}{d\ln c}\right) D_{2} \right] \nabla c + \frac{i_{2}t_{+}}{z_{+}F} + c_{+}v_{0} = -D_{2}\nabla c + \frac{i_{2}t_{+}}{z_{+}F} + c_{+}v_{0}$$
(6.2)

$$N_{-} = \left[-\left(1 - \frac{d\ln c_0}{d\ln c}\right) D_2 \right] \nabla c + \frac{i_2 t_{-}}{z_{-}F} + c_{-} v_0 = -D_2 \nabla c + \frac{i_2 t_{-}}{z_{-}F} + c_{-} v_0 \tag{6.3}$$

where N_+ and N_- are the negative and positive ion molar fluxes, respectively; t_+ and $t_$ are the transport number of cations and anions into which a molecule of electrolyte LiPF₆ dissociates, respectively; z_+ and z_- are the charge number of the positive and negative ions, respectively; c_+ and c_- are positive and negative ion concentration, respectively; and v_0 is the solvent velocity. The magnitude of the $d \ln c_0$ is zero if the initial Li⁺ concentration is constant. The value of v_0 usually is assumed as 0. Therefore, equations 6.2 and 6.3 are reduced to:

$$N_{+} = -D_2 \nabla c + \frac{i_2 t_{+}}{z_{+} F} \tag{6.4}$$

$$N_{-} = -D_2 \nabla c + \frac{i_2 t_{-}}{z_{-} F} \tag{6.5}$$

The electroneutrlity requires:

$$\sum_{i} z_i c_i = 0 \tag{6.6}$$

For the lithium salt, the charge number $z_{+} = 1$ and $z_{-} = -1$. Therefore, Equation 6.6 is changed to:

$$c_{+} = c_{-} \tag{6.7}$$

The current density can be expressed as:

$$\mathbf{i}_2 = -k_2 \nabla \phi_2 + k_2 \frac{2RT}{cF} \left(1 + \frac{d\ln f_{\pm}}{d\ln c} \right) \left(1 - t_{\pm} \right) \nabla c \tag{6.8}$$

Substituting i_2 with Equation 6.8, equations 6.4 and 6.5 become:

$$N_{+} = (-D_{2} + \frac{2k_{2}t_{+}t_{-}RT}{c_{+}z_{+}F^{2}})(1 + \frac{d\ln f_{\pm}}{d\ln c})\nabla c_{+} - \frac{k_{2}t_{+}}{z_{+}F}\nabla\phi_{2}$$
(6.9)

$$N_{-} = (-D_2 + \frac{2k_2t_-2RT}{c_-z_-F^2})(1 + \frac{d\ln f_{\pm}}{d\ln c})\nabla c_- - \frac{k_2t_-}{z_-F}\nabla\phi_2$$
(6.10)

Because the charged mobile species in the electrolyte cannot diffuse into the current collectors, the fluxes of the two charged mobile species are set as zero at the interface of the electrolyte and the current collectors, as shown in Figure 6.4. Finally, the periodic boundary conditions are applied at the upper and lower boundaries.

6.2.1.3 Separator

The separator is treated as a homogeneous matrix, as the microstructure of the separator is not explicitly modeled. Its porosity is considered through effective properties for diffusion coefficient D_2 and ionic conductivity k_2 in the Nernst-Planck equations 6.9 and 6.10. The relationships of $D_{2,eff}$, $k_{2,eff}$ and D_2 , k_2 are explained in equations 2.5 and 2.6.

6.2.1.4 Binder

In the model, the conductive binders are depicted as a continuous thin layer over the particle surface. The electrical charge balance in the binder obeys Ohm's law as Equation 2.9. On the other hand, the Nernst-Planck equation is extended over the domain occupied by binder. In other words, binder is modeled as being conductive for electronic and ionic charge.

6.2.1.5 Current Collector

The electrons are the only mobile charge carrier in the current collectors. Equation 2.9 is employed to determine the rate of electron transfer in the current collectors.

The voltage is set to zero at the left side of the left current collector in the battery. The constant current density is applied at the right side of the right current collector. The model simulates a galvanostatic condition.

6.2.1.6 Model Implementation

The current balance in the active particles, binders and current collectors was solved by the Electric Currents Interface in COMSOL $4.2^{\textcircled{R}}$; the diffusion in the active particles was solved by the Transport of Diluted Species Interface; the current balance and mass transport in the electrolyte were solved by the Nernst-Planck Equations Interface.

6.2.2 "Stress"Sub-model

The "Stress" sub-model computes the stress and deformation in the active particles and conductive binders. As described in Equation 2.34, the total strain is the summation of diffusion-induced eigenstrain, thermal strain and the mechanical strain in the elastic battery material. The Li concentration computed by the Electrochemical sub-model is used as input to solve for diffusion-induced strain. The thermal strain is neglected at this stage.

The boundary conditions are depicted in Figure 3.3. They are the same as those for the "Stress" sub-model in the multiphysics model in Section 3.1.3.



Figure 6.5: The boundary conditions for stress analysis.

The stress and deformation was solved by the Solid Mechanics (plane strain) interface from $\text{COMSOL}^{\textcircled{R}}4.2$.

6.3 Material Properties and Battery Parameters

6.3.1 Conductive Binder

The electric conductive performance of the binder in the electrode is controlled by binderparticle interaction [143], the ratio of conductive additive, and even the battery temperature. The electrical conductivity value of 400 S m⁻¹ is typical for PVDF material [143], which is adopted in this work.

The mechanical properties of the different binder types vary widely with temperature, additives, or the preparation method [149–153]. Figure 6.6 presents the stress strain curves of PVDF-HFP materials reproduced from literature data [150–152]. As seen, the response of the materials varies greatly from very flexible to have a moderate stiffness. In general, the material is capable of large deformation with the exception of the grade with 5% Chitin.



Figure 6.6: The strain-stress curves for P(VDF-HFP) materials [150–152].

In order to comprehensively investigate the stress in the binder, two types of the PVDF-HFP were selected: PVDF-HFP(FC1278) [152], a lower modulus material with E = 1.1MPa; and PVDF-HFP-LiClO₄ [150], a higher modulus material with a Young's modulus of E = 184 MPa.

The Prony series was employed to describe the viscoelastic behavior of PVDF-HFP (FC1278) [152], which was labeled in Figure 6.6 by green color. By fitting the stress re-

laxation curves calculated from the four element linear model for PVDF-HFP (FC1278) [152], the Prony series parameters were determined, as shown in Table 6.1.

i	Stress relaxation constant (Pa)	Relaxation time (s)
	$E_{\infty} = 0.52 \times 10^6$	
1	$E_1 = 0.045 \times 10^6$	$\tau = 100$
2	$E_2 = 0.89 \times 10^6$	$\tau = 700$
3	$E_3 = 0.0025 \times 10^6$	$\tau = 1500$
4	$E_4 = 0.088 \times 10^6$	$\tau = 3000$
5	$E_5 = 0.000207 \times 10^6$	$\tau = 8000$

Table 6.1: Prony series parameters for the stress relaxation modulus of PVDF-HFP (FC1278).

Figure 6.7 depicts the comparison of the simulated stress strain curve of the binder by the stress relaxation modulus in Table 6.1 and the experimental cyclic stress strain curve [152]. The cyclic stress strain curve was measured by a strain rate of 1% per minute. The simulated curve showed good agreement with the original stress strain curve.

Figure 6.8 presents the stress strain curve of the PVDF-HFP-LiClO₄. The material has an elastic modulus of 184MPa, a yield stress of 9.2 MPa and an ultimate tensile strength of 13.4 MPa. PVDF-HFP-LiClO₄ binder was described using a piece-wise linear plasticity



Figure 6.7: The comparison of the cyclic stress strain curves from simulation and experiment for PVDF-HFP (FC1278) [152].

law, as shown in Figure 6.8.

6.3.2 Other Battery Components

The mechanical properties of the other battery components are identical to those presented in the Chapter 3, as shown in tables 3.5, 3.6 and 3.7. In particular, the time dependent viscoelastic behavior of the separator is considered as expressed in Table 3.3. The temperature effect on the viscoelastic behavior is not involved.

Table 6.2 collects the other battery parameter used in the microstructure resolved model. For consistency, most battery parameters, such as the battery thickness and the active particle electrical conductivity are identical to the values in Table 3.4. The volume fraction of the conductive binder is 0.080 and 0.071 in the negative electrode and positive electrode,



Figure 6.8: The stress strain curve of the PVDF-HFP-LiClO₄[150]

respectively. Because the microstructure resolved geometry shown in the Figure 6.2 already reflects the electrode porosity and tortuosity, the Bruggeman relationship and exponent p are no longer needed in the electrode domain.

The temperature dependence of the physical properties is not considered in the current model. The values of OCP of the graphite and LiMn_2O_4 , the ionic conductivity k_2 and the diffusion coefficient D_2 of Li in the electrolyte, etc., are those at 25 °C.

6.4 Numerical Experiment

Figure 6.9 shows the FE mesh for the 2D microstructure resolved model. It includes 299996 triangular elements, and 2426258 degrees of freedom.

The solution was obtained using the "Direct (UMFPACK)" time dependent solver with

Quantity	Negative electrode	Positive electrode	Separator	Electrolyte	Cu foil	Al foil
$\frac{\text{Thickness}}{\frac{1}{2}L \ (\mu \text{ m})}$	50	87	26	/	10^{b}	10^{b}
Initial concentration $c_{ini} \pmod{\mathrm{m}^{-3}}$	14870^{b}	3900 ^b	/	1000^{b}	/	/
$\begin{array}{c} \text{Maximum concentration} \\ c_{max} \ (\text{mol m}^{-3}) \end{array}$	26390^{a}	22860^{a}	/	/	/	/
Volume fraction of active particles ε_a	0.520^{b}	0.430^{b}	/	/	/	/
Volume fraction of conductive binder ε_c	0.080^{b}	0.071^{b}	0.46^{C}	/	/	/
Electrical conductivity of solid phase k_1 (S m ⁻¹)	100^{a}	3.8^a	/	/	/	/

Table 6.2: Critical battery parameters used in the half-sized 2D microstructure resolved model.

a: Ref. [32]

b: estimated or assumed value.

c: Ref. [133]

a relative tolerance of 0.0001 and an absolute tolerance of 0.001 for all variables.

6.5 Model Validation

The "Electrochemical" sub-model in 2D microstructure resolved model was validated by comparing the simulated data with the experimental data from the same battery system. For comparison, simulations were also carried out using Newman's 1D battery model. Doyle et al. [32] measured the cell voltage of the a $\text{Li}_{x}\text{C}_{6}|\text{PP}|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ battery system, with the polymeric electrolyte 2M LiPF₆ in EC/DMC (the volume ratio 2:1) with the polymeric matrix PVDF-HFP. This experiment was simulated by the 2D microstructure resolved model with the same battery system and geometry parameters. Figures 6.10 (a) and (b) show the



Figure 6.9: The mesh for the geometry of the 2D microstructure resolved model. Sections (a) and (b) correspond to the zoomed-in regions. (a): mesh in the negative electrode; (b): mesh in the positive electrode.

cell voltage comparison at discharge rate 0.5C and 1C, respectively. Good agreement was obtained at both 0.5C and 1C.

The result from 2D microstructure resolved model had better agreement with the experiment result than that from 1D battery model at 1C. Whereas the 1D battery utilized uniform spherical shapes for the active particles, the 2D microstructure model employed realistic microstructure geometry, which has various particle shapes and sizes. A recent study revealed that the battery performance is affected by the battery microstructure [37]. During the discharge process, the graphite particles of smaller than average size, and of complex morphology induce the localized lithium depletion, which leads to an increase in the polarization losses of the anode [37]. As a result, the 2D microstructured resolved model predicts a lower cell voltage than the 1D Battery model, in which the active material is assumed as



Figure 6.10: The comparison of the predicted cell voltage with the experimental results [32]: (a) 0.5C; (b) 1C.

spherical particles of the same size.

6.6 Results and Discussion

The validated model was used to investigate the stress in the binder and active particles in the Li-ion battery. The numerical experiments for the stress in the binder were conducted with a discharge-charge cycle with a rate 2C, which equates to an input current density 19.2 A m⁻². The cycle consists of a discharge (0 s - 1000 s), open circuit (1000 s - 1500 s), charge (1500 s - 2500 s) and another open circuit period (2500 s - 3000 s). Two types of PVDF were selected for investigation: PVDF-HFP(FC1278) [152], a lower modulus material with E = 1.1 MPa; and PVDF-HFP-LiClO₄ [150], a higher modulus material with a Young's modulus of E = 184 MPa.

6.6.1 Concentration Change

Figure 6.11 summarizes the Li distribution in negative and positive electrodes at multiple points in time during the discharge and charge periods. Specifically, the points in time are 0, 500, and 1000 seconds (corresponding to the discharge) and 1500, 2000, and 2500 seconds (corresponding to the charge). The simulation result showed that the concentration distribution in the negative electrode was larger than that in the positive electrode. This was attributed to the smaller Li diffusion coefficient and larger particle size in the negative electrode.

As shown in Figure 6.11, the mass transport in the smaller particles (i.e., region β) was faster than that in the larger particles (i.e., region α). Furthermore, the particles with complex morphology (i.e., region γ) also showed faster Li diffusion. This effect of particle size and morphology on the Li diffusion was also reported by Smith et al. [37]. In the same electrode, the particles with small size or complex morphology result in a large surface area per volume, enabling faster mass transfer rates [37]. The local Li diffusion was enhanced in those edges and corners.



Figure 6.11: The Li concentration distribution in the negative and positive electrode at different times during discharge-charge cycle: (a) 0 s; (b) 500 s; (c) 1000 s; (d) 1500 s; (e) 2000 s; and (f) 2500 s. The unit for concentration in the graph is molm⁻³.

6.6.2 Stress in the Electrode

6.6.2.1 Stress in the Active Particles

The stress distributions in the active particles of negative and positive electrodes at different time frames are plotted in Figure 6.12 and Figure 6.13, respectively. The particles were surrounded by polymeric binders with low modulus. As seen, in the negative electrode, the stress value at the particle boundary was higher than that at the particle center during discharge, while conversely the stress at the boundary was lower than that at the particle center during charge. The trend was opposite in the positive particles. This observation was consistent with the result in Chapter 5. Furthermore, the high tensile stress was predicted at the particle boundary and particle center in both electrodes. The stress value of a sharp corner at the particle boundary may be even higher than that at the particle center.

The variation of the stress during discharge-charge cycles at the particle center (location (2) in Figure 6.12 and location (3) in Figure 6.13) and the sharp corner with the high stress (location (1) in Figure 6.12 and location (4) in Figure 6.13) was inspected in Figure 6.14. As shown, the maximum stress value in the negative electrode was much higher than that in the positive electrode. There are several factors resulting in the lower stress value in the positive electrode active particles. According to the analytical solution [18], the radial or tangential stress was proportional to the particle mechanical property, Li diffusion coefficient, partial volume ratio, particle size and local current density :

$$\sigma_{(r,or\theta)} \propto \frac{j_0 R E \Omega}{3F D(1-\nu)} \tag{6.11}$$



Figure 6.12: The first principal stress distribution in the negative electrode at different times during discharge-charge cycle: (a) 0 s; (b) 500 s; (c) 1000 s; (d) 1500 s; (e) 2000 s; and (f) 2500 s. The unit for stress in the graph is Pa.



Figure 6.13: The first principal stress distribution in the positive electrode at different times during discharge-charge cycle: (a) 0 s; (b) 500 s; (c) 1000 s; (d) 1500 s; (e) 2000 s; and (f) 2500 s. The unit for stress in the graph is Pa.

In this work, the average positive electrode particle size was 8.26 μ m, which was 0.6 time of the negative particle size. Moreover, the negative electrode surface area was about one sixth of the positive electrode surface area. As a result, the average local current density in the negative electrode was about 6 times of that in the positive electrode. This large average local current density was one of the critical reasons for the higher stress in the negative particle.

The maximum tensile stress was found at the sharp corner of the negative particle boundary at the end of discharge. The value of the first principal stress at location (1) was 470 MPa at 1000 s (the end of discharge), which was 4 times of the maximum stress value found in the negative particle center at 2500 s (the end of charge). In the positive active particles, the maximum stress value at the particle boundary was close to that at the particle center.

In order to reflect the effect of the sharp corner on the stress value, the stress history of a smooth surface point at the particle boundary was plotted at Figure 6.15. For a given particle, the points located at the small radius boundary and the large radius boundary were examined. The maximum first principal stress value of a smooth surface point at the negative particle boundary was approximately 200 MPa, which was less than one half of that at the sharp corner.

The maximum value of Von Mises stress in the smooth surface boundary points of positive electrode particles (location (7) and (8)) was around 85 MPa. It is higher than that in the sharp corner (location (4)). In contrast to the shape of the particle at location (4), the particles located at location (7) and (8) were long and narrow. This indicates that the Von Mises stress at the positive electrode particle was not highly affected by the sharp corner, but by the particle shape itself. The sharp corner effect was more obvious in the large active



Figure 6.14: The evolution of the stress components in the active particles. The stress curves were plotted from different locations: (a) negative electrode particle center, location (2) in Figure 6.12; (b) negative electrode particle boundary, location (1) in Figure 6.12; (c) positive electrode particle center, location (3) in Figure 6.13; (d): positive electrode particle boundary, location (4) in Figure 6.13.



Figure 6.15: The evolution of the stress components at the normal point of particle boundary. The stress curves were plotted from different locations: (a) negative electrode particle boundary with small radius, location (5) in Figure 6.12; (b) negative electrode particle boundary with large radius, location (6) in Figure 6.12; (c) positive electrode particle with small radius, location (7) in Figure 6.13; (d) positive electrode particle boundary with large radius, location (8) in Figure 6.13.

particles, for example, the negative electrode particles.

6.6.2.2 Stress in the Binder

Figure 6.16 presents the distribution of the first principal stress in the two types of binders at the end of discharge. Because of the thinness of the binder layer relative to the model, one has to zoom-in to see the distribution. The zoomed-in area corresponds to the location of maximum stress. The higher stresses were found at regions near sharp corners of the particles, between the particles, or between the particles and current collector.



Figure 6.16: The contour of the first principal stress in the binder corresponding to different binder materials at the end of discharge (1000 s): (a) PVDF-HFP(FC1278), E=1.1 MPa; (b) PVDF-HFP-LiClO₄, E=184 MPa. The unit for stress in the graph is Pa.

The histories of the principal stresses and Von Mises stress in the binders PVDF-HFP(FC1278)

(low modulus) and PVDF-HFP-LiClO₄ (high modulus) were plotted in Figure 6.17. The stress varied with the cycle, reaching the maximum at the end of discharge, relaxing some-what during the open circuit period and reducing to near zero at the end of charge. For the battery system in this study, the binder stress was always higher in the negative electrode. This may be due to the larger particle size in the negative electrode. The high modulus binder had a higher stress magnitude. The maximum Von Mises stress was about 10 MPa in the high modulus binder as compared to 0.18 MPa in the low modulus binder. The ratio of the maximum stress between the two types of binders was about 56. The maximum value of the first principal stresses in PVDF-HFP-LiClO₄ at the negative electrode was 15.2 MPa, which was higher than the tensile strength 13 MPa shown in Figure 6.8. This result indicated that in this battery system, PVDF-HFP-LiCl₄ binder may fail during discharge.

Figure 6.18 plots the strain histories. The strain levels were about 20% and 7% for the low modulus and high modulus binders, respectively. Since the material's elongation tends to reduce with improving in strength, binders with lower modulus appear to have advantages over the higher modulus one in terms of reducing binder related failure, particularly for active particles with large deformation. This result is consistent with the experimental observation that flexible binders improve the cycle life of silicon anode [154].

6.6.3 The effect of Discharge Rate

In order to examine the effect of discharge rate on the stress at the different locations of the active particles, the first principal stress and Von Mises stress at both the particle center and boundary under discharge rate 2C, 4C and 6C were compared in Figures 6.19 and 6.20, respectively. As the figures indicate, the battery stopped discharging earlier under the higher discharge rate as discussed in Chapter 4. These results also indicate that under the discharge



Figure 6.17: Stress history in binder: (a) binder with low modulus at a location in the negative electrode shown in Figure 6.16 (a); (b) binder with low modulus at a location in the positive electrode in Figure 6.16 (a); (c) binder with high modulus at a location in the negative electrode in Figure 6.16 (b); (d) binder with high modulus at a location in the positive electrode in Figure 6.16 (b).


Figure 6.18: Strain history in binder: (a) binder with low modulus at a location in the negative electrode shown in Figure 6.16 (a); (b) binder with low modulus at a location in the positive electrode in Figure 6.16 (a); (c) binder with high modulus at a location in the negative electrode in Figure 6.16 (b); (d) binder with high modulus at a location in the positive electrode in Figure 6.16 (b).

rate of 6C, the smallest stress magnitude can be attributed to the earliest determination of the discharge process.

Under the same DOD, the first principal stress magnitude was increasing with the increase of the discharge rate. The maximum stress value appeared at the sharp corner of the negative particle boundary, and reached 810 MPa at the end of discharge (DOD = 0.55) at 4C.

The effect of discharge rate on Von Mises stress was most pronounced at the positive particle boundary. The maximum Von Mises stress value at the positive particle boundary was 630 MPa at the end of discharge of 4C, compared to 380 MPa at the end of discharge of 2C. At the center of the negative and positive particles, the Von Mises stress value was not obviously affected by the discharge rate.

Several developed models [15, 24, 35, 157] for the stress in the active particles and the measured results [155, 156] for the stress in the electrode have been established. The results of the previous simulation indicated that the radial and tangential components of stress are increasing with the discharge/charge rate but at the low rate range. After reaching a peak of stress at a certain discharge/charge rate, the stress started decreasing at higher rates due to the earlier battery termination [157]. In this work, the first principal stress under different discharge rate showed the same trend. A wide range of the stress values existed among previously simulated and experimental results even for the same electrode material. Specifically, the maximum stress value ranged from 10 MPa to 400 MPa for the stress in the graphite electrode [155, 156]. It should be noted that there were several factors that may be responsible for the wide range of stress values observed. The first factor was attributed to the lack of experimentally measured property data for various constituents of the composite electrode [155]. The second factor was the neglected complex geometry of the active particle. For all the previously available models, the active particles were assumed to



Figure 6.19: The evolution of the first principal stress in the active particles under different discharge rate: (a) negative electrode particle center, location (2) in Figure 6.12; (b) negative electrode particle boundary, location (1) in Figure 6.12; (c) positive electrode particle center, location (3) in Figure 6.13; (d) positive electrode particle boundary, location (4) in Figure 6.13.



Figure 6.20: The evolution of the Von Mises stress in the active particles under different discharge rate: (a) negative electrode particle center, location (2) in Figure 6.12; (b) negative electrode particle boundary, location (1) in Figure 6.12; (c) positive electrode particle center, location (3) in Figure 6.13; (d) positive electrode particle boundary, location (4) in Figure 6.13.

be with regular geometry, such as sphere or cylinder. In addition, the previous models only considered the stress in the individual particles; while the effect of the surrounding materials on the active particle stress was largely ignored. In this work, the maximum Von Mises stress value and the first principal stress value at the negative electrode particle center were 95 MPa and 52 MPa at 6C, respectively, which were within the stress value range from previous results. Furthermore, the maximum stress value at the sharp corner at the particle boundary exceeded the predicted value by the previously developed models substantially. This reflects the effect of the localized particle's complex geometry on the stress in the active particles. The latter was impossible to examine if the previous models or experimental measurements were employed.

The stress field in an electrode may lead to the electrode morphological change [158]. The graphite anode suffers from particle cracking and damage resulting in surface structure disordering upon prolonged cycling [159, 160]. As seen in Raman spectra, the graphite electrode shows an increased intensity of the carbon D-band (1350 cm⁻¹) with respect to G-band (1580 cm⁻¹) in a cyclic Li-ion battery [155, 161]. Such structure damage has a direct effect on the thickness and composition of the solid-electrolyte-interphase (SEI) layer [162, 163]. It is particularly true for the active particles under high intercalation/deintercalation rate [159]. This work provides a quantifiable method for the characterization of the stress field and evolution in the electrode. It adds to the current state of knowledge on the relationship of electrode mechanical damage and morphological change at microstructure level, especially for the instances with high intercalation/deintercalation rate.

The effect of discharge rate on the stress in the binder was examined next. Figures 6.21 and 6.22 compared the stress value at the locations showing high stress value at both PVDF-HFP(FC1278) and PVDF-HFP-LiClO₄, respectively. The stress change in the binder under

different discharge rates was not so obvious as in the active particles. Under the same DOD, both the first principal stress and Von Mises stress magnitudes increased slightly with the discharge rate. The battery operation rate was not the dominant factor for the stress in the binder.

6.7 Summary

A 2D microstructure resolved multiphysics model including electrochemical and mechanical analysis has been developed. The realistic microstructure was represented in the model. It was used to study the stress in the active particle and the polymeric binder of a $\text{Li}_{x}\text{C}_{6}|\text{PP}|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell.

The stress in the negative electrode particle was higher than that in the positive electrode particle. The larger particle size and higher average local current density were the critical reasons. The effect of the irregular particle shape on the stress in the electrode particles was examined. The maximum stress value was at the sharp corner of the negative electrode particle boundary. The value was much higher than that at the particle center or the smooth surfacer point at the particle boundary.

In the polymeric binders, the maximum stress was found in regions near sharp corners of the particles, between the particles, or between the particles and current collector. The binder stress was higher in the negative electrode where the particle size was larger. The maximum stress was observed at the end of discharge. The binder with a higher modulus exhibited higher stresses. The stress in the binder was proportional to its modulus while the strain remained at the order of 10-20%. Flexible binders appear to have advantages over the more rigid binders in terms of reducing binder related failure. The effect of the discharge



Figure 6.21: The evolution of the first principal stress in the polymeric binder under different discharge rate. The stress curves were plotted from high stress location with different binder material: (a) PVDF-HFP(FC1278) (low modulus), location (1) in Figure 6.16(a); (b) PVDF-HFP(FC1278) (low modulus), location (2) in Figure 6.16(a); (c) PVDF-HFP-LiClO₄ (high modulus), location (3) in Figure 6.16(b); (d) PVDF-HFP-LiClO₄ (high modulus), location (4) in Figure 6.16(b).



Figure 6.22: The evolution of the Von Mises stress in the polymeric binder under different discharge rate. The stress curves were plotted from high stress location with different binder material: (a) PVDF-HFP(FC1278) (low modulus), location (1) in Figure 6.16(a); (b) PVDF-HFP(FC1278) (low modulus), location (2) in Figure 6.16(a); (c) PVDF-HFP-LiClO₄ (high modulus), location (3) in Figure 6.16(b); (d) PVDF-HFP-LiClO₄ (high modulus), location (4) in Figure 6.16(b).

rate on the stress in the binder was limited.

Chapter 7

Conclusion and Future Work

7.1 Summary and Conclusion

A multiphysics model for the stress analysis of the separator in a basic Li-ion battery cell has been developed. Three groups of phenomena that occurred inside the battery cell were considered in order to perform the stress analysis. They are electrochemical, thermal and mechanical phenomena. Besides mechanical stress, the intercalation stress and thermal stress in a separator were investigated in this study. This work is the first work that computes the stress in battery components within a multiphysics framework with ongoing electrochemical reaction.

In this model, the multi-physics equations were solved concurrently using four coupled sub-models at different scales. The battery electrochemical kinetics, current balance, ionic transport and mass transport were solved by a 1D macroscopic "Battery"sub-model and a pseudo 2D "Electrode"sub-model based on an existing 1D battery model in $\text{COMSOL}^{\textcircled{\text{R}}}$, where the porous electrode theory and the concentrated solution theory were employed. The thermal behavior was considered by the 1D "Thermal"sub-model. The local model was used to simulate the heat generation in a Li-ion battery. The stress analysis at the level of a battery cell was conducted with a 2D idealized meso-scale RVE "Stress"sub-model of the battery cell. In order to consider the intercalation stress in the separator, the Li flux in the 1D "Battery"sub-model was mapped to the active particle surface to calculate the Li

concentration in the sub-model. The battery temperature obtained from the "Thermal" submodel was also mapped to the "Stress" for thermal stress calculation. The multiphysics model was implemented in $\text{COMSOL}^{(\widehat{\mathbf{R}})}$, a commercially available multiphysics code.

The major limitation of the model is the inability to get a converged solution for the multiphysics problem when a contact condition between materials with a large difference in stiffness was introduced, as in the case between the separator and active particles. To overcome this obstacle, a continuum mesh had to be used at the separator and electrode interfaces. The stress revealed by this model, at best, may represent the condition in the separator where the particle roughness created a nonslip condition in the local area.

The developed multiphysics model was used to investigate the stress in polymeric separator PP in a $\text{Li}_{x}\text{C}_{6}|\text{PP}|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ cell, with the liquid electrolyte 1M LiPF₆ in a solvent of EC/DMC (2:1 by volume). The measured thermo-viscoelastic property of the separator was used in the work.

The "Thermal" sub-model was validated against available experimental data in terms of cell temperature rise and heat generation rates and then used in the investigation of relationships among the battery temperature rise, cell utilization and the design parameters. The thickness of battery components had a great impact on Li⁺ concentration polarization. The batteries with a thin component thickness had a lower temperature rise and better battery utilization. Reducing the active particle size was most efficient in improving the cell utilization when Li diffusion in the negative particles became dominant.

The simulation results from "Stress" sub-model provided new insights into the battery components deformation in a discharge/charge cycle. It was observed that the net cyclic dimensional variation of the battery cell was determined by the difference of the volume change of the two electrodes and this amount may be regulated by optimizing the porosity of the two electrodes.

The electrode particle made small indention into the separator under pressure. The maximum stress in the separator was found in indented areas. The stress state and its magnitude in the separator depended upon the particle size, particle packing, and the boundary constraint of the battery cell. The effects of interaction and thermal are not simple summation and hence must be considered concurrently. The results indicate that under normal operation conditions the stress level in the separator is far from in danger of immediately yield or rupture in the center of the cell.

In summary, the multiphysics model developed in this study can be used to investigate the stress in the separator, the heat generation in the battery, and the relationship among electrochemical, thermal and mechanical phenomena. Due to the lack of the complete set of model parameters and experimental data, the model was qualitatively rather than quantitatively validated. However, as the homogenized active particle size and porosity were considered in the 1D "Battery" sub-model and pseudo 2D "Electrode" sub-model, the multiphysics cannot consider the effect of electrode microstructure and its evolution on the battery performance.

In order to involve the real microstructure effect, a 2D microstructure resolved model was developed in Chapter 6 for the same $\text{Li}_{x}\text{C}_{6}|\text{PP}|\text{Li}_{y}\text{Mn}_{2}\text{O}_{4}$ battery system. This 2D model was constructed based on the real electrode geometry. There were two sub-models sharing the same geometry in the model: "Electrochemical" sub-model and "Stress" sub-model. The "Electrochemical" sub-model computes the spices and charge transport, and electrochemical reaction. The "Stress" sub-model computes the intercalation induced strain, the mechanical strain and the stress. At this stage, the heat generation and thermal effect is not considered. The 2D microstructure model was used to investigate the stress in the active particles and conductive binders.

By using the 2D microstructure resolved model, The effect of the irregular particle shape on the stress in the electrode particles was examined. The maximum stress value was at the sharp corner of the negative electrode particle boundary. The value was much higher than that at the particle center or the normal particle boundary point. Furthermore, the stress in the negative electrode particle was larger than that in the positive electrode particle. The larger particles size and average local current density were the critical reasons.

In the polymeric binders, the maximum stress was found in regions near sharp corners of the particles, between the particles, or between the particles and current collector. The binder with a higher modulus exhibited higher stresses. The stress in the binder was proportional to its modulus while the strain remained at the order of 10-20%. Flexible binders appear to have advantages over the more rigid binders in terms of reducing binder related failure.

7.2 Outlook of Future Work

This work developed a finite-element based multi-scale, multiphysics approach to investigate the stress in a Li-ion cell. It is validated and used to predict the stress in the separator in $\text{LiC}_6|\text{Li}_2\text{MnO}_4$ battery system, as it is one of the systems with a complete set of model parameters and experimental data.

The application of the current model can be expanded to battery systems with high capacity electrode materials, which is one of the most active topics in Li-ion battery research.

Compared to graphite, Sn, Ge and Si have 10 times better volumetric capacity and 2-10 times better specific capacity. Employing these materials will significantly improve the energy density of the batteries. However, the cyclic stability of the electrodes with high capacity materials in general is rather poor. A problem accompanied by high Li storage capacity is the large volume changes during charging and discharging cycles. To improve the cycle life, electrodes with various sizes, geometries and constructions have been investigated experimentally. A model that can assess the battery performance and stress development in systems with these electrodes will be invaluable. It will provide insight into the relationships between different parameters. It can also be used in design optimization.

A main challenge in multiphysics model development is to obtain the material properties and parameters required for the multiphysics model for these systems.

Among all high capacity anode materials, Si has received most attention. Crystalline Si was found to go through a series of phase changes and eventually becomes amorphous Si when reacting with Li⁺ [165]. Shenoy et al. [164] and Zhao [158] employed the first principal model to calculate the SOC dependent elastic properties of Li-Si alloys. The results indicated that the struture change of the lithiation of crystalline Si electrode renders the Si anode based system the capability of large plastic deformation. Zhao et al. [166] proposed a phenomenological model to describe the yield surface of Si with Li interaction. The model prediction was in good agreement with the stress measurements of Si film during cyclic intercalation/deintercalation [167]. This model may be incorporated into the present multiphysics model to investigate the battery with Si anode. Similar work is required for other high capacity material systems.

Besides influencing the deformation behavior of the host, Li concentration [168] and stress state [15] also influence the Li diffusion in the host material. Further experiments and numerical investigations are required to consider these effects in the multiphysics model for high capacity electrodes. Another challenge in modeling Li-Ion battery with high capacity electrodes is the numerical technique itself. As stated in Chapter 4, models built upon COMSOL[®] had convergence problems when modeling contact between materials with large difference in stiffness and a continuous mesh had to be used. With electrodes capable of large volume variation, the issue with contact modeling needs to be resolved.

The current microstructure resolved model is limited to 2D. The local level porosity and tortuosity in 2D electrode geometry are not the same as those in the realistic 3D geometry. The current imaging techniques can reveal 3D microstructures to certain accuracy. The mesh generation tools are available to automatically generate the mesh for 3D microstructure geometry. However, the computer resource required to solve 3D models far exceeds the current capability.

APPENDICES

Appendix A

Non-Linear Least-Square Subroutine

The following program is the non-linear least-square subroutine for creep compliance of Celgard 2400 at 40 $^{\circ}$ C. The subroutine for creep compliance at different times is the similar but using different original creep compliance data.

clear

x0 = [0.1;20;100;20;49;10]; % initial point, active set algorithm only

xdata = [2.04, 4.04, 10.04, 101.05, 308.06, 640.08, 921.99, 1199.01]; % different time

ydata = [1082.967, 1120.411, 1175.19, 1386.174, 1563.476, 1734.761, 1839.002, 1919.932];

% creep value corresponding to different time value

[xe, resnorm] = lsqcurvefit(@creep, x0, xdata, ydata); % nonlinear curve-fitting least-square

T1=0.1; % retardation time

T2=100; T3=1000; T4=10000; T5=100000; j=xe(1)*xe(1)+xe(2)*xe(2)*(1-exp(-xdata/T1))

*100000 + xe (3) * xe (3) * (1-exp (-xdata/T2)) * 150000 + xe (4) * xe (4) * (1-exp (-xdata/T3))

+xe (5)*xe (5).*(1-exp (-xdata/T4))*14+xe (6)*xe (6).*(1-exp (-xdata/T5));

% Prony series expression for creep curve

plot (xdata,j,'+') % plot original creep curve

hold

plot (xdata,ydata,'*') % plot nonlinear curve-fitting curve

legend ('Fitted Curve', 'DMA Data'); % add legend

Appendix B

Laplace Transformation Subroutine

The following program is the Laplace transformation subroutine to obtain stress relaxation function for Celgard 2400 at 40 °C. The subroutine for stress relaxation function at different temperature is similar but using different creep constant data. This program is written by Mathematica 8.

 $\begin{array}{l} J0 = 1027 \quad \ \ \, *\ creep\ constant \ast \\ J1 = 87.85 \\ J2 = 365.21 \\ J3 = 0.821 \\ J4 = 3850 \\ J5 = 178 \\ \tau_1 = 0.1 \quad \ \ \ \, *\ retardation\ time \ast \\ \tau_2 = 100 \\ \tau_3 = 1000 \\ \tau_4 = 10000 \\ \tau_5 = 100000 \\ J = J0 + J1 \ast (1 - e^{-\frac{t}{T_1}}) + J2 \ast (1 - e^{-\frac{t}{T_2}}) + J3 \ast (1 - e^{-\frac{t}{T_3}}) + J4 \ast (1 - E^{-\frac{t}{T_4}}) + J5 \ast (1 - E^{-\frac{t}{T_5}}) \\ \ast \ \, Prony\ series\ of\ creep\ compliance \ast \end{array}$

JS = LaplaceTransform[J, t, s] * Laplace transformation of creep compliance*

 $GS = (1/s^2)/JS$ * stress relaxation function in Laplace domain* InverseLaplaceTransform[GS, s, t] * inverse Laplace transformation*

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