ABSTRACT

KIM, SANGWOOK. Stress at Electrode-Electrolyte Interface in Lithium-ion Batteries via Multiphysics Modeling. (Under the direction of Dr. Hsiao-Ying Shadow Huang.)

Since carbon dioxide from petroleum-derived fuels has become an environmental issue, the need for alternative energy sources increases dramatically. One of the most promising energy solutions is the use of lithium-ion batteries as an energy storage system. They exhibit a few favorable characteristics, such as their low cost, high thermal stability, high electrochemical performance, and high specific capacity. However, lithium-ion batteries show capacity loss and impedance rise on the surface of cathode particles during charging and discharging in several conditions. It has been suggested that high current-rates (C-rates) during discharging play an important role in the mechanical and structural deterioration of lithium-insertion materials, thereby progressively reducing the capacity of lithium-ion batteries with each charge and discharge cycle (referred to as “rate-capacity fade”). Yet our basic knowledge of how electrode material mechanical stress states contribute to the battery performance and stability is currently extremely limited, hindering materials innovation and the ability to use lithium-ion batteries as energy storage systems.

The main objective of this research is to investigate the mechanical stresses on the interface between the cathode and the electrolyte (i.e., a half-cell system). LiFePO₄ is used as a cathode material and the combination of several different kinds of electrolyte is considered. Multiphysics finite element models incorporating a Fluid Flow module (CFX), a Transient Thermal module, a Static Structural module, and additional Application Customization Toolkits (ACTs) in ANSYS are developed to study mechanical stresses in the half-cell battery system during discharging.
Our results provide a better understanding of mechanical stresses on the interface between the electrode and the electrolyte in lithium-ion batteries in several conditions. We explore (i) the impact of the porosity of electrode-electrolyte interface, (ii) the impact of porous electrodes in a lithium-ion half-cell, and (iii) the impact of phase transformation in porous electrodes. Specifically, we study effects of C-rate, volume fraction (porosity), viscosity, and lithiation stage during a half-cell system discharging. Moreover, our simulations demonstrate that both electrode and electrolyte material properties have greater effects when investigating mechanical stresses on the electrode-electrolyte interface. These computational models would aid on mitigating higher stresses in cathode particles to ensure longer battery cycle life.
Stresses at Electrode-Electrolyte Interface in Lithium-ion Batteries via Multiphysics Modeling

by
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Mechanical Engineering

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Dr. Alexei V. Saveliev
DEDICATION

To my parents, Soon-tae and Il-ran Kim, and My sister, Yeaeun Kim

Nothing would be possible without your support.

Thank you for always encouraging me.
BIOGRAPHY

Sangwook Kim was born in Busan, South Korea, on January 3rd, 1990. He matriculated at Pusan National University (Busan, Korea) in 2008. He served two years from 2010 at Korea Army. After that, he received his Bachelor of Science degree in Mechanical Engineering from PNU in 2014. He decided to study abroad to expand his academic and develop global leadership. In 2014, he enrolled in graduate school at North Carolina State University (Raleigh, NC) for pursuing his Master of Science degree in Mechanical Engineering. His main research field is stress analysis in lithium-ion batteries using multiphysics modeling.
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# TABLE OF CONTENTS

TABLE OF CONTENTS .......................................................................................... v
LIST OF TABLES ................................................................................................. vii
LIST OF FIGURES ............................................................................................... viii

CHAPTER 1: INTRODUCTION .............................................................................. 1
   1.1 Lithium-Ion Battery ................................................................................. 1
   1.2 Promising LiFePO_4 Electrode ................................................................. 4
   1.3 Research at National Laboratory .............................................................. 6
      1.3.1 Sandia National Laboratory ............................................................... 6
      1.3.2 Brookhaven National Laboratory ....................................................... 9
   1.4 Current State-of-Art and Limitation ......................................................... 11
   1.5 Objectives of this Study ........................................................................... 13

CHAPTER 2: LITERATURE REVIEW .................................................................. 15
   2.1 LiFePO_4 as a Cathode material ............................................................... 15
   2.2 Electrolyte ............................................................................................... 24
   2.3 Solid-Electrolyte Interphase (SEI) ........................................................... 29
   2.4 Phase Transformation across Electrode .................................................. 32
   2.5 Diffusion-Induced Stress ......................................................................... 37

CHAPTER 3: MODEL DEVELOPMENT ............................................................... 43
   3.1 The Impact of the Porosity of Electrode-Electrolyte Interface ............... 47
   3.2 The Impact of Porous Electrodes in a Lithium Ion Half-Cell .................. 51
   3.3 The Impact of Phase Transformation in Porous Electrodes ................... 54

CHAPTER 4: SIMULATION RESULTS AND DISCUSSION .............................. 58
   4.1 Stress Analysis of the Porosity of Electrode-Electrolyte Interface .......... 58
      4.1.1 Effect of C-rate .................................................................................. 59
      4.1.2 Effect of Porosity ............................................................................... 60
      4.1.3 Effect of Viscosity .............................................................................. 62
      4.1.4 Effect of Lithiation ............................................................................. 63
      4.1.5 Conclusion ......................................................................................... 66
### 4.2 Multiphysics Models for Stress Analysis of Porous Electrodes

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.1 Effect of C-rate</td>
<td>69</td>
</tr>
<tr>
<td>4.2.2 Effect of Volume Fraction</td>
<td>70</td>
</tr>
<tr>
<td>4.2.3 Effect of Viscosity</td>
<td>74</td>
</tr>
<tr>
<td>4.2.4 Conclusion</td>
<td>75</td>
</tr>
</tbody>
</table>

### 4.3 Phase Transformation Effect in Porous Electrodes via Multiphysics Modeling

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.1 Lithiation</td>
<td>77</td>
</tr>
<tr>
<td>4.3.2 Effect of C-rate</td>
<td>80</td>
</tr>
<tr>
<td>4.3.3 Effect of Volume Fraction</td>
<td>86</td>
</tr>
<tr>
<td>4.3.4 Conclusion</td>
<td>91</td>
</tr>
</tbody>
</table>

### CHAPTER 5: SUMMARY AND CONCLUSIONS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Future Work</td>
<td>95</td>
</tr>
</tbody>
</table>

### REFERENCES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
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<td>REFERENCES</td>
<td>96</td>
</tr>
</tbody>
</table>

### APPENDIX

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix A: Material Property and Supplementary Information</td>
<td>106</td>
</tr>
<tr>
<td>A1: Electrode Material Property Change during Discharging</td>
<td>106</td>
</tr>
<tr>
<td>A2: Material Property of Electrolyte</td>
<td>107</td>
</tr>
<tr>
<td>A3: Supplementary Information on Model 1</td>
<td>108</td>
</tr>
<tr>
<td>A3: Supplementary Information on Model 2</td>
<td>113</td>
</tr>
<tr>
<td>A4: Supplementary Information on Model 3</td>
<td>118</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 1: Thermal stability characteristics and other factors in cost and environmental issues for battery materials [1].................................................................................................................................................. 5
Table 2: Lithium ion diffusivity and electronic conductivity of cathode materials [15]. 12
Table 3: Summary of simulations to present........................................................................................................ 14
Table 4: A candidate of organic electrolyte for lithium-ion batteries....................................................... 24
Table 5: Material properties for cathode and electrolyte .................................................................................. 45
LIST OF FIGURES

Chapter 1
Figure 1: Comparison of the different battery technologies in terms of gravimetric(x-axis), and volumetric(y-axis) energy density [2]................................................................. 2
Figure 2: Working mechanism of lithium-ion batteries during discharging [3]............. 3
Figure 3: Comparison of various cathode materials; LiCoO2, LiMn2O4, LiNiO2, and LiFePO4 [1]..................................................................................................................... 5
Figure 4: SOC mapping obtained via scanning transmission X-ray microscopy (a) 26µm, (b) 18µm, and (c) 6µm from the current collector [6]............................................. 7
Figure 5: (a) The number of particles in terms of particle size, and (b) the fraction of delithiated particles plotted as a function of percentile of particle size (lithium-rich particles are in color red and lithium-poor particles are in color green) [6].................... 8
Figure 6: Schematic illustration for multi-particle LiFePO4 system [7]............................. 10

Chapter 2
Figure 7: Comparison of the discharge capacity of various LiFePO4 electrodes at 25 °C [17]................................................................................................................................. 16
Figure 8: Simulation snapshots of 50% SOC electrodes discharged at different C-rates [20]......................................................................................................................... 17
Figure 9: The voltage as a function of the capacity at (a) the first cycle, and (b) the second cycle. The phase fraction of FePO4 during charging as a function of the cell position (y) at (c) the first cycle, and (d) the second cycle in C/7 [18]......................... 18
Figure 10: Discharge capacity versus cycle number for various LiFePO4 electrodes in 0.2 C-rate [18].................................................................................................................... 20
Figure 11: Normalized 7Li MAS NMR spectra of (a) carbon coated LiFePO4, and (b) pure LiFePO4 at 25 °C [19]. ............................................................................................................... 21
Figure 12: The SEM images of LiFePO4 carbon coated electrode (a) before cycling, (b) after 10 cycles, (c) after 30 cycles, and (d) after 60 cycles [23]. ............................... 22
Figure 13: (a) Average SOC (γ) from current collector to separator, and (b) intercalation stresses at the surface of the particles across the electrode during discharge [24]. ................................................................. 23
Figure 14: (a) Fe-ion dissolution from LiFePO4 olivine powders in different electrolytes at 30 °C, and (b) unstable behavior of a LiFePO4 olivine electrode in acidic electrolyte [29]. .................................................................................................................. 26
Figure 15: (a) Simulated porous electrode microstructure, and (b) resultant stream lines highlight the tortuous path [33]. ..................................................................................... 27
Figure 16: Average lithium content gradient from cathode to anode at cell depths of discharge (DODs, i.e., % overall lithiated \(= 50\%\)) as a function of (a) porosity, and (b) C-rate for the three different particle-size distributions [21]................................. 28
Figure 17: General reactions at an electrode, an electrode surface region, and bulk solution [34]. ........................................................................................................................................ 29
Figure 18: The Nyquist plots of carbon coated LiFePO$_4$ after 5 charge–discharge cycles. (a) 100%, (b) 50%, and (c) 0% SOC at 303 K [39]. ................................................................. 30
Figure 19: SEM images of (a) pristine cathodes, (b) pristine anodes, (c) cathodes after 15-day storage, and (d) anodes after 15-day storage [38]. .............................................. 31
Figure 20: (a) XRD spectra in terms of SOC from starting material to 95% SOC, and (b) unit cell volumes and the normalized crystalline phase fraction of triphylite and heterosite [39]. ..................................................................................................................... 33
Figure 21: Illustration of the shrinking-core model with the juxtaposition of the two phases and the movement of the phase boundary [11]. ......................................................... 35
Figure 22. (a) Contour plots for lithium concentration according to the lithium intercalation, and (b) anisotropic misfit between FePO$_4$ and LiFePO$_4$ along 3 directions according to one-dimensional lithium diffusion along [010] [42]. .................................................. 36
Figure 23: (a) Dimensionless concentration profile, (b) radial stress, and (c) tangential stress in terms of location in the spherical particle [45]. .................................................... 39
Figure 24: Diffusion-induced stress fields in a particle using (a) the isotropic model, and (b) the anisotropic model [46]. ..................................................................................................... 40
Figure 25: Effect of (a) porosity of anode, and (b) particle size on the total stress along the thickness of the anode [24]. ........................................................................................................ 41
Figure 26: Maximum and minimum stress in terms of C-rate (dashed: 5.5 µm, dotted: 55 µm, and solid: 165 µm electrodes) [47]. ...................................................................................... 42

Chapter 3

Figure 27: (a) Geometry, and (b) mesh of the model 1 composed of electrolyte and cathode domains. ......................................................................................................................... 47
Figure 28: Project schematic simulation in ANSYS including Fluid Flow (CFX), Transient Thermal, and Static Structural modules. ................................................................. 48
Figure 29: (a) Geometry, and (b) mesh of the model 2 composed of electrolyte and cathode domains. ....................................................................................................................... 51
Figure 30: Project schematic simulation in ANSYS including Fluid Flow (CFX), and Static Structural modules. ................................................................................................. 53
Figure 31: (a) Geometry, and (b) mesh of the model 3 composed of electrolyte and cathode domains. ................................................................................................................... 54
Figure 32: Project schematic including Fluid Flow, Static Structural modules, and Application Customization Toolkit (ACT). .................................................................................. 57
Chapter 4
Figure 33: (a) Velocity vector of electrolyte across electrolyte and electrode domains, and (b) velocity profiles at 3 different locations in the half-cell system (red: inlet boundary, blue: middle of the electrolyte domain, and green: middle of the electrode).

Figure 34: Influences of varying C-rate on the normalized normal stress and shear stress (porosity of 0.25 and EC is used as an electrolyte).

Figure 35: Relationship between porosity and normalized normal stress (EC is used as an electrolyte).

Figure 36: The effect of electrolyte viscosity on normal and shear stresses at 1C (porosity of 0.25).

Figure 37: Concentration profile calculated by the transient thermal module in ANSYS. Each model represents lithiation of (a) 20%, and (b) 80%.

Figure 38: Local concentration in terms of diffusion distance. Each concentration distribution shows lithiation of 20% (a) and 80% (b).

Figure 39: Relationship between stresses and lithiation stage at 1C (porosity of 0.25 and EC is used as an electrolyte).

Figure 40: Molar volume misfits when lithium-poor phase and lithium-rich phase exist.

Figure 41: Contour plots of stress and locations of position 1, 2, and 3 in (a) electrode domain and (b) a zoom-in top view of the electrode domain. Snapshots are taking from the 1C model with the volume fraction of 15.5%.

Figure 42: Influences of C-rate on normalized normal and shear stresses at position 1 (volume fraction of 15.5% and EC is used as an electrolyte).

Figure 43: Streamline of model 2 in 1C with the volume fraction of (a) 6.5%, (b) 15.5%, and (c) 30%.

Figure 44: Contour plots of normal stress (y-axis) in 1C with volume fraction of (a) 6.5%, (b) 15.5%, and (c) 30% at the lithiation of 10%.

Figure 45: Effect of volume fraction on normalized normal stress in 1C at the lithiation of 10% (EC is used as an electrolyte).

Figure 46: Effect of the viscosity of electrolyte on normalized normal stress at specific location in the 1C model at the lithiation of 10% (volume fraction of 15.5%).

Figure 47: Concentration distribution at the lithiation of (a) 0%, (b) 15.8%, and (c) 83% in cathode in a 1C model (volume fraction of 15.5%).

Figure 48: (a) Contour plot of lithiation at 50% lithiation in 1C (volume fraction of 15.5%), and (b) a 10-nodes tetrahedral type element.

Figure 49: Contour plot at lithiation stage of (a) 0%, (b) 5%, (c) 10%, (d) 20%, (e) 30%, (f) 50%, (g) 75%, and (h) 100% for 1C model with volume fraction of 15.5%.

Figure 50: Contour plots of normal stress for the model with volume fraction of 15.5% at 50% lithiation in (a) 1C, and (b) 6C.
Figure 51: Effect of C-rate on normal stress at the position 1 during lithiation (volume fraction of 15.5% and EC is used as an electrolyte). ................................................................. 84
Figure 52: Relationship between the surface concentration and the dimensionless discharging time for the models with volume fraction of 15.5% and EC is used as an electrolyte. .................................................................................................................. 85
Figure 53: Effect of C-rate on the normalized strain energy during lithiation (volume fraction of 15.5% and EC is used as an electrolyte). .................................................................................................................. 86
Figure 54: Contour plots of normal stress for the model with volume fraction of (a) 3.3%, and (b) 26.8% particle at 50% lithiation in 1C (EC is used as an electrolyte). ..... 87
Figure 55: Effect of volume fraction on normal stress in (a) 1C, (b) 6C, and (c) combined results (EC is used as an electrolyte). ............................................................. 89
Figure 56: Effect of volume fraction on normalized strain energy (a) 1C, and (b) 6C (EC is used as an electrolyte). ............................................................................................. 90
CHAPTER 1: INTRODUCTION

1.1 Lithium-Ion Battery

Since carbon dioxide from petroleum-derived fuels has become an environmental issue, the need for alternative energy sources and the replacement of the internal combustion engine increases. The use of lithium-ion batteries is one of the most promising power sources. Lithium-ion batteries have been used for a wide range of applications such as portable electronics, power tools, and transportation [1]. Especially, the lithium-ion batteries show good potential for the application on hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and electric vehicles (EVs). The main reasons why lithium-ion batteries are now the prevailing rechargeable battery system are due to their low cost, low toxicity, high thermal stability, high electrochemical performance, and high specific capacity compared to commonly used batteries such as Ni–Cd and Ni–MH portable batteries [2].

Gravimetric and volumetric energy densities, which are important properties for cathode materials, determine the energy release rate and energy storage capacity per unit weight or volume. Since a lighter battery with the same energy capacity is easier to carry around, the gravimetric energy density is especially important for portable devices. Especially, in case of electric vehicles, the volumetric energy density becomes a determinant factor, because with the same energy capacity, a smaller battery is easier to fit into a car. Figure 1 demonstrates that lithium-ion batteries show higher gravimetric energy density (W·h·kg⁻¹) and volumetric energy density (W·h·l⁻¹), which are strongly related to the ability to deliver energy in the system.
Figure 1: Comparison of the different battery technologies in terms of gravimetric(x-axis), and volumetric(y-axis) energy density [2].
Figure 2 below portrays how lithium-ion batteries work. The lithium-ion battery cell is made up of five essential components; a positive and a negative electrode, electrolyte, a separator, and current collectors. During the charge and discharge process, lithium ions are shuttled between an anode and a cathode through electrolyte. When lithium ions reached the cathode surface, lithium ion insertion (intercalation) occurs, and it causes diffusion-induced stress (DIS). Graphite is commonly used as an anode, whereas various materials such as LiCoO$_2$, LiMn$_2$O$_4$, LiNiO$_2$, and LiFePO$_4$ are used as a cathode. Moreover, organic-carbonate solvents such as ethylene carbonate (EC) and dimethyl carbonate (DMC) with a lithium salt dissolved are commonly used as an electrolyte.

![Diagram of lithium-ion battery working mechanism during discharging.](image)

**Figure 2:** Working mechanism of lithium-ion batteries during discharging [3].
1.2 Promising LiFePO₄ Electrode

In 1997, Padhi et al. [4] proposed LiFePO₄ as a cathode material, which shows a higher capacity (170 mAh/g) as high as LiCoO₂. It also exhibits high volumetric energy (970 WhL⁻¹), and volumetric power (1236 WL⁻¹) compared to the four mainstream cathode materials as shown in Figure 3 [1]. Since LiFePO₄ is made from non-toxic materials and the abundant transition metal (160 billion tons in the Earth), it is an environmental-friendly and cheaper material (Table 1).

Moreover, one of the prominent problems of lithium-ion batteries is safety, attributed primarily to the material’s thermal stability [5]. In 2013, the United States Federal Aviation Administration (FAA) ordered a review into Boeing 787 Dreamliner due to the battery overheating problems. The lithium-ion batteries of Boeing 787 have used LiCoO₂ as a cathode material. Table 1 shows that LiFePO₄ exhibits the lowest exothermic peak temperature (289°C) and heat flow (-6 Wg⁻¹). Exothermic peak temperature can be used as a description of self-reaction temperature. The lower the peak temperature, the safer a material is. Negative value of heat flow means electrochemical reaction of electrode is endothermic. Therefore, LiFePO₄ shows the higher thermal stability during charge and discharge process.
Figure 3: Comparison of various cathode materials; LiCoO₂, LiMn₂O₄, LiNiO₂, and LiFePO₄ [1].

Table 1: Thermal stability characteristics and other factors in cost and environmental issues for battery materials [1].

<table>
<thead>
<tr>
<th></th>
<th>LiCoO₂</th>
<th>LiMn₂O₄</th>
<th>LiNiO₂</th>
<th>LiFePO₄</th>
</tr>
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<tr>
<td>Exothermic peak temperature (°C)</td>
<td>367</td>
<td>302</td>
<td>348</td>
<td>289</td>
</tr>
<tr>
<td>Exothermic heat flow (Wg⁻¹)</td>
<td>20</td>
<td>7</td>
<td>33</td>
<td>-6</td>
</tr>
<tr>
<td>Environmental pollution</td>
<td>toxic Co</td>
<td>good</td>
<td>heavy metal Ni</td>
<td>good</td>
</tr>
<tr>
<td>Battery cost</td>
<td>expensive</td>
<td>moderate</td>
<td>cheap</td>
<td>cheap</td>
</tr>
<tr>
<td>Storage of transition metal (×10⁶ ton)</td>
<td>8.3</td>
<td>99.7</td>
<td>48,000</td>
<td>160,000</td>
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</tbody>
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1.3 Research at National Laboratory

Interesting research on lithium-ion batteries have been conducted by several national laboratories and universities. In this section, a few studies conducted by U.S. national laboratories, such as Sandia National Laboratory and Brookhaven National Laboratory, are introduced.

1.3.1 Sandia National Laboratory

For better performance in lithium-ion batteries in electric vehicles, medical equipment, and aircrafts, Sandia National Lab has been conducting research using LiFePO$_4$ as a cathode material in lithium-ion batteries. Chueh et al. [6] studied the particle-by-particle pathway of lithium intercalation, which is the ability of a molecule to be inserted and extracted from two other molecules.

In Figure 4, the lithium-poor particles are represented in color green and indicate nearly charged, while lithium-rich particles are represented in color red and indicate nearly discharged. It has been observed that the average lithium content of the particles (i.e., state-of-charge, SOC) shows nearly same across the cathode, suggesting that lithium ion transport through the electrolyte is relatively fast even under a 1 discharging current-rate (C-rate). A nC-rate requires $1/n$ hour to fully charge and discharge the battery. Furthermore, only a small fraction of the particles has both lithium-rich and lithium-poor regions during discharging (i.e., few particles with mixed phase marked in yellow are observed). Therefore, the time needed to completely charge individual LiFePO$_4$ particle is much shorter (about 50 times shorter) than the time needed to charge the entire electrode.
Figure 4: SOC mapping obtained via scanning transmission X-ray microscopy (a) 26µm, (b) 18µm, and (c) 6µm from the current collector [6].

From Figure 4, their experimental results suggest that most particles are ellipsoidal, therefore the particle size is later expressed as a length along the long axis of the ellipse.
Figure 5 demonstrates the particle-size distributions of all the single-phase particles. The two vertical lines (i.e., a red and a green line) in the Figure 5a indicate the average particle size of lithium-rich particles and lithium-poor particles. It has been observed that the average particle size is 256 nm for lithium-rich LiFePO₄ particles and 294 nm for lithium-poor LiFePO₄ particles. Even though there is a difference of average particles size between lithium-rich and lithium-poor LiFePO₄, Figure 5b displays the fraction of delithiated particles (in color green) and lithiated particles (in color red) plotted as a function of percentile of particle size. That is, lithiation state depends weakly on the particle size. It suggest that increases in particle size does not influence the fraction of delithiation. This result is contrary to the common expectation that smaller particles would delithiate before larger ones.

Figure 5: (a) The number of particles in terms of particle size, and (b) the fraction of delithiated particles plotted as a function of percentile of particle size (lithium-rich particles are in color red and lithium-poor particles are in color green) [6].
1.3.2 Brookhaven National Laboratory

At the Brookhaven National Laboratory, Wang et al. [7] have used X-ray microscopy to track the phase transformation process at nano-scale resolution during charging and discharging. They focused on the reasons why charging under high C-rate constrains LiFePO$_4$ battery performance. Figure 6 compares phase transformation mechanism and intercalation pathway at fast and slow charging rates for a multi-particle LiFePO$_4$ system. It suggests that in a multiple LiFePO$_4$ particle system, phase transformation occurs concurrently at slow C-rate, whereas it proceeds inhomogeneously at faster C-rate [7]. Even at the end of discharging, an incomplete phase transformation marked in red is still detected at faster C-rate (i.e., 5C). To improve the ionic and electron conductivity, they tried to relieve inhomogeneity of phase distribution by using low active material loading and liquid electrolyte. However, inhomogeneity of the phase distribution still remains unsolved in spite of their efforts. The observed inhomogeneity at high C-rates has not been solved until now, thus is regarded as prominent issue, which needs to be settled as soon as possible.
Figure 6: Schematic illustration for multi-particle LiFePO$_4$ system [7].
1.4 Current State-of-Art and Limitation

Currently, lithium-ion batteries have become commercially available. Due to their high gravimetric energy density, lithium-ion batteries have become the choices of the energy storage systems for laptops, cell phones, and many other portable applications. For example, Samsung SDI continues to develop lithium-ion batteries for portable electronic devices. One of latest batteries, called ICR18650-32A, has 3200mAh current capacity and 12Wh energy capacity [8]. It has the highest capacity among the cylindrical-type lithium-ion batteries and it provides increased hours of laptop usage.

Moreover, lithium-ion batteries are commonly used in HEV, PHEV, and EV because of their high volumetric energy density. BMW has released a PHEV in 2015, called BMW i8. It has a 7.1 kWh pack, which suggests that BMW i8 can operate 37 km (23 miles) without gas [9]. Since BMW i8 have an additional internal combustion engine, the battery pack can be charged during driving with gas. TESLA has developed a high profile EV, which has received a lot of attention. It is reported that the 85 kWh lithium-ion battery in model S (85D) has an ability to deliver 230 miles (370 km) [10].

Even though lithium-ion batteries have been commercially used in industry due to their many advantages, they have some obstacles and limitations. First of all, LiFePO₄ has relatively low electronic conductivity and lithium ion diffusivity comparing to other commonly used cathodes such as LiMn₂O₄ or LiCoO₂ (Table 2). Low electronic conductivity and lithium ion diffusivity of LiFePO₄ results in considerable ohmic drops within the electrode [11]. Ohmic drops cause decrease in the terminal voltage during discharge and increase in voltage needed to charge. Secondly, it has been noted that the electrode displays capacity loss in several conditions [12]. Even though a fast C-rate is required to provide a
better acceleration for EV, LiFePO$_4$ limited high-rate capability, with considerable loss in utilization with a high C-rate [11]. Moreover, capacity loss is very significant with the longer period of charge and discharge cycles or storage [13]. Thirdly, an irreversible charge loss occurs on the solid-electrolyte interphase (SEI) is observed [14]. It is noted that the SEI plays negative roles on the battery performance via irreversible charge losses, and it harms the battery safety by forming an additional layer on the electrode surface.

Table 2: Lithium ion diffusivity and electronic conductivity of cathode materials [15].

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<tr>
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<th>Lithium Ion Diffusivity [cm$^2$·s$^{-1}$]</th>
<th>Electronic Conductivity [S · cm$^{-1}$]</th>
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<tr>
<td>LiCoO$_2$</td>
<td>$10^{-10}$ ~ $10^{-8}$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>$10^{-11}$ ~ $10^{-9}$</td>
<td>$10^6$</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>$10^{-15}$ ~ $10^{-14}$</td>
<td>$10^9$</td>
</tr>
</tbody>
</table>
1.5 Objectives of this Study

It has been observed that the capacity fade with a high C-rate or with a long period of cycling is strongly related to the mechanical stresses inside lithium-ion batteries [12]. Moreover, it has been experimentally observed that stresses due to intercalation and phase transformation can cause local fractures in the active materials of lithium-ion batteries [16]. Yet our basic knowledge of how electrode material mechanical stress states contribute to the battery performance and stability is currently extremely limited, hindering materials innovation and the ability to use lithium-ion battery as an energy storage system.

The main objective of this research is to investigate the mechanical stresses on the interface between the cathode and the electrolyte (i.e., a half-cell system). Three distinct multiphysics finite element models are developed aiming to understand (i) the impact of the porosity of electrode-electrolyte interface, (ii) the impact of porous electrodes in a lithium ion half-cell, and (iii) the impact of phase transformation in porous electrodes. A Fluid Flow module (CFX), a Static Structural module, a Transient Thermal module, and additional Application Customization Toolkits (ACTs) in ANSYS are utilized and effects of C-rate, volume fraction (porosity), viscosity, and lithiation on internal stresses inside the electrode are investigated. Table 3 below provides a summary of simulations that are carried out within developed models. Parameters used in the models will discuss in Chapter 3.
Table 3: Summary of simulations to present

<table>
<thead>
<tr>
<th>Lithiation</th>
<th>C-rate</th>
<th>Volume Fraction (Particle Size)</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td>0% ~ 100%</td>
<td>1C 5C 10C 20C</td>
<td>0.1 0.25 0.5 0.75</td>
</tr>
<tr>
<td>Model 2</td>
<td>10%</td>
<td>1C 5C 10C 20C</td>
<td>6.5% (75nm) 15.5% (100nm) 23.6% (115nm) 30% (125nm)</td>
</tr>
<tr>
<td>Model 3</td>
<td>0% ~ 100%</td>
<td>1C 2C 6C 8C</td>
<td>3.3% (60nm) 8% (80nm) 15.5% (100nm) 26.8% (120nm)</td>
</tr>
</tbody>
</table>
CHAPTER 2: LITERATURE REVIEW

2.1 LiFePO$_4$ as a Cathode material

LiFePO$_4$ is considered as one of the promising materials for a cathode as discussed in Chapter 1.2, however, the capacity loss is very critical at higher C-rate. To overcome this problem, Shrinivasan and Newman [11] have suggested to reduce the capacity loss by decreasing the particle sizes and to improve the conductivity of LiFePO$_4$ by coating the particles with a layer of carbon. With this concept, experimentalists have starting fabricating LiFePO$_4$ with nano-scale particles and carbon coatings [17][18][19]. In Figure 7, LPK142, LPK132, and LPK140 indicate the electrode with carbon coated nano-scale particles (1.5 to 2\%wt of carbon, size ranges from 50 to 250nm), carbon free nano-scale particles, and carbon free micro-scale LiFePO$_4$ particles (size ranges from 1 to 5 μm), respectively. Guerfi et al. [17] have reported that the carbon free nano-scale cathode (i.e., LPK 132) exhibits 50% capacity improvement at 10C compared to the carbon free micro-scale cathode (i.e., LPK 140). Moreover, positive effect of carbon coating on the battery performance was confirmed by comparing LPK142 with LPK132.
Figure 7: Comparison of the discharge capacity of various LiFePO$_4$ electrodes at 25 °C [17].

In spite of that the electrode with nano-scale particles exhibits high performance, it is observed battery degrades due to inhomogeneous electrochemical reaction across the cathode, however. Using synchrotron-based X-ray microscopy, Li et al. [20] investigated 3,000 individual particles at various C-rates and measured a fraction of actively intercalating particles in the electrode at different state of charge (SOC) (Figure 8). They have reported that more lithiated particles (marked in red) are located near the separator, and more delithiated particles (marked in green) are observed at a high C-rate. This inhomogeneous lithiation across the electrode was also observed by Strobridge et al. [21]. Moreover, Figure 8 displays that the size of delithiated particles (marked in green) is larger than that of lithiated particles (marked in red). They concluded that an inhomogeneous active population of particles in the electrode directly impacts a decreased in the cycle life and electrochemical performance of lithium-ion batteries.
Figure 8: Simulation snapshots of 50% SOC electrodes discharged at different C-rates [20].

Strobridge et al. [21] have measured a fraction of nano-scale LiFePO$_4$ electrode to investigate inhomogeneous reaction by using X-ray diffraction (XRD). They have reported that the fraction of LiFePO$_4$ decreases along with the diffusion direction (y-direction) at both the first and the second cycle (Figure 9b, d) because of lithium diffusion limited-kinetics in the electrolyte across the cathode. Moreover, it has been observed that the fraction of LiFePO$_4$ decreases more drastically at the second cycle especially between 15µm and 150µm. More specifically, the gradient of lithium content in the particles, which indicates the inhomogeneous reaction causing battery degradation, is 1.6 Li fraction/mm at the first cycle (scan #6, green line in Figure 9b) and 2.7 Li fraction/mm at the second cycle (scan #7, green...
line in Figure 9d). To understand the reduced battery performance due to the inhomogeneous reaction, a simulation have been performed to examine the hypothesis that the decrease in electronic conductivity at the second cycle affects the inhomogeneity across the electrode. With the same geometry and parameters in the simulations, Strobridge et al. [21] varied the electronic conductivity to observe the change of the battery performance. Their result suggests that an expansion and a contraction of particles during cycling have caused a decrease in electronic conductivity of LiFePO₄, which negatively affects the battery performance.

Figure 9: The voltage as a function of the capacity at (a) the first cycle, and (b) the second cycle. The phase fraction of FePO₄ during charging as a function of the cell position (y) at (c) the first cycle, and (d) the second cycle in C/7 [18].
Several studies have suggested that carbon coating could potentially overcome the capacity loss in LiFePO$_4$ [17][18]. For example, Cho et al. [18] have conducted experiments to examine the effect of carbon content in the cathode. They have used different carbon fraction, 1.25wt.% (Product-0), 1.67wt.% (Product-1), 2.28wt.% (Product-2), and 2.54 wt.% (Product-3), as an additional layer on the surface of cathode, respectively, and compared the battery performance. Figure 10 compares the discharge capacity of pure LiFePO$_4$ with various LiFePO$_4$/C samples. It has been observed that an increase in carbon content of samples shows a reduced capacity loss during cycling, which is related to the increase in electronic conductivity. However, the electrode containing too much carbon (i.e., Product-3 with 2.54 wt.% carbon) shows lower performance comparing to Product-1 (with 1.67wt.% carbon) and Product-2 (with 2.28wt.% carbon) due to the carbon thickness. They have reported that LiFePO$_4$ coated with a thin and uniform carbon film can deliver maximum discharge capacity of 151mAh$^{-1}$ at 0.2C and sustain 415 cycles with 80% of capacity retention [18]. Higher performance of the carbon coated LiFePO$_4$ particles are found due to the higher electron conductivity and more nucleation from more surface area, comparing to a carbon free electrode [22].
Figure 10: Discharge capacity versus cycle number for various LiFePO$_4$ electrodes in 0.2 C-rate [18].

Dupré et al. [19] have utilized $^7$Li magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS) to study the influence of carbon coating of LiFePO$_4$ during storage at the room temperature. Through normalized $^7$Li MAS NMR spectra, the reactions of the interphase are evaluated after aging (Figure 11). After one month of contact with electrolyte, the detected NMR signal for the carbon-free LiFePO$_4$ has increased significantly compared to the carbon coated LiFePO$_4$. This suggests that the reaction of the carbon-free electrode is aggravated more than that of carbon coated electrode during storage at the room temperature.
Figure 11: Normalized $^7$Li MAS NMR spectra of (a) carbon coated LiFePO$_4$, and (b) pure LiFePO$_4$ at 25 °C [19].
Another important issue regarding the battery degradation is that cracks are observed in LiFePO₄ after cycling. Wang et al. [23] have investigated cracks on the LiFePO₄ particles using XRD and SEM. Small flaws were observed in some particles after 10 cycles (Figure 12b). Figure 12c demonstrates that the crack becomes more obviously after 30 cycles. They believe that the cracks, which related to the performance degradation, may be caused by high internal strain energy during lithium intercalation. Thus, the importance of investigating mechanical stresses and strain energy in electrode particles during charging and discharging becomes more significant.

![Figure 12: The SEM images of LiFePO₄ carbon coated electrode (a) before cycling, (b) after 10 cycles, (c) after 30 cycles, and (d) after 60 cycles [23].](image-url)
Reganathan et al. [24] have published a mathematical model to develop a correlation between the mechanical properties and the performance of the porous battery electrodes. In their study, $\gamma$ is expressed as the ratio of average concentration of lithium in the particle and $\tau$ is defined to present normalized SOC:

$$\gamma = \frac{c_{i,j}}{c_{i,j}^{\text{max}}}, i = p$$

(1)

$$\tau = \left[ \frac{\int_{i} \gamma}{\int_{i} \gamma^{\text{max}}} \right]_{c/33}, i = p, m = \text{given rate of discharge}$$

(2)

As shown in Figure 13a, the ratio of average concentration of the particles (i.e., $\gamma$) across the thickness of the cathode could be realized in terms of normalized SOC (i.e., $\tau$). It has been reported that once the concentration on the surface is saturated when $\tau$ is 80%, phase transformation initiates near the separator causing a drastic increase in average concentration $\gamma$ near the separator above 80% (Figure 13a). Because of the phase transformation, the magnitude of the stress across the electrode increases until $\tau = 80\%$ (single phase) (Figure 13b), and the stress starts to decrease in this point (not shown in figure).

Figure 13: (a) Average SOC ($\gamma$) from current collector to separator, and (b) intercalation stresses at the surface of the particles across the electrode during discharge [24].
2.2 Electrolyte

The electrolyte plays an important role in the performance of lithium-ion batteries. Generally, battery electrolytes are optimized for maximizing conductivity and electrochemical stability [25], [26]. Table 4 lists candidates for organic carbonate electrolyte for lithium-ion batteries.

Table 4: A candidate of organic electrolyte for lithium-ion batteries

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Melting point [°C]</th>
<th>Boiling point [°C]</th>
<th>Dipole moment [10⁻³⁰ Cm]</th>
<th>Viscosity [mPa·s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene Carbonate (PC)</td>
<td>-54.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>241.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>16.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.4711&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethylene Carbonate (EC)</td>
<td>36.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>238&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.87&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.900&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Diethyl Carbonate (DEC)</td>
<td>-43.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>126.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.15&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.749&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td>4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>90&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.95&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.585&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Nazri and Pista [26], <sup>b</sup>Muhuri and Hazra [27], and <sup>c</sup>Rodríguez et al. [28]

For a maximum conductivity of electrolyte, propylene carbonate seems suitable for lithium-ion batteries since it has higher dipole moment, the measure of molecular polarity, which ensures higher dissociation of the lithium salt [29]. However, the viscosity of propylene carbonate is significantly high compared to other electrolyte such as ethylene carbonate, diethyl carbonate, and dimethyl carbonate. Therefore, linear carbonate (i.e., diethyl carbonate and dimethyl carbonate) with low viscosity, related to high fluidity, needs to be added to assure a fast ionic movement [30]. To compensate the low conductivity of the electrolyte with the low viscosity, thin electrode stacks with a thickness around 200-400 µm
is commonly used for lithium-ion batteries [25]. Moreover, doubling the concentration of lithium ion in the electrolyte can increase the capacity up to 15% [31]. Therefore, studying transport of lithium ion in the electrolyte is of importance.

Aurbach et al. [32] have studied the effect of acidic and non-acidic electrolyte on carbon coated cathodes during storage. In Figure 14a, sample #1 containing 3% carbon and sample #2 containing nearly 1.5% of carbon are compared. When they stored the carbon coated cathode in non-acidic electrolyte (i.e., EC-DMC/LiClO₄), Fe-ion dissolution is negligible. Fe-ion dissolution means the loss of the active mass from the electrode and indicates that cathode has become deteriorated. Even at a higher temperature (60°C), Fe-ion dissolution is also negligible. As the solution becomes more acidic, the dissolution of Fe-ion becomes pronounced and it causes an unstable behavior of electrode (Figure 14b). As expected, the higher temperature also leads to more dissolution of Fe-ion. Particularly, dissolution becomes very noteworthy in water contaminated solution (i.e., EC-DMC/LiPF₆ + 100ppm H₂O). It is confirmed that effect of commonly used acidic-electrolyte on cathode during storage period is significant.
Generally, tortuosity refers to the ratio of the diffusivity in the free space to the diffusivity in the porous medium. Figure 15 displays the simulated porous electrode microstructure and resultant stream line highlight the tortuous path in the electrolyte. In the composite matrix, the diffusion path length increases because lithium-ions are forced to flow around or through the particles [33]. The increased diffusion path length due to the porous medium makes the macroscopic resistivity of the cell increase, and it results in a significant decrease in the total delivered power density and the capacity of the power source.
**Figure 15:** (a) Simulated porous electrode microstructure, and (b) resultant stream lines highlight the tortuous path [33].

Using *in-situ* energy-dispersive X-ray diffraction, Strobridge et al. [21] have analyzed the average lithium content gradient across the electrode with three different particle size distributions, to study the magnitude of the inhomogeneity, the porosity, and C-rate effects. Figure 16a shows that when the porosity increases to 35% (i.e., relatively low volume fraction), the lithium concentration gradient decreases, which can be related to a higher effective diffusivity of the ions in the electrolyte. Figure 16b suggests that the lithium concentration gradients increase with C-rate. It also suggested that the lithium ion diffusion in the electrolyte becomes more limiting at higher C-rate [21].
Figure 16: Average lithium content gradient from cathode to anode at cell depths of discharge (DODs, i.e., % overall lithiated = 50%) as a function of (a) porosity, and (b) C-rate for the three different particle-size distributions [21].
2.3 Solid-Electrolyte Interphase (SEI)

Figure 17 demonstrates overall electrode reactions characterized by a reduction-oxidation mechanism including mass transfer, and chemical reactions [34]. Although an electrode region and a bulk solution region were commonly studied in many papers [20][23][35][36], it is now realized that more research about electrode surface region is needed. Especially, among electrode surface regions, solid-electrolyte interphase (SEI) growth at an interface between the negative electrode and the electrolyte is one of the most focused research areas [37]. Furthermore, it has been reported that lithium ions must also travel through an additional layer between the cathode and the electrolyte, which is similar with the SEI observed on an anode [38][39].

![Diagram of general reactions at an electrode, an electrode surface region, and bulk solution](image)

**Figure 17:** General reactions at an electrode, an electrode surface region, and bulk solution [34].
The experimental results from Ju et al. [39] suggest the charge exchange process should take place at the interface between LiFePO$_4$ and the electrolyte for pure phase LiFePO$_4$ electrode. From the Nyquist plot in Figure 18, after cycling for 5 times, the SEI is formed on the cathode surface. The migration process of lithium ions through the SEI layer leads to the manifestation of the additional semicircle in the Nyquist plots. Strobridge et al. [21] used XRD to map the evolution of the inhomogeneous electrochemical reaction in electrodes. Their results also show that the poorer electronic wiring could result from both the expansion and the contraction of the particles during cycling and the formation of a SEI layer [21].

Figure 18: The Nyquist plots of carbon coated LiFePO$_4$ after 5 charge–discharge cycles. (a) 100%, (b) 50%, and (c) 0% SOC at 303 K [39].
Zhong et al. [40] have used an electrochemical method to investigate SEI film on the surface of the both electrode. Figure 19 below portrays SEM images of electrodes. After 15-day storage, the surfaces of both cathode and anode become coarse (Figure 19c and d) caused by the formation of SEI films. Generally, SEI films deteriorate surface structures of the electrodes. The SEI formation was also confirmed by an increasing internal resistance from 13.8 mΩ to 14.7 mΩ after 15-day storage. The internal resistance is caused by the SEI formation since the other resistances including lithium ion diffusion resistance in the electrolyte, charge transfer resistance, and Ohm contact resistance are typically the same for each electrode due to the same battery materials used and in the battery assembly technologies adopted [40].

Figure 19: SEM images of (a) pristine cathodes, (b) pristine anodes, (c) cathodes after 15-day storage, and (d) anodes after 15-day storage [38].
2.4 Phase Transformation across Electrode

Investigating phase stability and phase transformation of electrodes is very important to the battery performance. As current is transferred from the anode to the cathode, an electrochemical reaction occurs inside the particle and it can be represented as below equation 3.

\[
\begin{align*}
\text{charging} & : \quad \text{Li}_x\text{FePO}_4 \rightarrow \text{FePO}_4 + x\text{Li}^+ + xe^- \quad (0 \leq x \leq 1), \\
\text{discharging} & : \quad \text{FePO}_4 \rightarrow \text{Li}_y\text{FePO}_4 + x\text{Li}^+ + xe^-
\end{align*}
\]

where \( x \) represents lithium concentration in the particles.

Phase transformation in cathode during charging and discharging has been studied using XRD by Meethong et al. [41]. Figure 20a compares a sequence of XRD spectra in terms of SOC. In XRD spectra, “H” represents heterosite (i.e., lithium-poor phase), “T” represents triphylite (i.e., lithium-rich phase), and “C” denotes the graphite. As charging proceeds, the heterosite peak increases and the triphylite peak decreases at the same time in the XRD spectra. As shown in Figure 20b, the fraction of triphylite (\( \text{Li}_{1-x}\text{FePO}_4 \), lithium-rich phase) and heterosite (\( \text{Li}_y\text{FePO}_4 \), lithium-poor phase) phase changes linearly with the SOC, where \( x \) and \( y \) is close to 0 and 1, respectively. Additionally, it has been also observed that the unit cell volume changes 6.6% due to the phase transformation, and it is mainly related to the volume misfit causing diffusion-induced stress (DIS) during charging and discharging, which will be discussed in Section 2.5.
Figure 20: (a) XRD spectra in terms of SOC from starting material to 95% SOC, and (b) unit cell volumes and the normalized crystalline phase fraction of triphylite and heterosite [39].
The shrinking-core model for a single particle of LiFePO$_4$ has been developed to investigate phase transformation (Figure 21). During discharging, an electrochemical reactions initiates when lithium ions and electrons reach the surface of a single phase particles ($\text{Li}_y\text{FePO}_4$). The phase transformation proceeds from $\text{Li}_{1-x}\text{FePO}_4$ (lithium-rich phase) to $\text{Li}_y\text{FePO}_4$ (lithium-poor phase) due to the electrochemical reactions. As lithium ions continuously traverse from the surface toward the core of particles, lithiation reaction occurs simultaneously. Finally, whole particle is composed of a single phase particles ($\text{Li}_{1-x}\text{FePO}_4$) [11].

Neglecting any migration effects, and assuming a concentration-independent diffusion coefficient the governing equation for this process can be written in spherical coordinates as follows:

$$\frac{\partial c_s}{\partial t} = D_{\text{Li}} \frac{\partial^2 c_s}{\partial r^2} + \frac{2D_{\text{Li}}}{r} \frac{\partial c_s}{\partial r}$$

Equation 4 is solved with the boundary conditions,

$$D_{\text{Li}} \frac{\partial c_s}{\partial r} = 0 \at r = 0,$$

$$c_s = c_0 \at t = 0,$$

where $D_{\text{Li}}$ is diffusivity of lithium ion in the electrode, $c_0$ is concentration of FePO$_4$, and $c_s$ is concentration of LiFePO$_4$. 


The simulation results from Tang et al. [42] suggest that LiFePO$_4$ expands along [100] and [010] but contracts in the [001] direction upon phase transformation caused by lithium intercalation. As shown in Figure 22a, phase transition occurs from a corner because particle corners are the most favored nucleation sites. Anisotropic growth is caused by the anisotropic misfit strain between FePO$_4$ and LiFePO$_4$. The linear misfit strain, caused by volume change during phase transition between FePO$_4$ and LiFePO$_4$, is the largest along [100] (5%) and the smallest along [001] (-1.9%) (Figure 22b) [42]. The misfit strain becomes a critical reason of diffusion-induced stresses during phase transformation.
Figure 22. (a) Contour plots for lithium concentration according to the lithium intercalation, and (b) anisotropic misfit between FePO$_4$ and LiFePO$_4$ along 3 directions according to one-dimensional lithium diffusion along [010] [42].
2.5 Diffusion-Induced Stress

Lithium insertion and removal in lithium-ion battery electrodes can result in diffusion-induced stresses (DIS) upon phase transformation. Capacity fade and fracture of electrode, one of the most significant problems in electrode materials, can be associated with DIS [43][44]. Cheng et al. [45] adopted a thermal stress analysis approach to investigate DIS based on the similarity of the law of heat conduction (Fourier’s law) and Fick’s laws of diffusion. The diffusion equation in the bulk of the insertion electrode is as follows:

\[
\frac{\partial \Theta_I}{\partial t} = D_I \nabla^2 \Theta_I, \tag{7}
\]

where \(D_I\) is intercalate diffusion coefficient, \(\Theta_I\) is the local concentration.

The stress-strain relationships can be expressed in spherical coordinate system as following equation:

\[
\varepsilon_r = \frac{1}{E} \left( \sigma_r - 2\nu \sigma_\theta \right) + \frac{1}{3} \Omega_c \Theta_I, \tag{8}
\]

\[
\varepsilon_\theta = \frac{1}{E} \left[ (1 - \nu) \sigma_\theta - \nu \sigma_r \right] + \frac{1}{3} \Omega_c \Theta_I, \tag{9}
\]

where \(E\) is Young’s modulus, \(\nu\) is Poisson’s ratio, \(\Omega\) is the partial molar volume of the solute, and \(c\) is the concentration of sites available for lithium insertion. The solutions for the normal and tangential stresses are expressed as following equation:

\[
\sigma_r(r) = \frac{2\Omega_c}{9(1-\nu)} \left[ \Theta_I^{av}(R) - \Theta_I^{av}(r) \right], \tag{10}
\]

\[
\sigma_\theta(r) = \frac{\Omega_c}{9(1-\nu)} \left[ 2\Theta_I^{av}(R) + \Theta_I^{av}(r) - 3\Theta_I(r) \right], \tag{11}
\]

where \(\Theta_I^{av}(r) \equiv (3/r^3) \int_0^r r^2 \Theta_I(r) dr\) is the average concentration in the spherical volume of radius \(r\) within the particle of radius \(R\).
From the results presented in the Figure 23a below, it can be seen that when the dimensional time \(\tau\) increases, lithium ions move from the surface \((r/R=1)\) towards the center of the particle \((r/R=0)\). When dimensionless time \(\tau = 0.4\), dimensionless concentration \(\frac{(\Theta_I(r,t)-\Theta_0)}{\Theta_R-\Theta_0}\) shows nearly consistent across the electrode, suggesting the particles are fully lithiated. Figure 23b and c demonstrate that dimensionless radial stress is always in tension in the particle, while tangential stress show tension and compression. It has been observed that radial stress initially increases until the dimensionless time \(\tau = 0.0578\) and followed by a decrease at a center of particle. In case of dimensionless tangential stress, the highest stress is observed at the center of particle when \(\tau = 0.0578\). Thus, both tangential and radial stress increase initially followed by a decrease after reaching certain point.
Figure 23: (a) Dimensionless concentration profile, (b) radial stress, and (c) tangential stress in terms of location in the spherical particle [45].
Malavé et al. [46] have investigated mechanical behaviors within Li$_x$CoO$_2$ cathode particles via isotropic and anisotropic computational models. Figure 24 compares DIS fields using isotropic and anisotropic models at $t = 1820s$ (nearly 50% discharged) during 1C. In both cases, compressive stresses observed in the particle interior, while the stresses near the particle surfaces are tensile stresses [46]. The simulation results suggest that the anisotropic model predicts higher tensile stresses than the isotropic model. Especially, higher tensile stresses, which are likely to cause crack initiation and fracture, are observed at the concaved area indicated by arrow. These results suggest that DIS is largely related to analysis models and surface shapes of particles.

Figure 24: Diffusion-induced stress fields in a particle using (a) the isotropic model, and (b) the anisotropic model [46].
Renganathan et al. [24] have developed a mathematical model to simulate the generation of DIS during the discharge process. They have reported that the intercalation process, related to the elastic deformation of the material, must be considered to quantify the stress generated in the electrode. To simulate the intercalation process, they also used the approach similar to that used to account for thermally induced stresses in a material. The effect of porosity and the particle size in the anode on DIS have been analyzed (Figure 25). It has been observed that the stresses increase with a decrease in the porosity and an increase in the particle size of negative electrode.

Figure 25: Effect of (a) porosity of anode, and (b) particle size on the total stress along the thickness of the anode [24].
A lithium ion cell-sandwich mathematical model with porous electrodes has been proposed by Christensen [47] to investigate DIS. It is observed that peak tensile stresses occur at the center of particles and peak compressive stresses occur at the surface of the particles. Figure 26 below represents that higher C-rate and larger particles result in a higher DIS. Besides, it could be observed that extensive fracturing of the cathode occurs exclusively in the region closest to the separator [47].

Figure 26: Maximum and minimum stress in terms of C-rate (dashed: 5.5 µm, dotted: 55 µm, and solid: 165 µm electrodes) [47].
CHAPTER 3: MODEL DEVELOPMENT

Several published studies have focused on the topic of the effect of mechanical stress in lithium-ion batteries [24][46][45][47][48]. However, these studies emphasized only one component of the battery cells (i.e., only cathode, anode or electrolyte). To better understand electrochemical and mechanical relations in lithium-ion batteries, factors such as (dis)charging current rate (C-rate), the volume fraction of the electrode, the viscosity of the electrolyte, and the phase transformation of the electrode materials, ought to be considered as a whole. Three distinct multiphysics finite element models of half-cell systems (i.e., with electrolyte and cathode materials) are developed in ANSYS Multiphysics (ANSYS, Inc., Canonsburg, Pennsylvania, USA).

Model 1 sets up a foundation for studying stresses on the interface between the electrolyte and the electrode. The advantage of this model is that we could investigate variations of mechanical stresses in lithium-ion batteries by different combinations of the porosity, C-rate, and electrolyte viscosity. Moreover, due to the simple geometry of the model, it allows us to evaluate resulting mechanical stresses on the interface between the electrode and the electrolyte quickly. Based on the results, a determinant factor contributing to the stress-induced degradation of the battery could be derived. However, this model is oversimplified by considering the electrode as a continuum media.

To this end, the second multiphysics model is developed: a porous medium with various spherical particle sizes in cathode is included in the model 2, by adopting Vijayaraghavan’s study [33]. Due to the nature of a porous medium, several interfaces between the electrode and the electrolyte can be studied. More insights of the effect of the C-
rate, the volume fraction, and electrolyte viscosity are deduced. Based on the results of the second model, we have a better understanding of the electrochemistry-induced mechanical stresses in porous electrodes.

To further capture phase transformation induced by lithium ion diffusion in electrode materials, a third multiphysics finite element model is developed. In this model, shrinking-core model developed by Shrinvasan and Newman [11] is extended by considering several particles and electrolyte. Specifically, changes of the materials properties of the electrode (from lithium-poor phase to lithium-rich phase) are coupled with the lithiation stage during discharging. Stresses at electrode-electrolyte interface in lithium-ion batteries are reinvestigated, particularly on the effects of the C-rate and the volume fraction. Table 5 lists the material properties for cathode and electrolyte used in this study.
Table 5: Material properties for cathode and electrolyte

<table>
<thead>
<tr>
<th>Ethylene Carbonate (EC)</th>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density</td>
<td>ρ</td>
<td>1.321 g·cm⁻³</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>Molar Mass</td>
<td>M</td>
<td>88.06 g/mol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
<td>η</td>
<td>1900 Pa·s</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td>Density</td>
<td>ρ</td>
<td>1.0635 g·cm⁻³</td>
<td>[28]</td>
</tr>
<tr>
<td></td>
<td>Molar Mass</td>
<td>M</td>
<td>90.08 g/mol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
<td>η</td>
<td>585 Pa·s</td>
<td></td>
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<td></td>
<td>Molar Mass</td>
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<tr>
<td>FePO₄</td>
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<td>Eₓ</td>
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<td>[49]</td>
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<tr>
<td></td>
<td></td>
<td>Eᵧ</td>
<td>121.12 GPa</td>
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<td></td>
<td>Eₗ</td>
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<td>Shear Modulus</td>
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<td></td>
<td></td>
<td>Gᵧₗ</td>
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<td></td>
<td></td>
<td>Gₓₗ</td>
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<tr>
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<td>Poisson’s Ratio</td>
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<td>υᵧₗ</td>
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<td></td>
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<td>υₓₗ</td>
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<td><strong>LiFePO₄</strong></td>
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<td>Elastic Stiffness</td>
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<td>C₂₂</td>
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<td></td>
<td>C₃₃</td>
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<td></td>
<td>C₅₅</td>
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<td>C₁₂</td>
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<td></td>
<td>C₁₃</td>
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<td>Eₗ</td>
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<tr>
<td>Shear Modulus</td>
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<td>Gᵧₗ</td>
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<td>Gₓₗ</td>
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<td></td>
<td>νᵧₗ</td>
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<td><strong>FePO₄ ↓ LiFePO₄</strong></td>
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<td>Elastic Stiffness</td>
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<tr>
<td></td>
<td>C₂₂</td>
<td>162.9 GPa</td>
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<td></td>
<td>C₃₃</td>
<td>181.1 GPa</td>
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<td></td>
<td>C₄₄</td>
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<td></td>
<td>C₅₅</td>
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<td></td>
<td>C₆₆</td>
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<tr>
<td></td>
<td>C₁₂</td>
<td>61.1 GPa</td>
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<td></td>
<td>C₁₃</td>
<td>54.9 GPa</td>
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<td>C₂₃</td>
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<tr>
<td></td>
<td>ΔVᵧ</td>
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<tr>
<td></td>
<td>ΔVₗ</td>
<td>-0.013</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[49] [50]
3.1 The Impact of the Porosity of Electrode-Electrolyte Interface

Figure 27a demonstrates the geometry of the model 1 used in the simulations. In order to model the interface between the electrolyte and the cathode, two 0.3μm × 0.3μm × 0.3μm domains are adopted: one of them is for electrolyte and the other one is for the cathode. The domain size is designed to be resembled 300nm thick LiFePO₄ films developed by Sauvage et al. [51]. Thus, the long edge of the simulation domain is set to L=0.6μm. The surface marked in green indicates the electrode-electrolyte interface. Particularly, Fluid-Porous Interface was used in this Fluid Flow module (CFX), in which the cathode material is considered as a continuum media with various porous ratios to simulate the solid domain as a porous electrode. Figure 27b portrays the mesh of the finite element model. The element model contains 1024 elements with the 8-nodes hexahedral (H8) element type. Moreover, the simulations are conducted in a steady-state and ionic flux is not considered as it is our first step to understand the impact of the porosity of electrode-electrolyte interface.

Figure 27: (a) Geometry, and (b) mesh of the model 1 composed of electrolyte and cathode domains.
Figure 28 below shows how the simulations based on the model 1 work in ANSYS. At first, the streamline of the electrolyte, where the lithium ions traverse, is calculated using the Fluid Flow module (CFX). Momentum loss of electrolyte occurs when electrolyte meets the surface of the electrode, and it causes mechanical stresses on the surface of the cathode. The C-rate dependent lithiation stage is calculated using the Transient Thermal module. By combining the results from the Fluid Flow and Transient Thermal modules, the mechanical stresses are investigated on the interface between electrolyte and cathode via the Static Structural module.

![Figure 28: Project schematic simulation in ANSYS including Fluid Flow (CFX), Transient Thermal, and Static Structural modules.](image)

In this simulation, the phase transformation from FePO₄ to LiFePO₄ during discharging is considered and the material properties of the electrode changes based on the following equation:

\[
[C(x)] = x[C]^{LiFePO₄} + (1 - x)[C]^{FePO₄}, \tag{12}
\]

where \([C(x)]\) is the phase transformation dependent anisotropic material property stiffness matrix, \([C]^{LiFePO₄}\) is the anisotropic material property stiffness matrix of LiFePO₄, and \([C]^{FePO₄}\)
is anisotropic material property stiffness matrix of FePO$_4$, and $x$ represents lithiation from the lithium-poor phase to the lithium-rich phase ($0 \leq x \leq 1$).

Equation 13 below indicates generalized Butler-Volmer kinetics usually describing the lithium insertion rate:

$$J = k_0 \frac{\alpha_{Li,yte}^{1-a} \alpha_{Li,s}^a}{\gamma_{TS}} \left[ \exp \left( -\frac{a\eta}{k_B} \right) - \exp \left( \frac{(1-a)\eta}{k_B T} \right) \right],$$

where $J$ is the lithium insertion rate, $k_0$ is the rate constant, $\alpha_{Li,yte}$ and $\alpha_{Li,s}$ are the respective activities of lithium in the electrolyte and in solid particles, $e$ is the elementary charge, $\eta$ is the reaction over-potential at the LiFePO$_4$/carbon/electrolyte triple-phase boundary, and $\gamma_{TS}$ is the activity coefficient of the transition state [52]. The 1C model has $J_{1C} = 0.19 \text{ A} \cdot \text{m}^{-2}$, the 5C model has $J_{5C} = 0.25 \text{ A} \cdot \text{m}^{-2}$, the 10C model is with $J_{10C} = 0.31 \text{ A} \cdot \text{m}^{-2}$, and the 20C model has $J_{20C} = 0.59 \text{ A} \cdot \text{m}^{-2}$ obtained from Li et al. [20]. To fulfill above insertion rate ($J$), the current density ($I$) at the inlet boundary was calculated by equation 14 since the current density can be expressed in terms of the velocities of the ions [36].

$$\frac{I}{F} = c_{(Li^+)} v_{(Li^+)} - c_{(PF_6^-)} v_{(PF_6^-)},$$

where $I$ is the current density, $F$ is Faraday’s constant, $c_{Li^+}$, $c_{PF_6^-}$, $v_{Li^+}$, and $v_{PF_6^-}$ indicates concentration of lithium ion and hexafluorophosphate ion, and velocity of lithium ion and hexafluorophosphate ion, respectively. To simplify the simulations, the concentration and the velocity of hexafluorophosphate ions are disregarded and we assumed that concentration of lithium ion are constant across the electrolyte.

To investigate the C-rate effects in our finite element models, we also assume that the velocity of lithium ions calculated above is used as an inlet velocity of the electrolyte. Furthermore, due to the process that lithium ions are forced to flow around or through the particles of cathode, resistant occurs on the surface of cathode in the half-cell system. That is,
it is assumed that an increase in macroscopic resistivity of the simulation domain is expressed as the momentum loss of electrolyte.
3.2 The Impact of Porous Electrodes in a Lithium Ion Half-Cell

The model presented in the previous section does not consider particle size, shape, and molar volume misfit, therefore, the second multiphysics model is developed: a porous medium with various spherical particle sizes in cathode materials. As shown in Figure 29a, model 2 consists of a $0.3\mu m \times 0.3\mu m \times 0.6\mu m$ rectangular domain for the electrolyte and several spherical particles as electrode materials. Moreover, symmetry boundary conditions and fluid-solid interface boundary conditions are adopted in the second model. Figure 29b displays the mesh of the finite element model. The element model contains 57456 elements with the 10-nodes tetrahedral (T10) element type.

![Figure 29: (a) Geometry, and (b) mesh of the model 2 composed of electrolyte and cathode domains.](image)

In this simulation, spherical and nano-size particles ranging from 75nm to 125nm are adopted to investigate the effect of electrode volume fraction; the particle size is selected from an experimental observation [53]. When the streamline passes around the cathode
particles, the resistant occurs on the electrode-electrolyte surface. The similar assumption in the model 1 that momentum loss of electrolyte causes pressure on the surface of cathode is also used. To determine inlet boundary conditions, the lithium ions’ transversal diffusion distance at a given time is estimated by the equation 15 [54]:

$$\delta_i(t) = \sqrt{D_i t}, \quad (15)$$

where $D_i$ is the diffusion coefficient of the electrolyte and $\delta_i$ is the estimated diffusion distance of lithium ion at a given time. Based on the estimated diffusion distance, the velocity of the electrolyte is calculated by dividing the diffusion length by the different discharging time due to different C-rates (i.e., 1C requires 3600s to reach a fully discharging, 5C requires 720s to reach a fully discharging). In this porous electrode half-cell model the diffusion coefficient of electrolyte is assumed to be a constant across the half-cell system, and with $D_{electrolyte} = 1 \times 10^{-10}m^2s^{-1}$ [55]. Details on how to calculate lithiation are discussed in the Section 4.1.4.

Figure 30 below demonstrates the multiphysics mechanism for stress analysis in the second model. To calculate the electrolyte flow around spherical particles, Fluid Flow module is used. Electrolyte flow produces fluid pressure on the interface between spherical particles and the electrolyte (i.e., solid-fluid interactions). As a result, pressured-induced mechanical stresses are generated in the half-cell system, which is then captured in the Static Structural module as the second step. In this step, spherical particles are modeled as anisotropic materials, as shown in Table 5. Since we focus on lithiation of 10% instead of transient lithiation, lithiation stage is calculated in CFX. From lithiation of 10%, lithium-rich phase and lithium-poor phase coexist in the electrode. Therefore, Transient Thermal model is not included in this model.
Figure 30: Project schematic simulation in ANSYS including Fluid Flow (CFX), and Static Structural modules.
3.3 The Impact of Phase Transformation in Porous Electrodes

Although reasonable results are obtained from the porous model (model 2) developed in the previous section, where the viscosity of the electrolyte and multiple interfaces are included, however, the C-rate dependent molar volume misfits, lithiation, and associated the phase transformation of the particle during discharging are not incorporated. Therefore, a third model is developed to address these factors. The geometry used in the model 3 is the same as the model 2, as shown in Figure 31. Specifically, changes of the material property of the electrode (from lithium-poor phase to lithium-rich phase) are coupled with the C-rate dependent lithiation stage during discharging in model 3.

![Figure 31: (a) Geometry, and (b) mesh of the model 3 composed of electrolyte and cathode domains.](image)

To simulate phase transformation during discharging, the shrinking-core model developed by Srinivasan and Newman [11] is adopted: the phase transformation of cathode materials is considered and the C-rate dependent volume misfits are adopted from the
experimental observations [56]. Thus, the importance of lithium-ion intercalation is further emphasized in the third model. The stress is calculated by following equation:

$$[\sigma] = [C]([\varepsilon] - 3\alpha \nabla \Phi),$$

where $\alpha$ is a volume expansion coefficient, $\nabla \Phi$ is the concentration gradients of lithium ion, and $[C]$ is the phase transformation dependent anisotropic material property matrix.

The driving force (flux) of the lithium ions movement is modeled by the heat flux. Since heat flux (flux of lithium ions) is an inlet boundary condition, heat energy (lithium-ion chemical potential) transfers through this domain. Lithiation can be simulated based on similarities between the heat equation (equation 17) and Fick’s second law of diffusion (equation 18).

$$\frac{\partial T}{\partial t} = -\alpha_T \Delta T,$$

$$\frac{\partial C}{\partial t} = -D \Delta C,$$

where $T$ is the temperature, $\alpha_T$ is a thermal diffusivity, $C$ is the concentration of lithium ion, and $D$ is the diffusion coefficient of lithium ion. In this simulation, the concept of heat transfer and temperature is used for simulating the diffusion and concentration of lithium ion. Thus, the limitation of the model is that the real effects due to the temperature and heat on lithium-ion batteries have to be disregarded.

In order to represent various C-rates, different mass fluxes ($J$) are determined to ensure enough time for lithium ion intercalation and diffusion in both electrolyte and cathode, where the 1C model has $J_{1C} = 0.125 W m^{-2}$, the 2C model has $J_{2C} = 0.25 W m^{-2}$, the 6C model has $J_{6C} = 0.75 W m^{-2}$, and the 8C model has $J_{8C} = 1 W m^{-2}$. In addition, a constant diffusion coefficients are used in the model, where $D_{electrolyte} = 1 \times$
$10^{-10} \text{m}^2\text{s}^{-1}$ [55], and $D_{\text{LiFePO}_4} = D_{\text{FePO}_4} = 1 \times 10^{-15} \text{m}^2\text{s}^{-1}$ [57]. Detail on how to calculate lithiation is discussed in the Section 4.3.1.

In this study, a computational model integrating experimental results [56] and theoretical analysis [11] is developed through a multiphysics analysis. As shown in Figure 32, the Fluid Flow and Static Structural module, and an Application Customization Toolkit (ACT) are used in the model 3. At first, the concentration distribution of the electrolyte, which enables lithium ions to move toward cathode, and the diffusion of lithium ions in each particles are calculated in the Fluid Flow module. The results generated in the Fluid Flow module are imported into the Static Structural module via a Fluid-Solid Interaction (FSI) transient extension, one of the ACT. FSI transient extension enables interpolating transient CFX results from the CFX mesh to the FEM mesh at each step of the structural analysis. Based on the transferred results from two modules, the diffusion-induced stresses on the cathode particles are calculated in the Static Structural module. Another ACT, called FE info extension, is also used to calculate the lithiation stage. FE info extension details nodes and elements related information in the mechanical interface.
Figure 32: Project schematic including Fluid Flow, Static Structural modules, and Application Customization Toolkit (ACT).
CHAPTER 4: SIMULATION RESULTS AND DISCUSSION

Sections below details the simulation results that were carried out by ANSYS Multiphysics. The results from the current study provide a better understanding of the mechanical stresses on the electrode-electrolyte interface of a lithium-ion half-cell system. Several parameters such as C-rate, volume fraction (porosity), viscosity, and phase transformation are considered in this study. Since it has been reported that tensile or compressive stresses are highly correlated to fractures in cathode particles [16] and highest stress is observed on the surface of electrode particles [46], we focus on normal stress on the surface of the electrode in our study.

4.1 Stress Analysis of the Porosity of Electrode-Electrolyte Interface

Model 1 aims to understand the influences of C-rate, porosity, viscosity, and lithiation on the interface between electrolyte and electrode. Figure 33a displays the velocity vector of electrolyte and Figure 33b shows dimensionless velocity profiles at different locations in the half-cell system: at the inlet boundary (marked in red, location 1), at the middle of electrolyte domain (marked in blue, location 2), and at the middle of electrode domain (marked in green, location 3). Since the maximum value at the middle of electrolyte domain is twice higher than that at the inlet boundary and non-slip boundary conditions are adopted, the electrolyte domain size is sufficient for fluid flow (i.e., electrolyte) to be fully developed. It has been observed that the maximum velocity increase by 4 times (i.e. 1/porosity) at the middle of electrode domain due to the porosity of 0.25 in the electrode.
Figure 33: (a) Velocity vector of electrolyte across electrolyte and electrode domains, and (b) velocity profiles at 3 different locations in the half-cell system (red: inlet boundary, blue: middle of the electrolyte domain, and green: middle of the electrode).

4.1.1 Effect of C-rate

Figure 34 below provides the simulation results that demonstrate the relationship between C-rates and the maximum normalized normal and shear stresses. Both normal and shear stresses increase with the increasing C-rate. This relationship was also observed in another battery chemistry (i.e., LiCoO$_2$) [46]. Moreover, the results suggest that normal stress is much higher than the shear stress and it is due to that lithium ions mainly transverse along the diffusion direction, which is normal to the electrode surface, thus higher normal stresses are generated. The similar phenomenon is also reported in LiFePO$_4$, where only electrode was simulated in that study [56]. From the results, higher C-rate results in higher stresses during discharging, suggesting damages caused by the mechanical stresses occur in the electrode. The results also provide quantitative data to support the hypothesis that batteries show the performance degradation (e.g., capacity loss) at higher C-rate.
Figure 34: Influences of varying C-rate on the normalized normal stress and shear stress (porosity of 0.25 and EC is used as an electrolyte).

4.1.2 Effect of Porosity

In the model 1, the porosity is calculated according to equation 19 below.

\[ \phi = \frac{v_v}{v_T} \]  

(19)

where \( v_v \) is the volume of the void-space, and \( v_T \) is the bulk volume of the material. Various porosities, 0.1, 0.25, 0.5, and 0.75, are considered and the resulting maximum stresses on the interface are analyzed. The plot in Figure 35 below represents that the normal stress decreases in a non-linear fashion as the porosity increases. It could be explained by the relationship of the porosity and the diffusion length in the porous media. Since decreasing in porosity causes an increase in the diffusion length, the electrolyte across the lower porosity
electrode needs to move faster to reach a fully discharging, and as a result, a larger normal stress is generated. This result is consistent with the theoretical analysis by Renganathan et al. [24]. We also conduct another simulation with a larger domain size (10μm) (not shown in this thesis), and a similar result about the effect of the porosity of the electrode to the stresses is also observed.

![Graph showing the relationship between porosity and normalized normal stress.](image)

**Figure 35:** Relationship between porosity and normalized normal stress (EC is used as an electrolyte).
4.1.3 Effect of Viscosity

Figure 36 demonstrates that normal and shear stresses increase with the increasing viscosity of electrolyte, suggesting that viscous force generated from the electrolyte has great influence. Moreover, the normal stress is affected by the electrolyte viscosity to a greater degree than the shear stress. The electrolyte Ethylene Carbonate has 3.25 times higher viscosity than Dimethyl Carbonate, and our simulation results show that the normal stress increase more than 3 times. It is confirmed that in spite of the higher conductivity properties in Ethylene Carbonate, the electrolyte with a higher viscosity plays a negative role in the battery performance due to the resulting higher mechanical stresses. It is also observed that the other properties of electrolyte, such as the molar mass and density, do not affect both normal and shear stresses that much.

Figure 36: The effect of electrolyte viscosity on normal and shear stresses at 1C (porosity of 0.25).
4.1.4 Effect of Lithiation

LiFePO$_4$ electrode undergoes a phase transformation during charging and discharging. Upon lithium intercalation and diffusion in cathode, lithium-poor phase (FePO$_4$) is transformed into lithium-rich phase (LiFePO$_4$) [11]. In this study, effect of lithiation of the electrode is incorporated and the study from ChiuHuang [56] is employed. The contour plots in Figure 37 shows lithium concentration profiles when the cathode is lithiated 20% and 80%. In this model, the property change according to lithiation stage is considered instead of C-rat dependent lithiation stage. Therefore, maximum concentration (marked in red) is imposed on the surface of lithium-poor phase electrode (marked in blue) to make concentration gradients. Concentration gradients is the driving force of lithium ion diffusion.

![Contour plots showing lithium concentration profiles](image)

**Figure 37:** Concentration profile calculated by the transient thermal module in ANSYS. Each model represents lithiation of (a) 20%, and (b) 80%.

The lithiation of the electrode is calculated by the following equation:

\[
\text{Lithiation stage} = \frac{\int_0^1 C_i \, dy}{\int_0^1 C_s \, dy},
\]  

(20)
where $C_s$ is the concentration when the surface of the cathode is fully saturated (i.e., $C_s = 1$) and $C_i$ is the concentration at $i$ ($0 \leq i \leq l$). $l$ is the total length of cathode (i.e., $0.3 \mu m$). In equation 20, $\int_0^l C_i \, dy$ indicates gray area whereas $\int_0^l C_s \, dy$ indicates sum of gray area and yellow area in Figure 38. Since lithium ion diffusion occurs proportional to the surface of the electrode, lithium-ion concentration change is completely independent along the x and z directions. Using equation 20, lithiation is calculated based on the local concentration distribution (Figure 38).

![Figure 38: Local concentration in terms of diffusion distance. Each concentration distribution shows lithiation of 20% (a) and 80% (b).](image)

As shown in Figure 39, both normal and shear stresses decrease in non-linear fashion as lithium lithiation increases, suggesting phase transformation has a great effect on mechanical stresses in the half-cell system. 80% lithiation means that electrode consists mostly of lithium-rich phase (LiFePO$_4$), while 20% lithiation indicates electrode consists most of lithium-poor phases (FePO$_4$). This trend is not consistent with the results obtained from ChiuHuang [56], and we believe it may be due to that volume misfits during lithiation.
are not included. Therefore, we reinvestigate effect of phase transformation and associated volume misfits in Section 4.3.2.

Figure 39: Relationship between stresses and lithiation stage at 1C (porosity of 0.25 and EC is used as an electrolyte).
4.1.5 Conclusion

The highest stress has been observed on the surface of electrode particles [46] and normal stresses are highly associated with the fracture in the electrode [16], therefore we focus on studying maximum normal stress on the surface between electrolyte and electrode in the model 1.

First, the effect of C-rate was investigated in Figure 34. Both normal and shear stresses increase with an increasing C-rate by adjusting inlet boundary conditions in our simulations. In other words, higher stresses at the electrode-electrolyte interface caused by higher C-rate during discharging, suggesting damages strongly related to the mechanical stresses occur in the electrode. Our results provide qualitative and quantitative information on mechanical stresses and could be used to support the experimental observation that the reduced performance such as capacity loss is caused by high C-rate discharging.

Secondly, Figure 35 portrays the effect of electrode porosity. It indicates that mechanical stresses on the electrode-electrolyte interface decreases exponentially as the porosity of electrode increases. In the low porosity electrode, an increase in diffusion length results in higher stress. Similar trend was also concluded in LiCoO$_2$ battery materials [24]. In the model with a larger domain size (10μm) (not shown in this thesis), similar result about the effect of the porosity of the electrode to the stresses is also observed.

Moreover, we also observed that an increase in the electrolyte viscosity causes higher normal and shear stresses (Figure 36). Even though high viscosity electrolyte ensures high ionic conductivity, it negatively affects the battery performance from a stress analysis point
of view. Furthermore, the results also suggest that the effects of molar mass and density of the electrolyte is less important than that of viscosity.

In case of lithium concentration, there is an inverse relationship between maximum stress and lithiation (Figure 39). That is, maximum stress on the surface decreases in a nonlinear fashion during discharging process. We suspect that it is because volume misfits during lithiation was not considered in the model 1, therefore further reinvestigation is conducted in next few sections. The results of this analysis contend that stress analysis on the surface of cathode is important during discharging process.
4.2 Multiphysics Models for Stress Analysis of Porous Electrodes

Several experiments have observed volume change (expansion and contraction) in LiFePO$_4$ cathode materials during lithiation [50][58], and therefore volume change and the pressure induced by electrolyte are considered in this study. To incorporate volume change in this study, lithiation stages are considered 10%, where 10% lithium-rich phase and 90% lithium-poor phase are included in the computational models by using the material property in Table 5. Since LiFePO$_4$ has relatively larger molar volume than that of FePO$_4$ and two phases are constrained at a coherent interface, volume misfits are observed. As shown in Figure 41, this higher volume misfit could lead to a tensile stress marked in red. On the other hand, electrolyte pressure causes compressive stress is acting on some parts of the model 2, marked in blue (Figure 41).

![Diagram](image)

**Figure 40:** Molar volume misfits when lithium-poor phase and lithium-rich phase exist.
Since maximum stress occurs on different locations in the model 2, we compare stresses at specific points: position 1, 2, and 3 (Figure 41). As expected, the stress at position 1 is much higher than stress at position 3.

![Contour plots of stress and location](image)

Figure 41: Contour plots of stress and locations of position 1, 2, and 3 in (a) electrode domain and (b) a zoom-in top view of the electrode domain. Snapshots are taken from the 1C model with the volume fraction of 15.5%.

### 4.2.1 Effect of C-rate

Figure 42 below shows that shear and normal stresses at the position 1 increase in a non-linear fashion as C-rate increases. A similar trend is also observed at the position 2 and 3. One interesting observation is that the shear stresses are higher than normal stresses. It is inconsistent with the result from model 1, however. We strongly believe that it is related to the porous electrode with multiple spherical particles. There is a need to further investigate the effect of various shapes of particles such as plate-like particles or ellipsoidal particles.
4.2.2 Effect of Volume Fraction

In this study, volume fraction is defined as the local ratio of the volume of cathode particles to the total physical volume. Because of total physical domain size is fixed, volume fraction is proportional to particle size. In Figure 43, streamlines of model 2 with various particle sizes are illustrated. It is assumed that lithium ions traverse along the streamline around spherical particles in this model. The streamlines show that the diffusion length increases with an increase in particle size, causing higher velocity of electrolyte in the space between particles.
Figure 43: Streamline of model 2 in 1C with the volume fraction of (a) 6.5%, (b) 15.5%, and (c) 30%.

Figure 44 displays contour plots of normal stress of the particle size of 75nm, 100nm, and 125nm. The models with 75nm, 100nm, 115nm, and 125nm particles have a volume fraction of 6.5%, 15.5%, 23.6%, 30%, respectively. The surface area of particles increases with the volume fraction, and it causes higher compressive stress caused by electrolyte at a higher volume fraction. Tensile stress is observed due to the volume misfits. However, this results suggest that compressive stress induced by electrolyte is more important factor than the volume misfits of particles at the stress analysis.
Figure 44: Contour plots of normal stress (y-axis) in 1C with volume fraction of (a) 6.5%, (b) 15.5%, and (c) 30% at the lithiation of 10%.

The effect of volume fraction on the normalized normal stress at each position is shown in Figure 45 below. As the volume fraction increases from 15.5% to 30% (i.e., more electrode particles), the normal stress increase by 131%. Studies have shown that with high volume fraction of cathode enabled by using nano-scale particles and carbon black [59], the higher battery performance is observed. From the stress analysis point of view, our results demonstrate that higher volume fraction of electrode (bigger particle sizes) produces higher stresses and may deteriorate the battery performance. It is also observed that the normal stress at position 1 is always higher than that at position 3. This can be explained by the
experimental results from Li et al. [20], suggesting more lithiation occurs near the electrode-electrolyte interface (i.e., more lithiation occurs at position 1 than that at position 3). Therefore, the stress induced by fluid pressure at position 1 is higher than any other position due to more lithiation at position 1.

Figure 45: Effect of volume fraction on normalized normal stress in 1C at the lithiation of 10% (EC is used as an electrolyte).
4.2.3 Effect of Viscosity

It has been reported that the most important properties of the electrolyte for ionic conductance are the viscosity and dipole moment [25]. Figure 46 below shows the effect of viscosity on the stress at each point. For each electrolyte, normal stress decreases in a non-linear fashion along the diffusion direction from position 1 to position 3. Even though the viscosity of EC is 3.2 times higher than that of DMC, the normal stress is 3.4 and 3.2 times higher when EC is used at the position 1 and the position 2, respectively. The results suggest that as the distance from the interface increases, the effect of the viscosity of the electrolyte becomes less important. Moreover, EC has 1.65 times higher dipole moment (i.e., suggesting higher ionic conductivity due to the dissociation of the lithium salt) than DMC, the stress increases more than 3 times at position 1 and 2. Even though EC has a higher dipole moment and high viscosity of electrolyte to ensure high fluidity (i.e., ionic movement), EC plays a negative role on the electrode from the stress analysis point of view. Therefore, DEC or DMC are recommended as electrolyte for lithium-ion batteries. However, EC should be added for assuring good cycling battery performance because EC shows very good film-forming ability for carbonaceous anodes [60].
Figure 46: Effect of the viscosity of electrolyte on normalized normal stress at specific location in the 1C model at the lithiation of 10% (volume fraction of 15.5%).

4.2.4 Conclusion

In the model 2, molar volume misfits and fluid pressure are considered to investigate mechanical stresses on the interface. Since Model 2 has several interfaces between the electrolyte and the electrode, the stresses at three specific positions are compared rather than the maximum stress on the interface (Figure 41).

First, the effect of C-rate was discussed in Figure 42. As expected, the maximum stresses at every position increase with the increasing C-rate. It is interesting to note that shear stresses is higher than normal stresses, which seems to be caused by the spherical shapes of particles.
Furthermore, the effect of volume fraction on normal stress at each position is investigated (Figure 45). The volume fraction is determined by the size and number of particles because electrolyte domain size is fixed. Due to a larger contact area between the electrolyte and the electrode, the model with volume fraction of 30% has 1.66 times higher normal stress than 15.5% volume fraction model at position 1. It is also observed that stress induced by fluid pressure at position 1 is always higher than any other position in the electrode and it is due to more lithiation occurs at the position 1.

Lastly, Figure 46 demonstrates the effect of viscosity on the stress at 3 locations in the electrode. It is observed that as the distance from the inlet boundary increases, the effect of viscosities is less important. Moreover, it is suggested that in spite of high conductivity property of the high viscosity electrolyte (i.e., EC), resulting mechanical stresses are higher than that when other electrolyte are chosen (i.e., DEC or DME).
4.3 Phase Transformation Effect in Porous Electrodes via Multiphysics Modeling

Reasonable results are obtained from the previous models where the viscosity of the electrolyte and multiple interfaces are included, however, during the course of this thesis, several factors are also important to be included. Therefore, a third model is developed to address factors such as, the C-rate dependent volume change due to the molar volume misfits, lithiation and associated the phase transformation of the particle during discharging. Within the model 3, several simulations were carried out to better understand the influences of C-rate, volume fraction during lithiation and to reinvestigate mechanical stresses at the electrode-electrolyte interface.

4.3.1 Lithiation

To adopt the concept of lithiation, we used a thermal stress analysis approach, which has been widely discussed [44] [48] [56]. Specifically, shrinking-core model developed by Shrinvasan and Newman [11] is used and the thermal diffusivity mimics lithium ion diffusivity. In this study, mass flux of lithium ion \( J \) is expressed as heat flux, and the temperature gradient represents lithium-ion concentration gradient. The concept depends on the similarities between lithium concentration distribution equation (equation 18) and temperature distribution equation (equation 17). The process of diffusion in both electrolyte and electrode is based on Fick’s second law (equation 18). Since the concept of heat and temperature is used for diffusion and concentration of lithium ion, effects of temperature and heat on material properties are disregarded. Once mass flux of lithium ion induced on the
inlet boundary, the lithium concentration changes as diffusion occurs (i.e., lithiation proceeds). Figure 47 represents a cross-sectional view of whole model which demonstrates concentration distribution in the electrolyte and the cathode. The lithiation of particles shows lithiation of 0%, 15.8%, and 83%, respectively. In this study, it is assumed that conductivity of electrolyte and electrode are constant and the diffusion coefficient are $D_{\text{electrolyte}} = 1 \times 10^{-10} \text{m}^2\text{s}^{-1}$ [55], and $D_{\text{LiFePO}_4} = D_{\text{FePO}_4} = 1 \times 10^{-15} \text{m}^2\text{s}^{-1}$ [57], respectively. Thus, the concentration of electrolyte changes more rapidly than that of the cathode. Even though lithium concentration of electrolyte indicates 100% concentration, only a surface of particles shows 100% concentration (i.e., fully saturated) and the lithiation of the electrode is still in progress.

![Concentration distribution](image)

**Figure 47: Concentration distribution at the lithiation of (a) 0%, (b) 15.8%, and (c) 83% in cathode in a 1C model (volume fraction of 15.5%).**

In Figure 48a demonstrating a full contour plot at lithiation of 50%, high concentration of lithium ion is marked in red and low concentration of lithium ion is marked
in blue. Figure 48b portrays a 10-nodes tetrahedral (T10) type element, which is used in this simulations. Based on the data from each element, lithiation of electrode can be calculated by following equation:

\[
\text{Lithiation stage} = \frac{\sum_{i} V_{i} \times \left( \frac{\sum_{j=1}^{10} C_{j}}{10} \right)}{V_{T}},
\]

where \( i \) is the number of elements, \( j \) is the number of nodes (10 nodes in each element), \( V_{T} \) and \( V_{i} \) indicates volume of particles for each element, and \( C_{j} \) is concentration of lithium ion at each nodes.

![Figure 48](image-url)

**Figure 48:** (a) Contour plot of lithiation at 50% lithiation in 1C (volume fraction of 15.5%), and (b) a 10-nodes tetrahedral type element.

Figure 49 shows contour plots of the electrode at various lithiation stages. When lithium ions insert into lithium-poor phase particles, lithium-rich phase is initially formed on the surface of particles (Figure 49a-c). While the phase boundary moves toward the center of the particle, the thickness of lithium-rich phase increases (Figure 49 d-g). At the last stage of lithiation (Figure 49h), only lithium-rich phase particles are observed.
Figure 49: Contour plot at lithiation stage of (a) 0%, (b) 5%, (c) 10%, (d) 20%, (e) 30%, (f) 50%, (g) 75%, and (h) 100% for 1C model with volume fraction of 15.5%.

4.3.2 Effect of C-rate

Figure 50 below displays contour plots of normal stress in the models with volume fraction of 30% in 1C and 6C, respectively. The stress field within the particles shows concentric, which is caused by the lithium concentration field shown in Figure 48a. As C-rate increases, the increases in the tensile and compressive stress are observed. The six times larger C-rate causes 1.62 times larger in tensile stress and 1.18 times larger in compressive stress. It is concluded that the tensile stress is strongly affect by C-rate. Moreover, higher tensile stress is observed near the center of particle, called diffusion-induced stress. The magnitude of maximum compressive stress is 4.05 and 2.94 times larger than that of maximum tensile stress in 1C and 6C, respectively. The results suggest that contraction of particles during discharging (due to phase transformation) and fluid pressure caused by the electrolyte is dominant factors comparing to the particle volume expansion during discharging. It is interesting to point out that the area marked in red and blue continuously...
decrease in stresses as the particles located away from inlet boundary. That is, particles near an inlet boundary show a higher stress than particles near outlet current collector. It is consistent with the experimental results from Strobridge et al. [21] where inhomogeneous reaction is reported. In addition, the higher stresses of particles closer to the electrode-electrolyte interface suggested there is a need to mitigate stresses at the separator as it is the location might occur mechanical damages in the battery during discharging.
Figure 50: Contour plots of normal stress for the model with volume fraction of 15.5% at 50% lithiation in (a) 1C, and (b) 6C.
The plot portraying the effect of C-rate on normal stress during lithiation is shown in Figure 51. The results show that higher C-rate causes higher normal stress. The maximum stress for 1, 2, 6, and 8C occurs when the lithiation is 0.34, 0.38, 0.49, and 0.59, respectively. It is apparent that as C-rate increases, the peak stress occurs at a higher lithiation. Our results are supported by a mathematical study from Lim et al. [61] and they have reported that the SOC (i.e., lithiation stage) is related to the maximum increased diffusion-induced stresses when increasing the particle size and intercalation rate, with a decreased lithium diffusion coefficient in LiCoO$_2$ batteries [61]. Our results confirm that peak stresses at higher C-rate occurs at a high lithiation stage in LiFePO$_4$ batteries. Moreover, the phenomenon of initially increasing stresses followed by a decrease has been observed in LiMn$_2$O$_4$ [16] battery chemistries. We believe that this result may support the idea of that volume expansion and contraction of particles during phase transformation should be included to better capture the stress evolution during discharging, where the maximum stress is observed at relatively high lithiation stage (Figure 51) instead of at the low lithiation in our model 1 (Section 4.1.4).
Figure 51: Effect of C-rate on normal stress at the position 1 during lithiation (volume fraction of 15.5% and EC is used as an electrolyte).

Figure 52 represents a relationship between the surface concentration and the dimensionless discharging time. As C-rate increases, the lithium concentration gradients increase. Since larger lithium concentration gradients contribute to the higher stresses based on the equation 16 (Section 3.3) [61], it is concluded that higher C-rate results in a higher stress on the cathode.
Figure 52: Relationship between the surface concentration and the dimensionless discharging time for the models with volume fraction of 15.5% and EC is used as an electrolyte.

Figure 53 compares strain energy variation at different C-rates. It is observed that higher C-rate leads to a higher strain energy. Our results supports the findings from Zhang et al. [48], suggesting that higher concentration gradients cause a higher strain energy. We also observe that the strain energy increases initially, reaches a peak value, and then decreases. The high elastic energy from the high C-rate models results in the instability of battery system and particle fracture [44]. From the appearance of Figure 53, it is suggested that higher C-rate plays a critical role in the rapid variation of the mechanical strain energy between lithiation of 0.2 and 0.6. We believe that the results are directly related to the capacity loss at the high C-rate in the lithium-ion batteries.
4.3.3 Effect of Volume Fraction

Since the electrolyte domain size is fixed, each model with particle sizes of 60nm, 80nm, 100nm, and 120nm indicates volume fraction of 3.3%, 8.0%, 15.5%, and 26.8%, respectively. Figure 54 below demonstrates contour plots of normal stress for the model with volume fraction of 3.3% and 26.8%. As a volume fraction increase, the increases in the tensile and compressive stress are observed. Interestingly, tensile stress at the cathode with volume fraction of 26.8% is 1.17 times larger than that of the 3.3% volume fraction model, while compressive stress increase by 2.13 times. From these results, it is obvious that compressive stress caused by electrolyte and volume change (expansion and contraction) during lithiation is a more critical factor. Moreover, the compressive stress in the electrode is
strongly affected by volume fraction of electrode. Based on intensive literature search and review, it is the first study reporting diffusion-induced stresses from the coupled effects of electrolyte and electrode.

Figure 54: Contour plots of normal stress for the model with volume fraction of (a) 3.3%, and (b) 26.8% particle at 50% lithiation in 1C (EC is used as an electrolyte).
Figure 55 demonstrates the impact of volume fraction on normal stress in 1C and 6C models. The results suggest that normal stress increases with the increasing volume fraction (i.e., particle size). This results match up with that of model 2. As the volume fraction increases, the surface area of cathode particles, where lithium intercalation occurs, increases. Therefore, higher stress is observed in models with higher volume fraction. Moreover, we also observe that the stress increases initially, reaches a peak value, and then decreases as lithiation proceed and the models with various C-rates show peak stress occurs at nearly the same lithiation stage. Figure 55a and b are combined in to show overall results about effect of C-rate and the volume fraction (Figure 55c). Since higher volume fraction and C-rate result in higher stress, battery degradation could be expected in these conditions.
Figure 55: Effect of volume fraction on normal stress in (a) 1C, (b) 6C, and (c) combined results (EC is used as an electrolyte).

Similar trends with the effect of volume fraction are observed in Figure 56. As lithiation proceeds, the strain energy first increases and then decreases in the models with different volume fractions. The highest value of strain energy for the same volume fraction can be found at approximate lithiation of 0.5. Moreover, it can be seen that higher volume fraction shows higher strain energy. This is consistent with the observations of Strobridge et al. [21]. It has been reported that when the porosity increases, the lithium concentration gradient, which indicates battery degradation, decreases. Similarly, the lithium concentration
gradient increases with a decrease in porosity [21]. That is, when we consider the relationship between volume fraction and porosity (volume fraction + porosity = 100%), higher volume fraction causes increases in lithium concentration gradient, which is strongly related the capacity loss.

Figure 56: Effect of volume fraction on normalized strain energy (a) 1C, and (b) 6C (EC is used as an electrolyte).
4.3.4 Conclusion

Through the model 3, the effect of various parameters on normal stress and strain energy is investigated. We first calculate the lithiation from local concentration during discharging process (Figure 47). Due to the similarity between Fick’s 2nd law and heat equation, temperature gradient is used in the ANSYS simulations to represent the concentration gradient.

First, the effects of C-rate on mechanical stresses and strain energy are compared in Figure 51 and Figure 53. Normal stress and strain energy increase with the increasing C-rate. This could be explained by the relationship between the surface concentration and dimensionless discharging time (Figure 52). As lithiation proceeds, the stress and strain energy increases initially followed by a decrease after reaching the peak. Moreover, peak stresses at higher C-rate occur at high lithiation stage in LiFePO₄ battery. It is supported by the results from Lim et al. [61]. By considering volume misfits during discharging, the maximum stress is observed at a relatively high lithiation stage instead of low lithiation one with lithium-poor phase.

Next, the impact of volume fraction of the positive electrode on the magnitude of stress is portrayed in Figure 55. We observed similar trends with effect of volume fraction. The contour plot in Figure 54 suggests that increases in volume fraction increase both compressive and tensile stress in particles due to the pressure from electrolyte and the diffusion-induced stresses.
CHAPTER 5: SUMMARY AND CONCLUSIONS

In this study, the coupled domains of electrolyte and the cathode particle are modeled to investigate the evolution of stress and strain energy during lithium-ion battery discharging. Model 1, model 2, and model 3 have been developed using Fluid Flow (CFX), Transient Thermal, and Static Structural modules in ANSYS Workbench. The main objective of this research is to provide a better understanding the effect of major parameters of cathode and electrolyte on the battery performance from the stress analysis point of view.

Since the highest stress is observed on the surface of electrode particles [46] and normal stress is highly associated with the fracture in the electrode [16], stresses on the interface between electrolyte and electrode are investigated in the model 1. Through the model 1, it can be concluded that there is a linear relationship between mechanical stresses on the surface of cathode when C-rate increases (Figure 34). That is, higher C-rate results in higher internal stress inside the electrode, which may accelerate the crack initiation and progression. The impact of porosity of the positive electrode on the magnitude of stress is discussed in Figure 35. It can be seen that stress on the interface decreases exponentially as the porosity of electrode increases. This result is consistent with the results reported by Renganathan et al. [24]. Similar trend is also observed when the simulations are conducted with a smaller cubic domain (0.3μm). Among electrolyte properties, an influence of the electrolyte viscosity is crucial to the stresses on the surface of cathode (Figure 36).
However, model 1 did not consider the particle shapes, sizes, and molar volume misfits. Thus, in the model 2, we consider several details of cathode particles (Figure 29). Because of many interfaces between the electrolyte and the electrode in the model 2, the stresses at the specific position are compared (Figure 41). As expected, the stress on the forefront of particles is higher than any other particles. The relationship between the maximum normal stress and other parameters such as C-rate, volume fraction, and viscosity is discussed. It is observed that there is a linear relationship between the maximum stress and C-rate (Figure 42). From Figure 45, it is observed that the model with volume fraction of 30% shows higher normal stress than the model with a volume fraction of 23.6% due to intercalating surface in the half-cell system. It is also observed that diffusion-induced stress at position 1 is higher than any other positions due to more lithiation occurs at that location. It has been reported that this inhomogeneous reaction causes the performance degradation [7],[20],[21]. The impact of viscosity is discussed in Figure 46. As the distance from inlet boundary increases, the effect of the viscosity is less significant. It is concluded that in spite of high conductivity property of Ethylene Carbonate (EC), it is not preferred to be use EC due to its higher viscosity might results in higher mechanical stresses.

Since the model 2 did not consider phase transformation during discharging, model 3 was developed to investigate the effect of various parameters on normal stress and strain energy. From the model 3, it is observed that the stress increases initially and after that stress decrease as lithiation proceed. This trend also has been reported in LiCoO$_2$ [61] and LiMn$_2$O$_4$ [16] battery chemistries. Moreover, normal stress and strain energy increase with an increasing C-rate (Figure 51 and Figure 53). It is due to that the surface concentration gradient is higher with higher C-rate (Figure 52). The impact of volume fraction of the
positive electrode on the magnitude of stress is portrayed in Figure 55. The contour plots in Figure 54 suggest that an increase in volume fraction (i.e., particle sizes) increases both compressive and tensile stress in the half-cell system. Moreover, the higher stress on the forefront of particles has been observed in most cases. It suggests there is a need to relief stresses at a specific location on the electrode-electrolyte interface. Simulation results from three models confirm relationships between mechanical stresses and many design parameters for lithium-ion batteries. It is apparent that the impact of phase transformation dependent mechanical properties and lithium diffusion cannot be neglected for the stress prediction. Furthermore, these results can be used to predict fracture in cathode, which plays negative roles in a battery system. Our study provides quantitative information of mechanical effects in lithium-ion batteries during discharging, specifically, on the interface between electrolyte and electrode.
5.1 Future Work

In this work, the simulation models have enormous potential for a future study. It has been reported that diffusion-induced stresses could possibly lead to the occurrence of Mode I, Mode II, and Mode III fractures [56]. With an initial crack inside particles of multiphysics models, fracture mechanics can be investigated more accurately during discharging.

Since both physics (fluid flow and static structural) were already considered in our study, we could further improve both electrolyte and electrode at the same time. It has been observed that lithium ion diffusion coefficient in electrolyte and cathode is highly affected by the temperature [17],[55]. If the temperature effect in both domains is considered, mechanical stresses on the electrode-electrolyte interface could be reinvestigated. Moreover, cathode material is strongly affected by the surface formation and particle shapes. We could also improve our model by adding coating of the particles with a layer of carbon on the surface of the particle or using plate-like particles, which show higher conductivity by decreasing diffusion distance for lithium ions.

Based on the developed models, another battery chemistries could be incorporated, such as LiCoO$_2$, LiMn$_2$O$_4$ by simply changing the material properties and phase transformation mechanisms. Ultimately, the model will be improved by considering a separator and anode materials to be a whole cell system. It will allow us better understand whole battery charging and discharging mechanisms during cycling.
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[Accessed: 08-Sep-2015].


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[58] Q. Liu, H. He, Z. Li, Y. Liu, Y. Ren, W. Lu, J. Lu, E. A. Stach, and J. Xie, “Rate-Dependent , Li-Ion Insertion / Deinsertion Behavior of LiFePO 4 Cathodes in Commercial 18650 LiFePO 4 Cells,” 2014.


APPENDIX
Appendix A: Material Property and Supplementary Information

A1: Electrode Material Property Change during Discharging

\[
\text{FePO}_4 + x\text{Li}^+ + xe^{-} \rightarrow x\text{LiFePO}_4 + (1-x)\text{FePO}_4
\]

\[
\text{Temp. } = 1 \quad \text{Temp. } = 0
\]

Figure A1: Phase transformation equation.

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Figure A2: According to phase transformation, change of elastic material properties (temperature 0: lithium-poor phase, temperature 1: lithium-rich phase).

Figure A3: Thermal properties of electrode.
A2: Material Property of Electrolyte

Figure A4: Material properties of Ethylene Carbonate.
### A3: Supplementary Information on Model 1

#### Figure A5: Mesh details of model 1 in Fluid Flow (CFX) module

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Figure A6: Mesh details of model 1 in Static Structural module
Figure A7: SOLID185 3D 8-Node Hexahedral Structural Solid element
Figure A8: Lithiation stage calculation in model 1.
Figure A9: Normal stress across electrode.
## A3: Supplementary Information on Model 2

**Details of "Mesh"**

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<td>Default (7.3255e-008 m)</td>
</tr>
<tr>
<td>Growth Rate</td>
<td>Default (1.20 )</td>
</tr>
<tr>
<td>Minimum Edge Length</td>
<td>5.e-008 m</td>
</tr>
</tbody>
</table>

| + Inflation                 |            |
| Patch Conforming Options    |            |
| Patch Independent Options   |            |
| Advanced                    |            |
| Defeaturing                 |            |

| + Statistics                |            |
| Nodes                       | 12655      |
| Elements                    | 57386      |
| Mesh Metric                 | None       |

**Figure A10: Mesh details of model 2 in Fluid Flow (CFX) module**
Figure A11: Mesh details of model 2 in Static Structural module
Figure A12: SOLID92 3D 10-Node Tetrahedral Structural Solid element
Figure A13: Top view of model2 with 75nm, 100nm, and 125nm particles.

Figure A14: (a) Pressure distribution caused by electrolyte, (b) normal stress, and (c) shear stress in 1C.
Figure A15: (a) Pressure distribution caused by electrolyte, (b) normal stress, and (c) shear stress in 5C.

Figure A16: (a) Pressure distribution caused by electrolyte, (b) normal stress, and (c) shear stress in 10C.

Figure A17: (a) Pressure distribution caused by electrolyte, (b) normal stress, and (c) shear stress in 20C.
A4: Supplementary Information on Model 3

![Image of a window showing material properties for LiFePO₄]

**Figure A18:** Thermal properties of LiFePO₄ in model 3.
Figure A19: Thermal properties of ethylene carbonate in model 3.
Figure A20: Surface nodes and elements to calculate surface concentration.