

**Designing a Thermal Management System for Lithium-Ion Battery
Packs Used in Electrical Vehicles**

by

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ABSTRACT

Lithium-ion batteries are well-suited for fully electric and hybrid electric vehicles due to their high specific energy and energy density relative to other rechargeable cell chemistries. Expanding considerations have been paid to rechargeable Li-ion batteries with the developing popularity of electric vehicles and hybrid electric vehicle. However, safety problems, high cost, and poor performance in low ambient temperatures and high current rates are big obstacles for commercial utilization of these batteries. Most of the mentioned limitations could be eliminated by proper thermal management. Temperature profile of the Li-ion cells has noteworthy impacts on the performance, safety, and cycle life of the battery. That is the reason little temperature gradient can prompt incredible loss in the performance of battery packs. Lately, various analysts recommend new procedures to suggest a superior thermal management on Li-ion batteries. Keeping the battery cells in an optimum range is the primary goal of battery thermal management.

In the first part of the study, a 3D model with new multilayer approach was developed to study the electrochemical-thermal behavior of the high capacity pouch type Lithium ion battery cells. In this approach, the 1D electrochemical module was coupled with the 3D thermal module using the COMSOL program which solves the differential equations numerically by finite element method (FEM). The developed Electrochemical-Thermal model was validated with the experimental measurements. The developed model was used to study the effects of multilayer structure and the number of electrodes on thermal behavior of the batteries for the first time in the literature. Then, the effects of cell dimensions and configuration were investigated on the temperature rise and nonuniformity of the battery cells.

In the second part, an air-based and a water-based thermal management system were developed, and the cooling performance of them were optimized. As cooling system, aluminum plates with mini-channel system was designed to a single-cell and battery packs. Design parameters, for example, channel number and width, inlet flow rate, and cooling material were optimized. As cooling material, water- and air-cooling performances were compared. Pressure drop and velocity profiles inside the channels were illustrated. Both internal and external temperature profiles of a single cell and battery packs were investigated with and without cooling systems.

In the last part, the optimized cooling systems were applied on the developed 4S1P battery modules. The needed inlet flow rates and power consumption values were calculated to keep the battery pack in an optimal operation temperature range (10-40 °C). The outcomes of this work showed that using upgraded mini-channel cooling plates adequately controls the temperature level and uniformity of the single cells and battery packs. With increasing the inlet flow rate, cooling efficiency can be as high as 60%.

ÖZET

Yüksek enerji ve güç yoğunluklarına sahip olmasından dolayı Li-iyon pillerin kullanım alanları gün geçtikçe artmaktadır. Özellikle yüksek güç gerektiren uygulamalarda getirdiği hacimsel ve ağırlıksal avantajlar otomotiv sektörünün de dikkatini çekmiştir. Sürekli değişkenlik gösteren yakıt fiyatları ve fosil yakıtların sebebiyet verdiği emisyon hacimleri elektrikli araçları alternatif taşıma araçları olarak sunmaya başlamıştır. Petrol üretimi olmayan ülkelerde elektrikli araçların kullanımının arttırılması, enerjide dışa bağımlılığı azaltılabilecek ve buna bağlı olarak da temiz enerji kullanımının çevresel etkileri kısa vadede görülebilecektir.

Her ne kadar Li-iyon bataryaların kullanımı teşvik edilse de güvenlik sorunlarından dolayı kullanım alanları yaygınlaşamamıştır. Isıl sürüklenmenin mümkün olduğu Li-iyon piller için gerekli önlemler alınmaz ise bataryanın yanması veya patlaması kaçınılmazdır. Bununla birlikte eğer optimum sıcaklıkta şarj-deşarj döngüsünde çevrilmez iseler bataryanın çevrim ömrü büyük oranda etkilenmekte ve kullanım süreleri azalmaktadır. Düşük sıcaklıklardaki gösterdiği zayıf performansı ile sadece soğutma değil aynı zamanda bataryayı ısıtmanın da önemli olduğunu görülmüştür. Bu sebeple Li-iyon pillerinin özellikle yüksek enerji ve güce ihtiyaç duyulan sistemlerde güvenle kullanılması için ısıl yönetim sistemlerinin özenle tasarlanması gerekmektedir.

Çalışmanın ilk bölümünde, yüksek kapasiteli poşet tipi Lityum iyon pil hücrelerinin elektrokimyasal-termal davranışını incelemek için yeni çok katmanlı yaklaşıma sahip bir 3D model geliştirilmiştir. Bu yaklaşımda, 1D elektrokimyasal modülü, diferansiyel denklemleri sonlu elemanlar yöntemi (FEM) ile sayısal olarak çözen COMSOL programı kullanılarak 3D termal modül ile birleştirildi. Geliştirilen Elektrokimyasal-Termal model deneysel ölçümlerle doğrulandı. Geliştirilen model, çok katmanlı yapı ve elektrot sayısının bataryaların ısıl davranışları üzerindeki etkilerini incelemek için kullanılmıştır. Daha sonra, hücre boyutlarının ve konfigürasyonunun, pil hücrelerinin sıcaklık artışı ve birörnekliliği üzerindeki etkileri araştırıldı.

İkinci bölümde, hava ve su bazlı bir termal yönetim sistemi geliştirildi ve soğutma performansı optimize edildi. Soğutma sistemi olarak, mini kanal sistemli alüminyum plakalar, tek hücreli ve pil paketlerine göre tasarlanmıştır. Tasarım parametreleri, örneğin, kanal sayısı ve genişliği, giriş debisi ve soğutma malzemesi optimize edildi. Soğutma malzemesi olarak su ve hava soğutma performansları karşılaştırıldı. Kanalların içindeki basınç düşüşü ve hız profilleri gösterildi. Tek bir hücrenin iç ve dış sıcaklık profilleri ve batarya paketleri soğutma sistemleri olan ve olmayan incelenmiştir.

Son bölümde, geliştirilen 4S1P akü modüllerine optimize edilmiş soğutma sistemleri uygulanmıştır. Pilleri optimum çalışma sıcaklığı aralığında (10-40 °C) tutmak için gereken giriş debisi ve güç tüketimi değerleri hesaplandı. Bu çalışmanın sonuçları, optimize edilmiş mini kanallı soğutma plakalarının kullanılmasının, tek hücrelerin ve pil paketlerinin sıcaklık seviyesini ve homojenliğini yeterince kontrol

ettiğini gösterdi. Giriş debisinin arttırılmasıyla soğutma verimliliği% 60'a kadar çıkabilir.



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ABBREVIATION

SLA	Single-layer approach
MLA	Multilayer approach
WCS	Water-cooling system
ACS	Air-cooling system
BTMS	Battery thermal management system



1 Chapter 1: Introduction

Fossil fuels are the main sources for supplying the world's energy demand. However, the world's energy policy is experiencing fundamental changes because of the environmental issues associated with the fossil fuels¹. The emission of carbon dioxide originating from the use of fossil fuels are among the key drivers of global climate change², air pollution, acid precipitation, ozone depletion, forest destruction, and emission of radioactive substances. The aforementioned issues need to be eliminated or diminished to achieve a bright energy future with minimal environmental impacts³.

Increasing global demand for energy associated with the world's decreasing fossil fuel reserves leads into ascending energy price. One solution to the approaching energy shortage is to make much more use of nuclear energy. However, reliability of nuclear energy as an alternative source for fossil fuels is argumentative. Furthermore, the issue of nuclear waste disposal is another obstacle. For example, after the Fukushima disaster in March 2011, Belgium closed nuclear plants between 2015 and 2025⁴.

The environmental issues associated with the fossil fuels and nuclear energy, necessitate usage of renewable energy sources. The main advantages of renewable technologies as clean energy sources are minimized environmental impacts and minimum secondary wastes production⁵. The main renewable energy sources include biomass, hydropower, geothermal, solar, wind and marine energies^{6, 7}. However, renewable energy sources are limited, and they are not sustainable in most regions. Therefore, high efficiency energy storage systems are needed to store the produced energies⁸. Storage systems including batteries (BESS), pumped hydro (PHS), flywheels (FES), compressed air (CAES), ultra-capacitors (UC), super magnetic energy storage (SMES), and hydrogen store energy in various forms like electrochemical, potential, kinetic, pressure, electromagnetic, chemical, and thermal⁹⁻¹¹.

Super capacitors and batteries play a crucial role in the storage of the electrical energy both in large-scale global energy systems and in more small-scale energy systems such as mobile devices. Besides mobile electric and electronic devices, increasing attentions have been paid to electrical vehicles (EVs) and hybrid electrical vehicles in terms of energy storage¹¹.

1.1 Electrochemical energy storage

Electrical Energy Storage (EES) is the process of converting electrical energy in to a form that can be converted back to electrical energy when needed. This process provides an opportunity to produce and store electricity of low demand and low generation cost and use it when either demand and generation cost is high, or electricity generation is limited¹²⁻¹⁶. Since storing electricity in the form of electricity is not either cheap or easy process, therefore it is stored in other forms to be used later. Our research focuses on electrochemical energy storage (Lithium ion batteries) and other EES systems are out of our research scope. Rechargeable batteries are the oldest form of

electricity storage devices that convert the chemical energy of the active material directly in to the electrical energy through a redox reaction. Figure 1.1 show the *Ragone* plot for the common energy storage devices; batteries, fuel cell, and capacitors.

Depend on the capacity of the batteries, a defined amount of electricity could be stored in the form of chemical energy by charging and converted to electricity by discharging the battery. During a charging process, an external electrical source applies to charge the cells. During a discharge, the released electrons from the electrochemical reactions are flowing through an external circuit to provide electricity. A battery is composed of several cells that are connected in series or parallel based on the defined capacity and voltage requirements. Each cell is composed of several layers and each layer is composed of five elements; positive and negative current collector, anode and cathode where the electrochemical reactions take place, and electrolyte/separator to enable ion exchange and prevent a short circuit between positive and negative electrodes¹⁷. Several types of rechargeable batteries have been developed that are discussed below:

1.1.1 Lead-acid batteries

Lead-acid batteries are the first known type of rechargeable batteries that are invented by Gaston Plante in 1859. It comprises lead metal, lead dioxide, and an electrolyte containing sulfuric acid and water. There are two major types of lead-acid

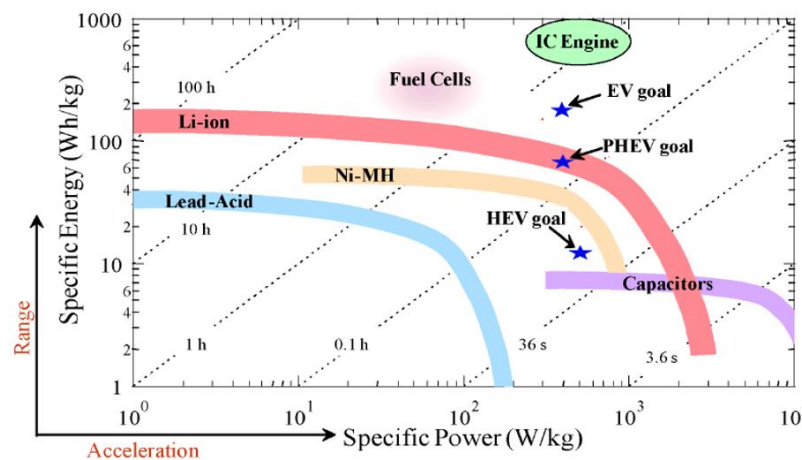


Figure 1.1 Ragone plots (specific power density versus specific energy density) for different batteries and energy storage devices¹⁸.

batteries including the flooded type which is used in automotive and industrial applications, and the sealed type which is used as power supplies.

Lead-acid batteries have high power density, high efficiency (70 – 90 %), and low cost (\$300–600/kWh) which makes them a popular choice for power supply, and power quality applications. However, low energy density (30–50 Wh/kg) and low cycle life (500–1000 cycles) makes these batteries unsuitable for energy storage applications¹⁹.

1.1.2 Nickle Metal Hydride batteries

Nickel Metal Hydride battery is the combination of positive nickel hydroxide, negative metal hydride, and nylon as a separator. As electrolyte material, KOH is filled between two electrodes. During charge state, the anode is in the metal hydrate form, and the cathode is in a nickel oxyhydroxide form. During discharge, the metal hydride is dehydrogenated to a metal alloy and hydrogen, which is electrochemically oxidized and combined with OH^- to form H_2O ²⁰.

NiMH batteries were used in the first type hybrid vehicles ¹⁹. These batteries offer specific energy up to 80 Wh/kg and they could operate even at higher current rates like 8C (8 Coulomb's). Due to the simplicity and aqueous electrolyte, NiMH cells in different sizes for different applications could be build, and they are still preferred as rechargeable batteries.

1.1.3 Sodium-Sulfur and Sodium-Metal Halide Batteries

Sodium-sulfur (Na-S) batteries comprises sodium and sulfur as the anode and cathode active materials, respectively. Both sodium and sulfur are light elements and subsequently they have high diffusion rates that makes Na-S batteries to benefit from high capacity and high energy density²⁰. High temperate sodium-sulfur battery technology brought new possibilities in energy storage applications since 1960. Sodium β -alumina, which is used as an electrolyte for Na-S batteries, show high ionic conductivity at 300 °C close to that of aqueous H_2SO_4 . This property of Sodium β -alumina makes it promising electrolyte to be used as a solid electrolyte in a high temperature electrochemical cell¹⁷. Synthesis and production of Na-S batteries require serious effort because of high temperature and corrosive media. However, after fabrication, these batteries require insignificant maintenance which makes them well candidate for large-scale energy storage applications.

1.1.4 Li-ion batteries

Compared to other commercially used batteries, lithium-ion batteries are known by high specific and volumetric energy density, high power output, and long cycle life²¹. With the developing fame of electric vehicles (EVs) and hybrid electric vehicles (HEVs), expanding consideration have been paid to rechargeable Li-ion batteries.

As shown in Figure 1.1, Li-ion batteries features with higher energy density, and higher specific power density compared to other battery types making them promising alternative energy source for vehicles. Nevertheless, due to the safety issues, high cost, and poor low temperature performance, these batteries have not been broadly conveyed industrially, which are difficulties identified with the thermal, and security issues²². LiFePO_4 as an active material (AM) for cathode, is a very promising material compared to the other materials such as LiCoO_2 , and LiMn_2O_4 due to the minimal cost, better safety profile, low toxicity, and a long cycle life.

1.2 Research objectives

Temperature profile of the Li-ion cells play a critical role on the capacity output, power output, security, calendar life, and cycle life of the battery. That is the reason little temperature change can prompt extraordinary loss in the performance of battery packs²³. As of late, building up another strategy to infer a superior thermal management on Li-ion batteries altogether has pulled in consideration of numerous investigates²⁴. Keeping the battery cells inside an ideal temperature run is the fundamental goal of battery thermal management and this venture. Following are the specific aims we cover in this project:

1. Improving a mathematical model for 20Ah cells to investigate Li-ion batteries electrochemical-thermal behavior throughout charge and discharge steps.
2. Investigating the effect of the number of layers and cell dimensions in battery performance.
3. Achieving desired capacity and voltage by designing proper cell modules considering the space that the battery occupies and the proper cooling system.
4. Calculation of the total heat increase produced during charge and discharge process in different modules at different ambient temperatures and different current rates, and specification of the needed cooling system characteristics.
5. Specification of the mini-channels cooling system designing parameters (such as the fluid to be used, inlet mass flow rates, mini-channel dimension and design, a number of cooling channels, the fabrication material, and the power needed for cooling system operation, based on the internal and external temperature distribution.
6. Improving a prototype based on the simulation results.
7. Comparison of the experimental and computational results.

1.3 Thesis structure

The thesis is organized as follows:

Chapter1: Introduces research importance along with the objectives.

Chapter 2: Covers literature review in electrochemical-thermal modeling of lithium ion battery along with the developed thermal management systems.

Chapter 3: Discusses the electrochemical-thermal model development and includes electrochemical model results.

Chapter 4: Includes the thermal model results, and discusses the effects of cell layers number, and cell dimensions on the thermal behavior.

Chapter 5: This chapter is about developing a thermal management system, and optimizing the design parameters including the channel width, the number of channel passes, inlet mass flow rate, and coolant type.

Chapter 6: Includes developing the battery modules experimentally and using the model. It also includes cooling performance of water-cooling system and air-cooling system at different ambient temperatures and different current rates.

Chapter 7: Covers the summery and future work.



2 Chapter 2: Literature Review

In this chapter, first, challenges associated with rechargeable batteries used in electrical vehicles (EVs) and hybrid electrical vehicles are discussed. Then, thermal management systems which are used to improve the electrochemical-thermal behavior of the batteries, are reviewed. Finally, the existing electrochemical-thermal models in the literature are reviewed.

2.1 Challenges with rechargeable Li-ion batteries used in EVs and HEVs

The application areas are increasing for the Li-ion battery technology with a high energy and power density. Particularly in hybrid and electric vehicles, their widespread applications attract many attentions^{25, 26}. It is expected that Li-ion batteries will be widely used in the near future²⁷. A typical electric vehicle battery comprises many Li-ion batteries coming together to provide enough power. Having a compact structure alongside its cost, safety, and the need to work at low temperatures is an inevitable necessity for the batteries used in EVs and HEVs. To solve these problems, there have been many efforts to develop new electrodes and electrolyte materials with better properties²⁸. Studies have shown that the active materials used in the electrodes are directly affected by the temperature of the cell²⁹.

Nelson et al. showed the necessity of a thermal management system if the long-term outcome of the "Freedom CAR and Vehicle Technologies" program is planned to be achieved³⁰. If the batteries are to be used for a long time, it is necessary to perform well temperature control and to operate at the optimum temperature range. Capacity utilization and cycle life of batteries operated at the optimum temperature

Table 2.1 Comparison of performance of current lithium ion cells

Cathode	LCO	LMO	NCA	NMC	LFP
Energy	Good	Good	Good	Good	Medium
Power	Medium	Medium	Medium	Medium	Good
Safety	Bad	Medium	Bad	Medium	Good
Cost	High	Low	High	Medium to High	Good
Low temperature	Medium	Medium	Good	Medium	Medium
High temperature	Medium	Bad	Good	Medium	Good
Cycle life	Bad	Medium	Good	Medium	Good

Calendar life	Good	Good	Good	Good	Good
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range increase and face none security threats. However, in a constantly changing current densities such as EV, inevitably, the batteries are exposed to different environments. Using the batteries in the mentioned circumstances leads to serious safety problems and so many researches are conducted to solve the safety issues related to the Li-ion batteries.

The performance of the electric vehicles according to the cathode chemistry was evaluated by Element Energy (Table 2.1) ³¹. It is emphasized that LiFePO_4 , which is the most effective one in terms of safety and cost, will be used in electric vehicles during the next ten years. For this reason, LiFePO_4 -based battery is being developed by many researchers ³²⁻³⁸. In the past, the batteries which were producing in a cylindrical structure with a low capacity (2.2 Ah), are now being produced in a compact and layered structure as high capacity (20 Ah) pouch type cells to be used in electrical vehicles. Today, lithium iron phosphate is known as the safest cathode material for the Li-ion batteries ³⁹.

In order to approach the 20 Ah capacity, the manufacturers produce cells either with large dimension and a smaller number of layers or with small dimensions and a greater number of layers.

There have been many efforts to investigate the components of the cell separately to develop the electrochemical-thermal characteristics of the batteries. To study the power performance of Lithium batteries, the details of carbon coating ⁴⁰, metal loading ⁴¹, electrical conductivity ⁴², particle size ⁴³, electrode thickness and porosity⁴⁴⁻⁴⁶ have been investigated precisely. All the mentioned parameters especially the electrode thickness have significant impacts on thermal issues of the lithium ion battery cells that are reviewed in the following section:

2.2 Thermal issues of Lithium ion battery

There have been many studies on effects of temperature rise and temperature nonuniformity on electrochemical and thermal performances of Li-ion batteries. In this section, common thermal issues of the Li-ion batteries such as capacity and power fading, Self-discharge, Thermal runaway, Electrical balances, and low temperature performance of the batteries are discussed briefly:

2.2.1 Capacity and power fading:

Specific energy (i.e., capacity) and specific power are two major parameters specifying a battery performance. Both available power and available energy/capacity of the batteries are decreasing during charge/discharge processes. The processes that are known to lead to capacity/power fading include: lithium deposition (overcharge circumstances), electrolyte/active material decompositions, phase change in the insertion electrode materials, and passive film formation on the electrode and current collector surfaces ⁴⁷⁻⁵⁰ all of which are related to temperature rise and nonuniform

temperature distribution along the battery packs and within the cells. Energy loss and power loss occurs as a result of transforming of active material into inactive phase and increased internal impedance rate, respectively⁵¹. Johnson et al. showed that capacity of the commercial batteries is fading by 10-40% during the first 150 cycles (charge-rest-discharge)⁵². Deshpande et al.⁵³ showed that charging/discharging the LiFePO₄ cells at higher ambient temperatures leads into faster capacity fade and lower cycle life (Figure 2.1).

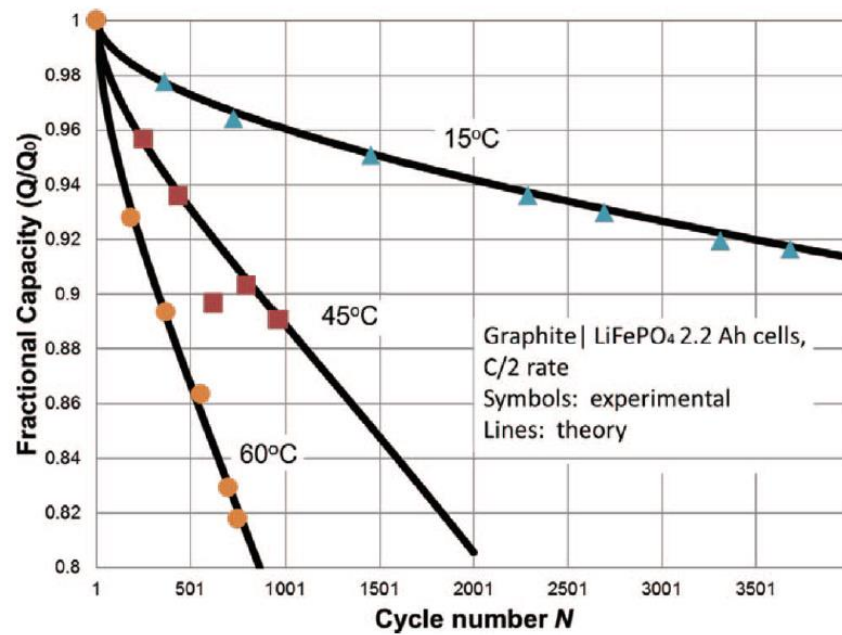


Figure 2.1. Capacity fading process of LiFePO₄ cell at different working temperatures⁵³.

2.2.2 Self-discharge:

Self-discharge is defined as a charge loss that occurs in a positive or negative electrode when the battery is not being used. Self-discharge is also a parameter that directly affects the calendar life (when the battery is not being used) of the battery. Secondary battery systems exhibit self-discharge rates ranging from 2% to 30% at room temperature, depending on system and battery configuration. The values tested in a one-month period are between 5% and 10% for lithium ion batteries. Capacity loss during storage is affected by storage conditions such as system structure and temperature. Secondary battery groups, such as lithium ion batteries, have a fast-self-discharge rate relative to the primary battery⁵⁴. At higher temperatures, Li ions on the surface of the active material dissolve in the electrolyte which results in increased electronic conductivity and rate of self-discharge⁴⁷.

2.2.3 Thermal runaway:

Thermal runaway is the process that happens when strongly exothermic reactions are accelerated by the elevated temperature. Because of thermal runaway phenomena, temperature of the cell increases due to the heat generation caused by the increasing rate of side reactions and oxygen release. The electrolyte is not stable at extreme working temperatures and is decomposed when the thermal runaway happens.⁵⁵⁻⁵⁹

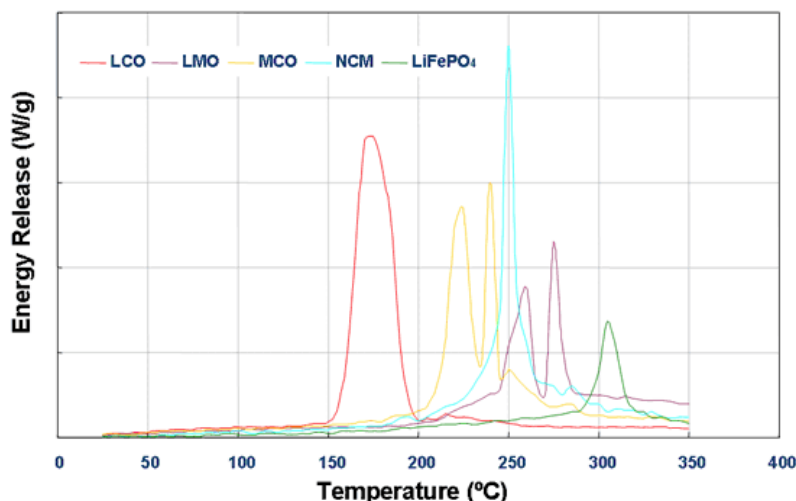


Figure 2.2. Thermal runaway point for different cathode materials (https://www.mpoweruk.com/lithium_failures.htm).

Furthermore, at high temperatures, the polymer separator melts and cause to short circuits between the cathode and the anode. Eventually as a result of metal oxide cathode material oxygen gas is released which enables burning of the electrolyte and gasses inside the cell and subsequently burning and even explosion of the battery pack if the heat is not dissipated properly⁵⁵. Figure 2.2 demonstrates the temperature at which the thermal runaway happens for different cathode materials of Li-ion cell. We can observe that Lithium Iron Phosphate (LFP) cathodes do not break down with the release of oxygen until the temperature rises to 310 °C. Furthermore, if the thermal runaway occurs in the cell with LFP cathode, much less energy is released. This could be clarified by the strong valence bond between the oxygen molecules in the phosphate material with the Phosphorus which is more difficult to break.

2.2.4 Electric balance:

Battery cells are connected in series (to achieve the desired capacity) or in parallel (to get the desired power) to get a battery module with specific features. Then the battery modules are connected again in series or parallel form to get the desired battery pack. If the capacity of the cells connected to each other in a series form does not match, then overall energy production of the battery will decrease. This can be

explained by the limitation that the weakest cell applies to the battery pack. In other words, the weakest cell will be overcharged if the battery gets fully charged. This can be dangerous for the battery and undesired side reactions could result in thermal runaway. Therefore, voltage of the single cells must be controlled to avoid electric imbalances⁶⁰⁻⁶³. Temperature of the cells directly affects their capacity and available power. Dickinson et al showed that capacity of the lead-acid batteries varies with the temperature⁶⁴. Therefore, temperature distribution in the battery modules and packs should be kept uniformly to ensure safety and better performance.

2.2.5 Low temperature performance:

Utilized power and utilized capacity rates are decreasing dramatically at low and subzero temperatures. Besides limited diffusion rate of Li ions decreased ionic conductivity of electrolyte at subzero temperatures leads to a significant drop in capacity utilization and as a result insufficient battery performance. There have been numerous research and attempts focusing on understanding the mechanisms which cause unsatisfactory battery performance at low temperatures, however, the exact mechanisms have not been fully understood yet.⁶⁵⁻⁶⁷

2.3 Review on Temperature Dependent Electrochemical Properties of Lithium Ion Batteries

The environmental issues associated with fossil fuels necessitate the use of alternative energy sources. Lithium ion batteries (LIBs) as rechargeable devices play a crucial role in electrochemical energy storage systems.⁶⁸ The application areas are increasing for Li-ion battery technology with high energy and power density. Particularly in hybrid and electric vehicles, their widespread applications attract much attention.^{25, 26} However, there is not widespread usage of these batteries due to the safety problems, cost, and thermal issues.^{21, 22, 69-71}

Battery life time and degradation rates are influenced by many external factors such as battery operating temperature, charge/discharge rate, depth of discharge (DOD), and time intervals between full charge cycles.⁷²⁻⁷⁶ Among these factors, temperature is the major parameter affecting the main aspects of the battery performance such as power output, capacity, safety, and cycle life of the battery.^{69, 77} For example, active material and electrolyte decomposition, changes at electrode/electrolyte interface (SEI layer growth, dissolution, and precipitation), and increased side reaction rates at higher operating temperatures result in capacity fading, power fading and thermal runaway.^{22, 78, 79} Similarly, reduced ionic conductivity of electrolytes, increased charge transfer resistance on electrolyte/electrode interface, high polarization of graphite anode (lithium plating), and limited diffusivity of lithium ions in electrodes result in low energy and power output at lower operation temperatures.⁷⁹⁻⁸¹ The aforementioned parameters directly influence battery economy. According to Motloch et al.⁸², 1°C temperature rise in a range of 30-40°C results in two month decrease in the battery

cycle-life. Figure 2.3 shows the optimal operation temperature range for the Li ion batteries for maximum cycle life.

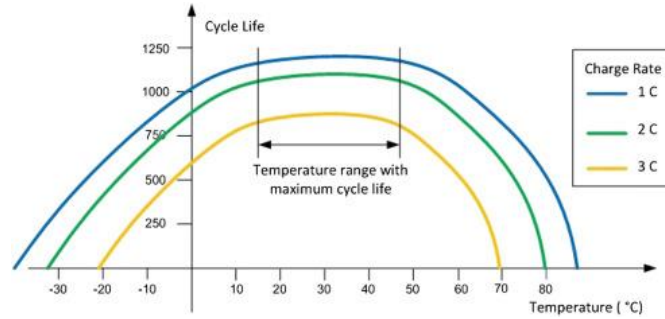


Figure 2.3. Lithium ion battery life vs. temperature and charging rate.^{72, 75, 83}

2.3.1 Thermodynamic Background

Knowledge of the thermodynamics of the Li ion batteries is essential for understanding the electrochemical behavior of the positive/negative electrode and the electrolyte during charge, discharge, overvoltage, cyclic aging and so on.⁸⁴⁻⁸⁶ Electrochemical reactions are essentially taking place on negative and positive electrode interfaces. In general, reduction or oxidation at one electrode are shown as:⁸⁴



where $< H >$ is the host structure and x is the electrode reaction advancement rate ($0 \leq x \leq 1$).

The change in the cell's standard free energy is expressed as:

$$\Delta G(x) = -nFE_0(x) \quad (2)$$

where n = number of transferred ions ($n = 1$ for Li^+), F = Faraday's constant (96,487 coulombs), and $E_0(x)$ is standard electromotive force which is given by:

$$E_0(x) = E_0^+(x) - E_0^-(x) \quad (3)$$

The change in the cell's standard free energy can also be expressed in terms of enthalpy $\Delta H(x)$ and entropy $\Delta S(x)$ as:

$$\Delta G(x) = \Delta H(x) - T\Delta S(x) \quad (4)$$

$$\Delta S(x) = F \left(\frac{\partial E_0(x, T)}{\partial T} \right)_{x, p} \quad (5)$$

$$\Delta H(x) = -F \left(E_0(x, T) + T \left(\frac{\partial E_0(x, T)}{\partial T} \right)_{x, p} \right) \quad (6)$$

where T is the absolute temperature and p is the pressure. According to the above equations, thermodynamic parameters of batteries such as enthalpy, entropy, standard Gibbs free energy, and standard electromotive force are strongly dependent on system

temperature, and, therefore, small variations in the temperature can change the crystallographic and electronic structures of the electrodes.⁸⁴

2.3.2 Energy Losses

The maximum amount of electric energy derived by the electrochemical oxidation and reduction of the electrodes is proportional to change in the standard free energy $\Delta G(x)$ of electrochemical couples as shown in equation (2). However, chemical energy cannot be fully converted to useful electric energy because of the polarization loss and cell internal impedance during discharge.⁸⁷⁻⁸⁹ The sources of polarization during charge/discharge are activation polarization and concentration polarizations which will be discussed in this section. Therefore, the cell potential E is derived as shown in equation (7):⁸⁹

$$E = E_0 \pm (\eta_a + \eta_c + iR_i) \quad (7)$$

where $\pm$ is + during charge and – during discharge, η_a and η_c are anode and cathode overpotentials, i is the charge/discharge current, and R_i is the cell internal impedance.

Activation polarization or charge transfer overpotential is the voltage loss associated with overcoming the energy barrier to the electrochemical reactions. It usually happens when the rate of oxidation or reduction reactions on electrodes are not sufficient to yield a desired current. To reduce the activation polarization, the electrode materials need to be highly porous to have maximum reaction rates. Activation polarization is a function of the operating temperature, SOC, and electrode properties, and can be expressed as in equation (8):⁸⁹

$$\eta_{ct} = \frac{RT}{\alpha nF} \ln \left(\frac{i}{i_0} \right) \quad (8)$$

The activation polarization can also be expressed as the Tafel equation:⁹⁰

$$\eta_{ct} = a + b \ln i \quad (9)$$

where $a = -\frac{RT}{\alpha F} \ln i_0$ and $b = \frac{RT}{\alpha F}$.⁹¹ Schematic representation of the Tafel equation is shown in Figure 2.4.

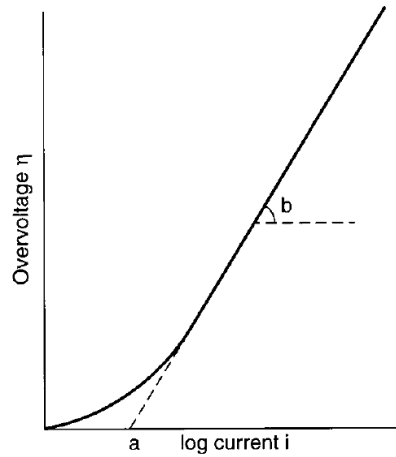


Figure 2.4. Schematic representation of the Tafel plot.⁸⁹

Concentration polarization is the mass transfer resistance associated with the concentration difference between the electrode surface and bulk of the electrolyte. To have a minimum concentration polarization, electrolyte diffusivity should be maximum to lower the mass transport limitations. The concentration polarization is given in equation (10):^{89, 92}

$$\eta_c = \frac{RT}{nF} \left(\frac{C_B}{C_E} \right) \quad (10)$$

where C_B is the bulk concentration of electroactive species, and C_E is the concentration in electrode.

The other energy loss source is the ohmic polarization or IR drop which is the voltage drop due to the internal impedance and is proportional to the current drawn from the cell. The total cell internal impedance is originated from the ionic electrolyte resistance and the electronic resistance of the electrode active material, current collectors, positive and negative tabs, and contact resistance between the current collectors and electrodes. Therefore, ionic conductivity of the electrolyte in conjunction with the electronic conductivity of the electrodes and current collectors should be high enough to lower the ohmic drop.⁹²

$$\eta_{ohmic} = -iR_i \quad (11)$$

Therefore equation (7) could be rewritten as:

$$E = E_0 \pm [(\eta_{ct})_a + (\eta_c)_a] + [(\eta_{ct})_c + (\eta_c)_c] + iR_i \quad (12)$$

equation (12) shows that some part of the useful potential is lost as a result of polarization and ohmic drop. This fact also is shown schematically in Figure 2.5. The open circuit potential (OCP) of the cathode and the anode can be approximated by Taylor's expansion as a function of the temperature and concentrations as in equation (13):⁹³

$$E_{0,j}(T, SOC) = E_{0,j}(T_{ref}, SOC) + \frac{\partial E_{0,j}}{\partial T} (-T_{ref}) \quad (13)$$

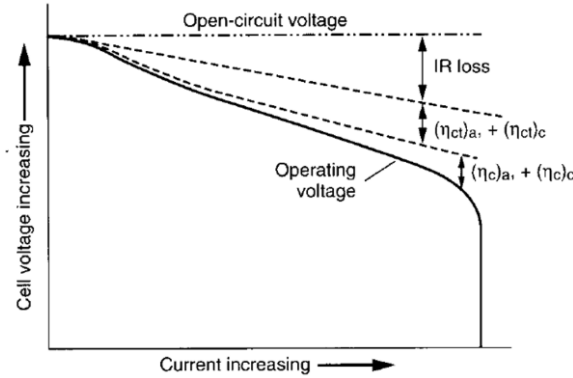


Figure 2.5. Typical polarization of a battery. ⁸⁹

2.3.3 Effects of temperature on resistances

Battery resistances are strongly temperature dependent parameters.^{94, 95} In the literature, three major resistances are considered for the Li ion batteries which are the ohmic resistance, surface film resistance, and charge transfer resistance.^{96, 97} Figure 2.6 illustrates an equivalent circuit model of the Li cell resistances.

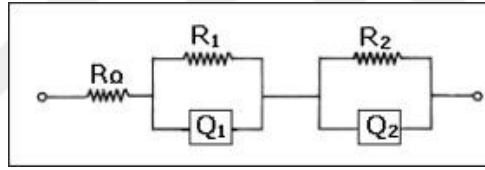


Figure 2.6. Equivalent circuit model of the cell impedances. ⁹⁸

where R_{Ω} , R_1 , Q_1 , R_2 , and Q_2 represent the ohmic resistance of the cell, resistance of the surface film on the electrode, constant phase element (CPE) of the surface film capacitance, charge transfer resistance, and constant phase element corresponding to double layer capacitance, respectively. ⁹⁸

2.3.3.1 Ohmic resistance

The ohmic resistance of the cell includes ionic resistance of the electrolyte and electronic resistance of the other cell components such as the electrodes materials, separator, current collectors, and cell terminals. In general, it specifies the capability of the cell to handle a certain current. ⁹⁹ The instantaneous voltage drop at the beginning of the discharge process is due to the ohmic resistance.

The operating temperature of the Li ion battery has opposite effects on the electrolyte ionic resistance and the electronic resistance of other electronic conductors. The ionic resistance of the electrolyte increases as the operating temperature decreases. Therefore, the more the temperature decreases, the greater the electrolyte ionic resistance will be.

However, the electronic resistivity of the electronic conductors increases with the temperature.¹⁰⁰ This can be clarified by the decreasing conductivity of the electric conductors with the increasing temperature as shown in equation (14):

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{k_B T}\right) \quad (14)$$

Andre et al.⁶² used electrochemical impedance spectroscopy to investigate the effect of operating condition such as temperature and state of the charge (SOC) on the electrochemical performance of commercial high power batteries. They showed that ohmic resistance is almost unaffected by the SOC (Figure 2.7) and it is strongly influenced by the operating temperature of the cell. Figure 2.8 shows that ohmic resistance (R_Ω) shows a nonlinear behavior with the temperature and has a three times higher value at -30°C than at 50°C .

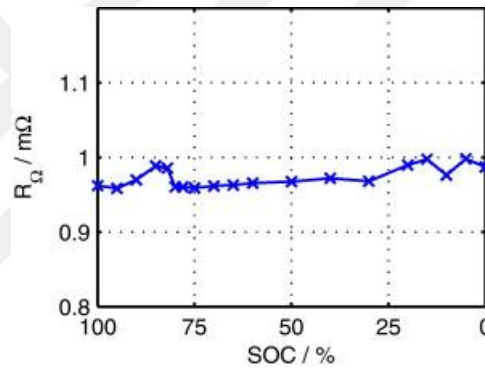


Figure 2.7. Influence of SOC on R_Ω at 24°C .

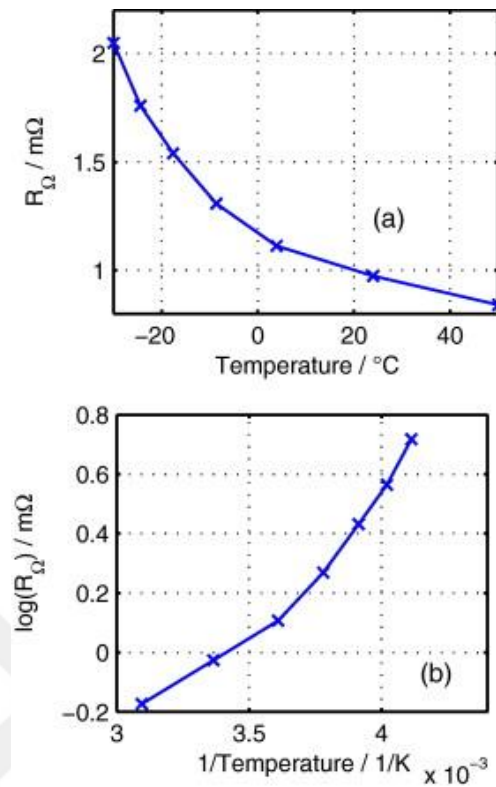


Figure 2.8. Influence of temperature (a) on R_{Ω} at 60% SOC and (b) Arrhenius plot of R_{Ω} .

2.3.3.2 Charge transfer resistance

The general form of electrochemical reactions taking place on the electrodes is shown in equation (1). The resistance associated with the charge transfer process on the electrode electrolyte interface is defined as the charge transfer resistance (R_{ct}). It is related to the reaction kinetics from the Butler-Volmer equation for charge transfer controlled electrochemical reactions¹⁰¹

$$R_{ct} = \frac{RT}{F I_0} \quad (15)$$

where I_0 is the exchange current density of the reaction, and it is a function of temperature and SOC. Suresh et al.¹⁰⁰ studied the impedance behavior of a commercial Li ion cell in the temperature range of -10 °C to 40 °C at indifferent SOC values. They calculated the values of I_0 at various temperatures and SOC values. As shown in Figure 2.9, the value of I_0 increases with both operating temperature and SOC.

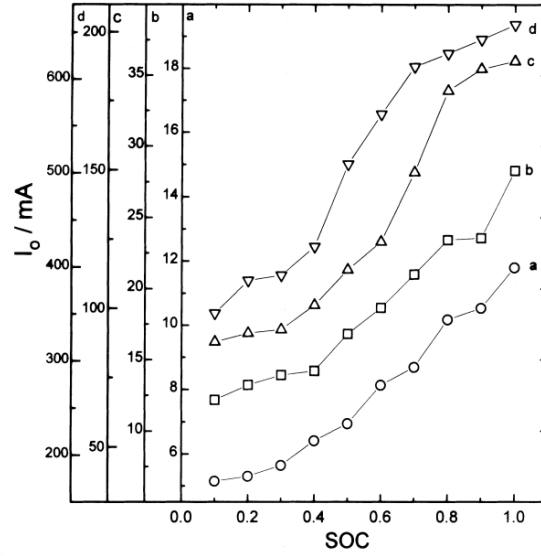


Figure 2.9. Variation of exchange current (I_0) with SOC at temperature (a) -10. (b) 0, (c) 20 and (d) 40 °C. Different scales on ordinate (a–d), respectively, correspond to the curves (a)–(d).¹⁰⁰

The exchange current density, I_0 , has a nonlinear relationship with Li ion concentration in solid phase as given in the equation below:

$$I_0 = F A k_s c^\alpha \quad (16)$$

where A , k_s , and α are electrode surface area, the reaction standard rate constant, and the transfer coefficient respectively. The solid phase concentration (c) can be given as:

$$c = c_s \cdot \text{SOC} \quad (17)$$

where c_s is the maximum concentration that can be taken from the electrode.

Therefore, c^α in equation (16) can be written as:

$$c^\alpha = c_s^\alpha \cdot \text{SOC}^\alpha = k_1 \cdot \text{SOC}^\alpha \quad (18)$$

Thus, combining equations (15), (16), and (18), we can write equation (15) as:

$$R_{ct} = \frac{RT}{F^2 A k_s k_1 (\text{SOC})^\alpha} \quad (19)$$

The reaction standard rate constant is obtained from the Arrhenius equation as a function of temperature:

$$k_s = A_0 \exp\left(-\frac{E_a}{RT}\right) \quad (20)$$

Then, equation (19) could be rewritten as:

$$R_{ct} = \frac{RT \exp\left(\frac{E_a}{RT}\right)}{F^2 A k_1 A_0 (\text{SOC})^\alpha} = \frac{kT \exp\left(\frac{E_a}{RT}\right)}{(\text{SOC})^\alpha} \quad (21)$$

where $k (= \frac{R}{F^2 A k_1 A_0})$ is a constant. The charge transfer resistance (R_{ct}) dependence on SOC and T can be obtained separately. In this approach, equation (21) needs to be written as in equation (22).

$$\ln \left(\frac{R_{ct}}{T} \right) = \ln k + \left(\frac{E_a}{R} \right) - \alpha \ln \text{SOC} \quad (22)$$

and then on differentiation, we obtain:

$$\frac{d \ln \left(\frac{R_{ct}}{T} \right)}{d \left(\frac{1}{T} \right)} = \frac{E_a}{R} \quad (23)$$

$$\frac{d \ln \left(\frac{R_{ct}}{T} \right)}{d \ln \text{SOC}} = -\alpha \quad (24)$$

By differentiation and rewriting equation (21) in terms of equations (23) and (24), Suresh et al.¹⁰⁰ evaluated the activation energy (E_a) and the transfer coefficient (α) by plotting the variation of $\ln \left(\frac{R_{ct}}{T} \right)$ with $\left(\frac{10^3}{T} \right)$, and variation of $\ln \left(\frac{R_{ct}}{T} \right)$ with $\ln \text{SOC}$. These plots are shown in Figure 2.10 and Figure 2.11, respectively.

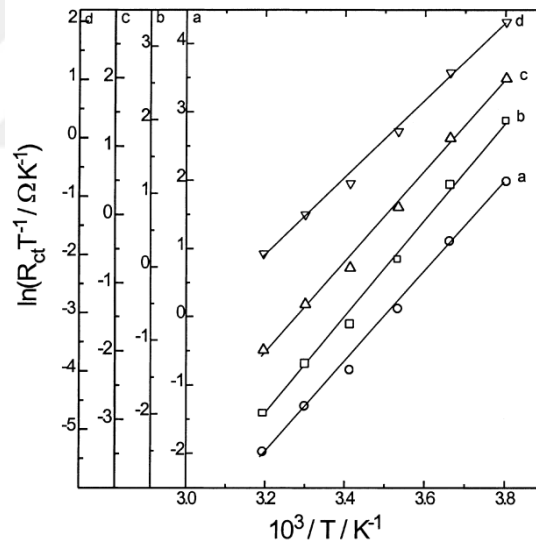


Figure 2.10. Plots of $\ln (R_{ct}/T)$ against inverse of temperature (T) for SOC (a) 1, (b) 0.8, (c) 0.5 and (d) 0.2. Different scales on ordinate (a–d), respectively, correspond to the curves (a)–(d).¹⁰⁰

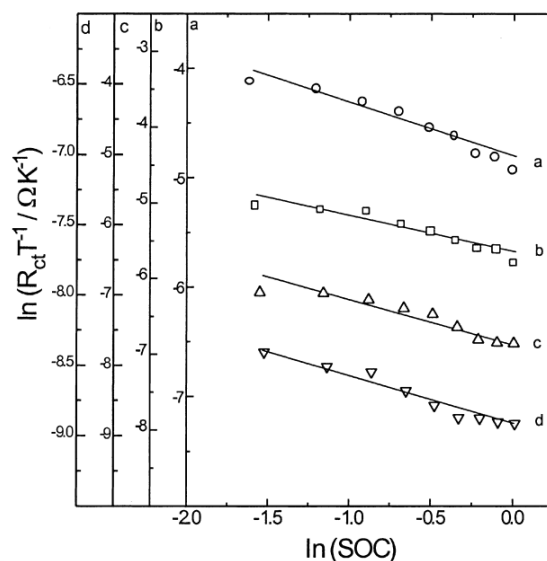


Figure 2.11. Plots of $\ln(R_{ct}/T)$ against SOC at temperature (a) -10, (b) 0, (c) 20 and (d) 40 °C. Different scales on ordinate (a–d), respectively, correspond to the curves (a)–(d).¹⁰⁰

Zheng et al.¹⁰² and Kumar et al.⁹⁸ found that the charge transfer resistance at the electrolyte/electrode interphase is the most temperature-dependent resistance source of the Li ion cells. Kumar et al.⁹⁸ showed that R_{ct} of LiCoO₂ cell drops from 4 Ω to nearly 0 Ω in a temperature range of -20 to 60 °C (Figure 2.12).

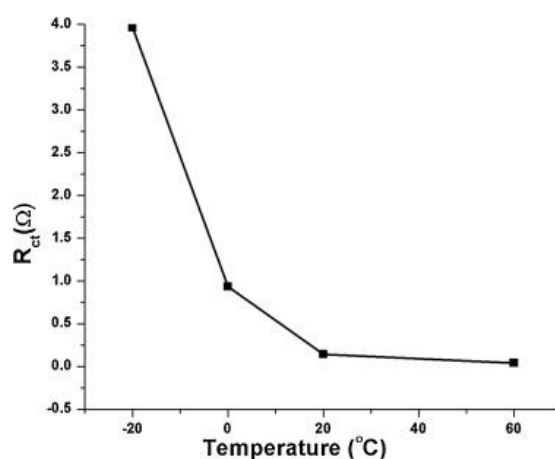


Figure 2.12. graph of charge transfer resistance against temperature.⁹⁸

2.3.3.3 Surface film resistance

The common electrolytes used in lithium ion batteries are not stable thermodynamically at negative electrode potential, and they are reduced and get chemically decomposed at the electrode/electrolyte interphase.^{103, 104} The decomposed products are not soluble in the electrolyte solution, and they precipitate and form a

protective film on the surface of electrodes. This protective layer is called solid electrolyte interphase (SEI) which protects the electrolyte components from being further reduced on the anode surface.^{78, 105} the resistance associated with the SEI layer is expressed as the charge transfer resistance (R_{SEI}). Suresh et al.¹⁰⁰ reported that the R_{SEI} is nearly unaltered with SOC, while there is a significant variance with the temperature (Figure 2.13). They showed that variation of the R_{SEI} with the temperature obeys Arrhenius' law, and its magnitude decreases with the increased temperature.

$$\frac{1}{R_{SEI}} = A_0 \exp\left(-\frac{E_a}{RT}\right) \quad (25)$$

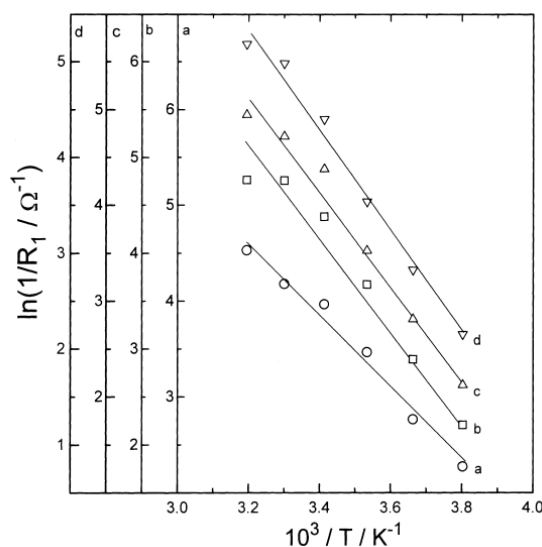


Figure 2.13. Plots of $\ln(1/R_1)$ against inverse of temperature (T) for SOC values (a) 1, (b) 0.8, (c) 0.5 and (d) 0.2. Different scales on ordinate (a– d), respectively, correspond to the curves (a)–(d).¹⁰⁰

2.3.3.4 Summary of the temperature dependence behavior of Li ion battery resistance

The effects of temperature on different cell resistances are discussed separately in the previous sections. Heins et al.⁹⁷ developed a new approach to investigate the formation process of the SEI layer on the electrode. They used temperature dependent electrochemical impedance spectroscopy to monitor and compare the respective resistances to obtain additional information about the formation mechanism of the SEI layer. Figure 2.14 shows the variation of $\ln(1/R)$ with $(1000/T)$ and the respective activation energy (E_a) values for the different resistances. It can be seen that the charge transfer resistance (R_{ct}) is the most temperature dependent resistance with the maximum activation energy value.

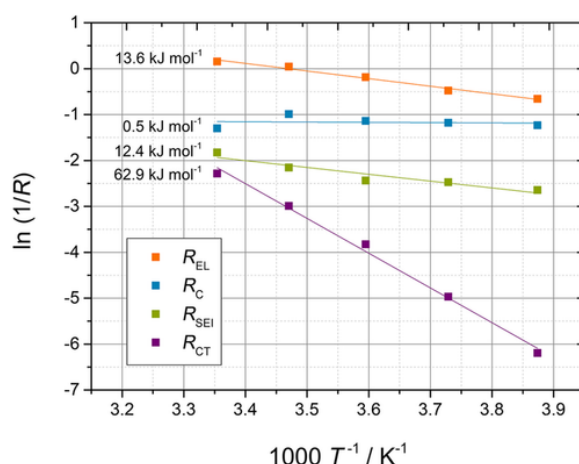


Figure 2.14. Arrhenius plots of the four identified processes derived from the resistances of the temperature-dependent spectra measured at a charge turnover of $Q=1.6$ mAh.⁹⁷

2.3.4 Temperature dependence physiochemical properties of batteries

A fundamental electrochemical model is necessary for understanding the electrochemical-thermal behavior of the Li ion batteries and designing a battery management system (BMS) and a battery thermal management system (BTMS).¹⁰⁶⁻¹⁰⁹ In the electrochemical model, the active materials are considered as spherical particles and a single particle-based physical model is being developed.^{110, 111} A simple diagram of a pseudo 2D Li-ion cell model is shown in Figure 2.15. The parameters used in the electrochemical-thermal models such as the kinetic reaction parameters, electrolyte conductivity, electrolyte and solid phase diffusivities, and open circuit voltage of the anode and cathode are mainly functions of material type, cell operating temperature, and concentration. The most temperature-dependent physiochemical properties of the Li ion cell are the electrolyte density, dynamic viscosity of the electrolyte, solid phase diffusion coefficient, exchange current density, electrolyte diffusion coefficient, electrode electronic conductivity, electrolyte ionic conductivity, and the chemical reaction rate.¹¹²

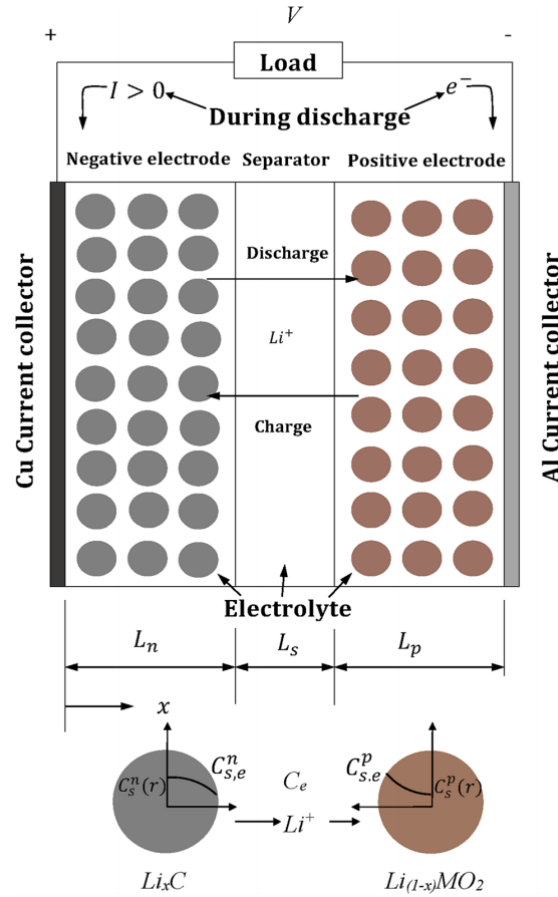


Figure 2.15. Schematic diagram of a pseudo 2D Li-ion cell model. ¹¹⁰

Zheng et al.¹⁰² reported the effect of temperature on the physiochemical properties of ionic liquid consisting of trimethylhexylammonium (TMHA) cation and bis (trifluoromethane) sulfonylimide (TFSI) anion containing different concentrations of LiTFSI salt. They fitted the experimental density and viscosity data of the TMHA- TFSI ionic liquid to the linear model shown in equation (26) and to Arrhenius' model shown in the equation (27), respectively. Figure 2.16-a shows a linear decrease of the solution density with the temperature, and Figure 2.16-b shows the decrease of the solution viscosity with the temperature for the TMHA-TFSI ionic liquid containing different concentrations of LiTFSI salt.

$$\rho = a + bT \quad (26)$$

$$\eta = A \exp\left(\frac{E_\eta}{RT}\right) \quad (27)$$

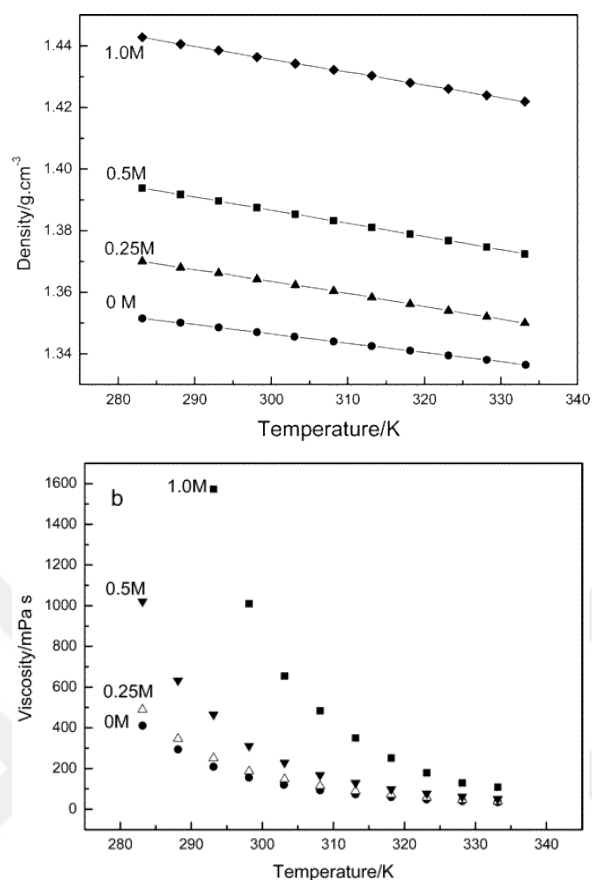


Figure 2.16. (a) Variation of solution density and (b) solution viscosity with temperature for TMHA-TFSI ionic liquid containing different concentrations of LiTFSI salt.¹⁰²

Zheng et al.¹⁰² also reported the temperature-dependence ionic conductivity for the ionic liquid containing different concentrations of LiTFSI salt which follows Arrhenius' law as shown in equation (28). Figure 2.17 shows the temperature dependence of ionic conductivity for the ionic liquid containing different concentrations of LiTFSI salt. The increase in the ionic conductivity of the solution with increasing temperatures is explained by the inverse proportion of the ionic conductivity with the solution viscosity. As shown in Figure 2.16-b, the viscosity of the solution decreases with the increasing temperature leading to easier movement and diffusion of the ions. Therefore, a decrease in the solution viscosity results in an increase in the ionic conductivity.¹⁰²

$$\sigma_e(T) = A \exp\left(-\frac{E_\sigma}{RT}\right) \quad (28)$$

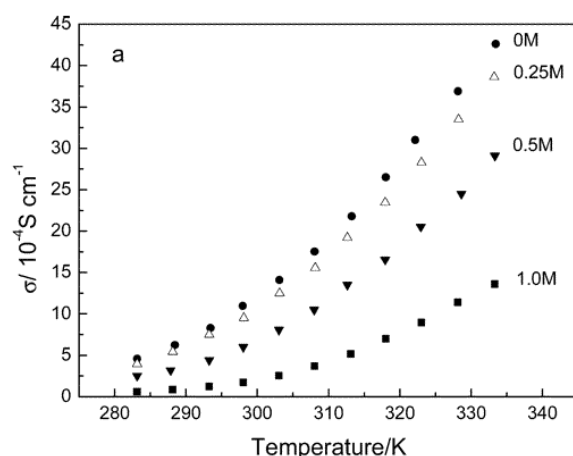


Figure 2.17. Variation of ionic conductivity with temperature for TMHA-TFSI ionic liquid containing different concentration of LiTFSI salt.¹⁰²

The temperature-dependent exchange current density can be expressed as:¹¹³

$$I_0(T) = A_{i0} \exp\left(-\frac{\Delta H_0}{RT}\right) \quad (29)$$

where the factor A_{i0} is the cell exchange current density multiplier, and ΔH_0 is the enthalpy of activation for the Li-Li⁺ reaction.

Kumar et al.⁹⁸ calculated the value of I_0 as a function of the temperature. As shown in Figure 2.18, the I_0 value changes from 5.5 to 730, when the temperature changes from -20 °C to 60 °C. Therefore, they reported that the low discharge capacity of the cell can be related to very low values of the I_0 at subzero temperatures.

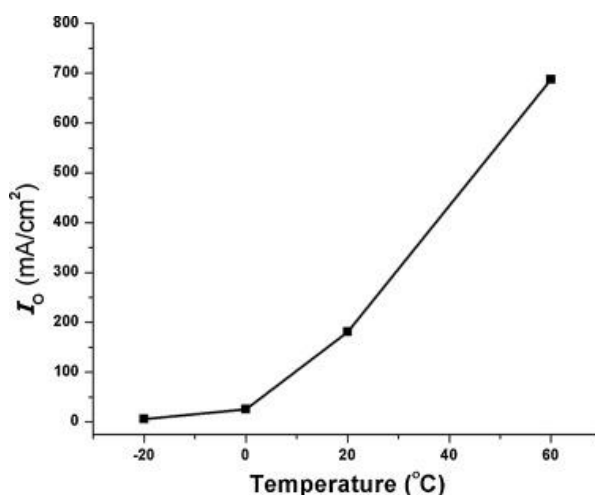


Figure 2.18. graph of exchange current density (I_0) with temperature (T).⁹⁸

The temperature dependence of the Li ion diffusion coefficient in the solid phase (D_s)^{93, 114, 115}, solid phase electronic conductivity (σ_s)¹¹⁶⁻¹¹⁸, and reaction constant (k_0)¹¹⁸, follows Arrhenius' law as in equations (30) – (33). The constant

diffusion coefficient $D_{s,Ref}$ at the reference temperature is a function of SOC, and is shown in equation (31).

$$D_s(T) = D_{s,Ref} \exp \left[\frac{E_{aD}}{R} \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right) \right] \quad (30)$$

$$D_{s,Ref} = 3.9 * 10^{-14} (1.5 - SOC)^{3.5} \quad (31)$$

$$\sigma_s = \frac{\sigma_{s,0}}{T} \exp \left(-\frac{E_a}{k_B T} \right) \quad (32)$$

$$k_0(T) = k_{0,Ref} \exp \left[\frac{E_{aR}}{R} \left(\frac{1}{T_{Ref}} - \frac{1}{T} \right) \right] \quad (33)$$

the temperature dependence of the Li ion diffusion coefficient in the electrolyte phase (D_e) is given as:¹¹⁸

$$D_e(C_e, T) = 10^{-\left[4.43 + \frac{54}{T - (229 - 5 \times 10^{-3} C_e)} + 0.22 \times 10^{-3} C_e \right]} \quad (34)$$

2.3.5 Temperature-dependence aging mechanisms

Identifying the exact aging mechanisms of Li ion batteries has been one of the main challenges for the researchers. There are numerous factors that independently influence battery capacity loss and resistance growth which make understanding of the aging mechanisms more complicated.⁵⁶⁻⁶⁰ The main factors known to influence the degradation rate of the Li ion batteries are the temperature 15, 61, low or high SOC 62, 63, and current 64. The degrading processes mainly take place in the electrodes, and there are significant differences between the aging mechanisms of positive and negative electrodes. The main known aging mechanisms can be summarized as:⁶⁵

- Structural changes of the insertion electrode
- Electrolyte decomposition
- Active material dissolution
- Phase change in the insertion electrode
- Passive film formation over electrodes and current collector surface

The operating temperature of the Li ion batteries greatly influences the electrochemical performance, cycle life, and safety of the batteries.^{5, 7, 66-68} It is also one of the main factors affecting the aging rate of the batteries. In recent years, many researchers have studied the effects of operating temperature on the aging mechanisms. Markevich et al.⁶⁹ studied the behavior of graphite electrode (comprising either synthetic flakes or round-shaped particles, meso carbon microbeads (MCMB) and meso carbon fibers (MCF)) at elevated temperature (up to 80 °C); Ramadass et al.⁷⁰ studied the capacity fade of Sony 18650 Li-ion cells at room temperature, 45 °C, 50 °C, and 55 °C; Handel et al.⁷¹ studied the thermal decomposition of the electrolyte, and Bodenes et al.⁷²

investigated the effects of high temperature on the aging process of positive electrode's binder, electrodes/electrolyte interfaces and positive active material. Uddin et al. 73 summarized the effects of high operating temperature on negative and positive electrodes, respectively. The effects of temperature on the degradation rate of electrodes will be discussed separately in the following section. The electrolyte aging mechanism is a part of electrodes aging and will not be discussed separately.

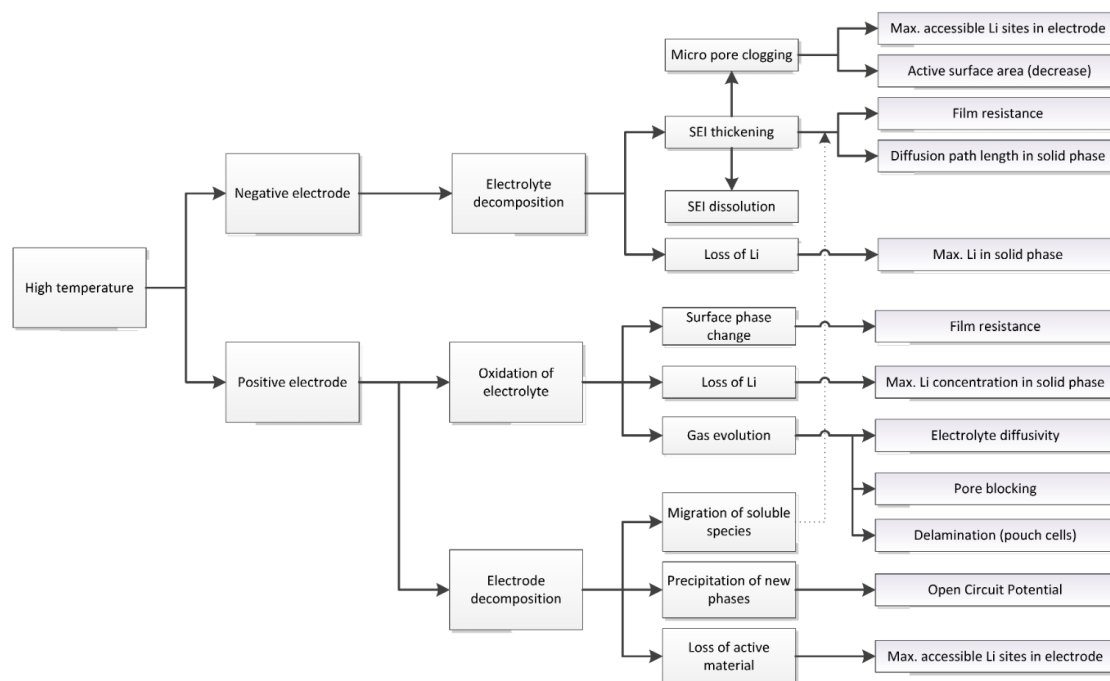


Figure 2.19. Flow chart showing the expected battery degradation caused by elevated temperatures. ¹¹⁹

2.3.5.1 Effect of temperature on the aging of a negative electrode

The most common materials chosen as the negative electrode for Li ion batteries are graphite, carbon, silicone or titanite. ^{120, 121} However, graphite anodes have some advantages over the other anode electrodes such as high capacity, low cost, long cycle life, low volume expansion, and safety. ^{120, 122, 123} The main aging mechanism of graphite electrode is believed to be formation and growth of solid electrolyte interphase (SEI) on the graphite surface with time. ⁴⁷ The SEI layer is developed through the reduction of electrolyte components and formation of passive film at zero potential on graphite surface. ^{49, 78, 124} Since the SEI layer is not fully permeable for the Li ions, the amount of recyclable Li ions decreases with the increasing thickness of SEI layer with cycles leading to capacity fading. ¹²⁵ Another possible graphite aging mechanism can be solvent co-intercalation into carbon and exfoliation of the carbon particles leading to the formation of carbon intercalation compounds (GIC). ^{126, 127} Growth of the GIC leads to irreversible capacity fading. ⁷⁴

The developed SEI layer is not thermally stable, and increased temperature can result in an increased degradation rate of the SEI layer.¹²⁸ The collapsed SEI layer must be replaced by a new one causing more Li ions to be lost. Moreover, the old broken layer fills the empty volumes resulting in decreased available surface area on an active material.¹²⁹ High temperature also accelerates formation of GIC. Leng et al.¹³⁰ used an electrochemistry-based model (ECBE) to investigate the effect of temperature on the aging behavior of a cycled Li ion battery within the temperature range of 25 °C to 55 °C. They study the impact of temperature on the aging rate of LCO electrode (cathode), graphite electrode (anode), and electrolyte separately. Figure 2.20 shows the degradation of m_2 of the cycled graphite electrode under different temperatures in which m_2 stands for the effectiveness of the graphite electrode in providing its stored Li-ions. Based on their study¹³⁰, both of the aging mechanisms of graphite electrode (SEI and GIC growth) lead into a larger degradation of m_2 at higher operating temperatures (Figure 2.20).

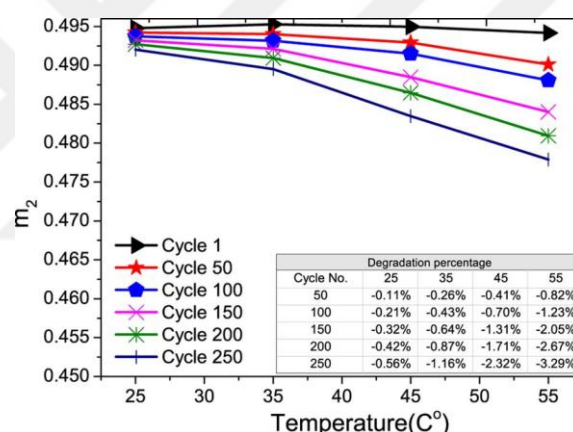


Figure 2.20. The aging of m_2 of graphite electrode vs. temperature.¹³⁰

On the other hand, the cold operating temperature in conjunction with the high charging rate and nonuniform current distribution result in lithium plating on the negative electrode.¹³¹ Lithium plating is defined as precipitation of the Li ions on the electrode surface when the potential of the electrode is very close to that of the lithium deposition potential. Therefore, lithium plating at lower temperatures decreases the amount of cyclable Li ions and results in capacity fading.^{132, 133} Uddin et al.¹¹⁹ has summarized the effects of low operating temperature on a negative electrode (Figure 2.21).

2.3.5.2 Effect of temperature on the aging of a positive electrode

Numerous studies have been done on the degradation mechanisms of the lithium metal oxide cathodes.¹³⁴⁻¹³⁷ Briefly, the changes that have been observed on the lithium oxide metals are:^{47, 78, 138-140}

- Degradation of active material

- Degradation of cathode components such as conductive agents, binder, corrosion of current collectors;
- Electrolyte oxidation and SEI formation
- Interaction between the aging products of a positive electrode (dissolved within the electrolyte) with a negative electrode

Leng et al.¹³⁰ studied the effect of temperature on degradation of LCO (LiCoO_2) cathode. Figure 2.22 shows the degradation of m_1 (defined as effectiveness of LCO electrode in storing Li-ions) with temperature during various cycle numbers. They found that degradation of LCO electrode could be related to two main mechanisms; formation of SEI layer and structural/phase change of the electrode. The aforementioned mechanisms reduce the reaction rate of Li ion insertion/de-intercalation and the charge transfer rates.^{141, 142} Furthermore, the influence of these mechanisms on degradation of the LCO electrode increases with temperature. This impact is more evident in long cycles (Figure 2.22).

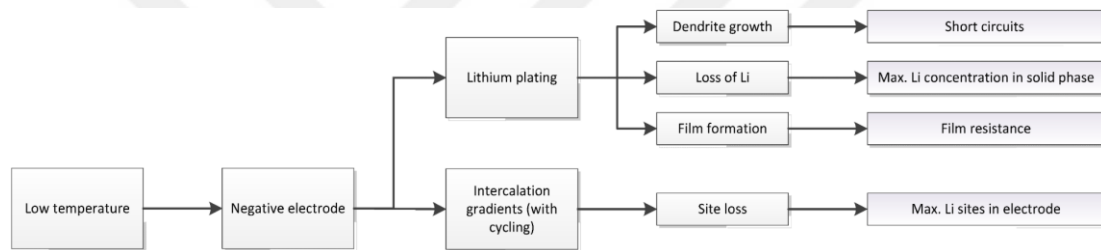


Figure 2.21. Graph demonstrating the impacts of cold temperature when cycling.¹¹⁹

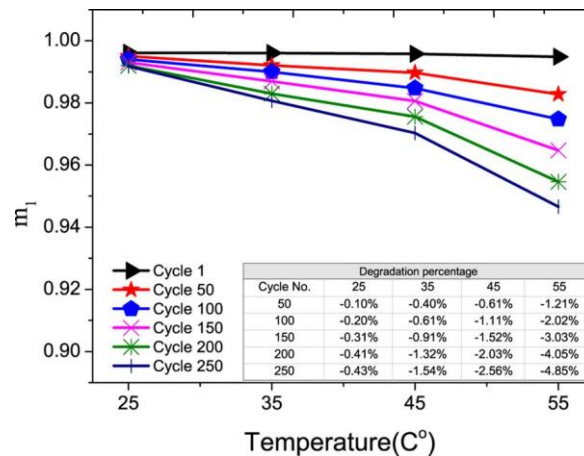


Figure 2.22. The percentage degradations vs. cycle number at various temperatures.

2.3.6 Modeling of temperature dependence degradation mechanism

Modeling the aging mechanisms and degradation rate is necessary for lifetime prognosis of the LIB¹⁴³ and reducing the time and the cost needed for the experimental aging tests.^{83, 144-146} There are numerous aging models in the literature such as models based on the neuronal networks (machine learning)¹⁴⁷⁻¹⁵², physiochemical models¹⁵³⁻

¹⁵⁵, and empirical models ¹⁵⁶⁻¹⁵⁹. Schimpe et al.¹⁶⁰ developed a detailed temperature-dependence empirical model for the calendar and cyclic aging that is reviewed in the following section.

2.3.6.1 Calendar aging model

Calendar aging is described as the capacity loss due to progress in time that occurs independent of charge/discharge cycling. The rate of calendar aging of the battery strongly depends on the temperature and SOC (potential that the battery is kept).¹⁶¹⁻¹⁶⁴ Schimpe et al.¹⁶⁰ reported a model predicting the cyclic aging with time in which the capacity loss is proportional to the square root of time.

$$Q_{l,Cal}(t) = K_{Cal}(T, SOC) \cdot \sqrt{t} \quad (35)$$

where K_{Cal} is a stress factor and is a function of time and SOC as shown in equation (36).

$$K_{Cal}(T, SOC) = K_{cal,Ref} \cdot f(T) \cdot f(SOC) \quad (36)$$

$K_{cal,Ref}$ is defined as the calendar reference stress factor at $T = 298.15$ K and $SOC = 50\%$. Schimpe et al.¹⁶⁰ proposed the following model for the temperature and SOC dependence calendar stress factor:

$$K_{Cal}(T, SOC) = K_{cal,Ref} \cdot \exp \left[\frac{-E_{a,Cal}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right) \right] \cdot \left(\exp \left[\frac{\alpha \cdot F}{R_g} \left(\frac{U_{a,Ref} - U_a(SOC)}{T_{Ref}} \right) \right] + k_0 \right) \quad (37)$$

where $E_{a,Cal}$ is the activation energy, R_g is the universal gas constant, $U_{a,Ref}$ is the open circuit potential at $SOC = 50\%$, and k_0 is a constant.

The calendar stress factor can be written separately as a function of temperature at constant SOC and as a function of SOC at constant temperature to calculate the unknown parameters by fitting the model to the experimental data. Therefore, the temperature dependence form of the K_{cal} at constant SOC can be written as in equation (38):

$$K_{Cal}(T, SOC = 50\%) = K_{cal,Ref} \cdot \exp \left[\frac{-E_{a,Cal}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right) \right] \quad (38)$$

Thus, by fitting the model data to the experimental data in a temperature range of 10 °C to 50 °C and constant $SOC = 100\%$ (Figure 2.23), the activation energy found to be 20592 J/mol.¹⁶⁰

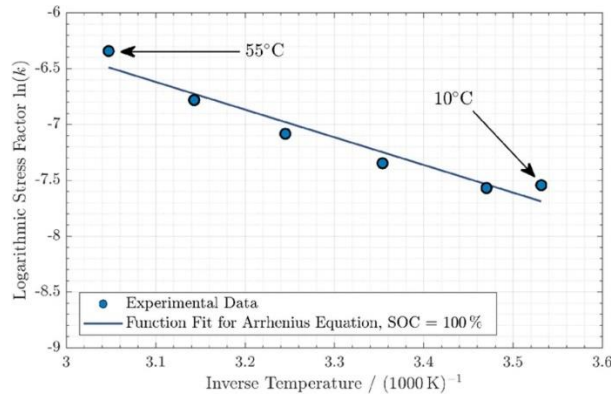


Figure 2.23. Arrhenius equation fit for temperature dependence of calendar stress factor at SOC = 100%.¹⁶⁰

The state of charge dependence of the calendar aging mechanism at constant temperature ($T = 298.15$ K) is expressed similar to the Tafel equation where the current is replaced by the calendar stress factor, and an additional constant k_0 is added as follows:

$$K_{\text{cal}}(T = 298.15 \text{ K}, \text{SOC}) = K_{\text{cal.Ref.}} \cdot \left(\exp \left[\frac{\alpha \cdot F}{R_g} \left(\frac{U_{a,\text{Ref}} - U_a(\text{SOC})}{T_{\text{Ref}}} \right) \right] + k_0 \right) \quad (39)$$

Schimpe et al.¹⁶⁰ take the values of U_a from Safari et al.¹⁶⁵ At reference temperature, $T = 298.15$ K, they set the $U_{a,\text{ref}}$ to $U_a(\text{SOC} = 50\%) = 0.1233$ V and fitted the data to Tafel equation (Figure 2.24), and they found the parameters α and k_0 to be 0.384 and 0.142, respectively.

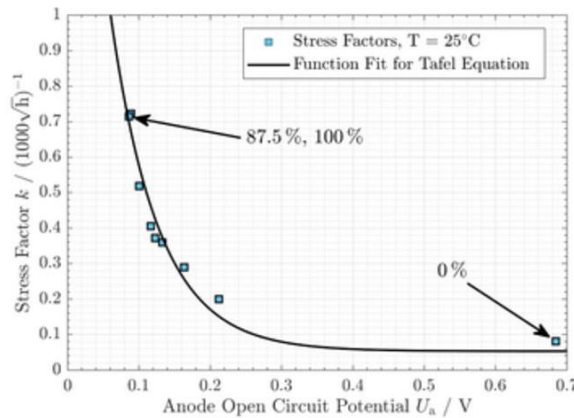


Figure 2.24. Fitting the Tafel equation function to anode open circuit potential dependence of calendar stress factor at $T = 25^\circ\text{C}$.¹⁶⁰

2.3.6.2 Cyclic aging model

Cyclic aging includes all the degradation processes when the battery is cycled in charge or driving mode.¹⁶⁶⁻¹⁶⁸ Cyclic aging mechanisms are different and depend on several factors. Schimpe et al.¹⁶⁰ proposed a model for the temperature and SOC

dependence cyclic aging and investigated the dominant cyclic aging mechanism separately. The main cyclic aging mechanisms are: ^{138, 160, 169, 170}

- High Temperature $Q_{L,Cyc,High\ T}$
- Low Temperature $Q_{L,Cyc,Low\ T}$
- Low Temperature, High SOC $Q_{L,Cyc,Low\ T\ High\ SOC}$

Thus, the temperature-dependent cycling aging models are different at low and high temperatures. At high temperatures, the cyclic aging is proportional to the total charge throughput during both charging and discharging (Q_{Tot}) as shown in equation (40).

$$Q_{L,Cyc,High\ T} = K_{Cyc,High\ T}(T) \cdot \sqrt{Q_{Tot}} \quad (40)$$

The cyclic aging stress factor is a function of the temperature which is expressed as:

$$K_{Cyc,High\ T}(T) = K_{Cyc,High\ T,Ref} \cdot \exp \left[\frac{-E_{a,Cyc,High\ T}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right) \right] \quad (41)$$

At low temperatures, the cyclic aging depends on both temperature and current rate, and it is proportional to the square root of charging aging, Q_{Ch} .

$$Q_{L,Cyc,Low\ T} = K_{Cyc,Low\ T}(T, I_{Ch}) \cdot \sqrt{Q_{Ch}} \quad (42)$$

The cyclic stress factor at low temperature as a function of the temperature and charging current is given as follows:

$$K_{Cyc,Low\ T}(T, I_{Ch}) = K_{Cyc,Low\ T,Ref} \cdot \exp \left[\frac{-E_{a,Cyc,Low\ T}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right) \right] \cdot \exp \left[\beta_{Low\ T} \cdot \frac{I_{Ch} - I_{Ch,Ref}}{C_0} \right] \quad (43)$$

where $\beta_{Low\ T}$ is a constant and C_0 is a nominal cell capacity.

The last cyclic aging mechanism is associated with the mechanism at low temperature at high SOC which is expressed as:

$$Q_{L,Cyc,Low\ T\ High\ SOC} = K_{Cyc,Low\ T\ High\ SOC}(T, I_{Ch}, SOC) \cdot \sqrt{Q_{Ch}} \quad (44)$$

For the mentioned mechanism, the cyclic aging stress factor is a function of the temperature, charging current, and SOC, and is expressed as follows:

$$K_{Cyc,Low\ T\ High\ SOC}(T, I_{Ch}, SOC) = K_{Cyc,Low\ T\ High\ SOC,Ref} \cdot \exp \left[\frac{-E_{a,Cyc,Low\ T\ High\ SOC}}{R_g} \left(\frac{1}{T} - \frac{1}{T_{Ref}} \right) \right] \cdot \exp \left[\beta_{Low\ T\ High\ SOC} \cdot \frac{I_{Ch} - I_{Ch,Ref}}{C_0} \right] \cdot \left(\frac{\text{sgn}(SOC - SOC_{Ref}) + 1}{2} \right) \quad (45)$$

The parameters obtained from fitting the data for cyclic aging can be found in the work of Schimpe et al. ¹⁶⁰

Overall, the combined calendar and cyclic aging can be expressed as follows:¹⁶⁰

$$Q_{\text{Loss}} = Q_{\text{L,Cal}} + Q_{\text{L,Cyc,High T}} + Q_{\text{L,Cyc,Low T}} + Q_{\text{L,Cyc,Low T High SOC}} \quad (46)$$

2.3.7 Effects of temperature gradient

Besides the absolute temperature of the battery cells, nonuniform temperature distribution between the battery cells and within each cell causes electric unbalances, poor battery performance, and capacity and power fading.^{25, 171-174} Temperature nonuniformity along the single cell layers causes nonuniform current density along the cell and, consequently, localized aging.^{77, 175-177} Troxler et al.¹⁷⁸ applied controlled temperature gradient between the cells of a battery pack with one hundred cells and proposed a model for the effect of temperature gradient on cell resistances. In this approach, they computed the equivalent resistance of sets of resistors that are connected in parallel, and each resistor is a function of temperature.

$$R_{\text{eff}} = \left[\sum_{i=0}^N 1/R(T(x_i)) \right]^{-1} \quad (47)$$

where R_{eff} is the effective resistor of a pack with temperature gradient between the cells, and R is a temperature dependence resistance parameter. They used Arrhenius equation to describe the solid-electrolyte interphase (SEI) resistance and charge transfer resistance as a function of temperature as in equation (48):

$$R(T) = R_{\text{ref}} \exp \left[\frac{-E_a}{R_{\text{gas}}} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \quad (48)$$

Klein et al.¹⁷⁹ studied the effects of temperature gradient on the nominal capacity of a 10Ah Li ion pouch type cell. They used a PID temperature controller to apply a controlled nonuniform temperature condition and performed Hybrid Pulse Power Characterization (HPPC) tests to figure out the instantaneous power capability effects. As shown in Figure 2.25, they found that the overpotential values increase as the temperature gradient (ΔT) increases. The overpotential sensitivity to ΔT value is more distinguished at lower temperatures. Moreover, temperature gradient influences the maximum capacity as the SOC decreases with increasing ΔT (Figure 2.25).

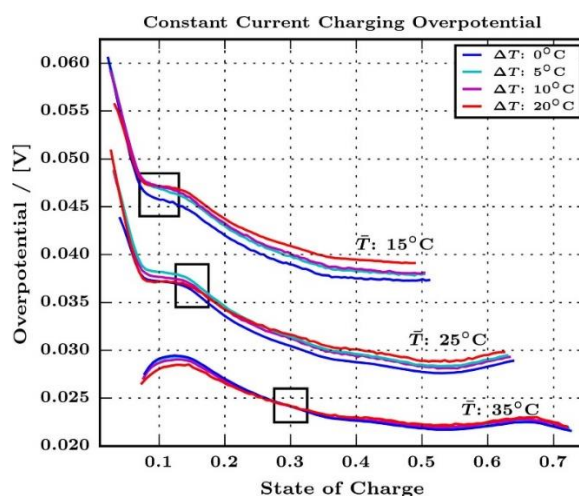


Figure 2.25. Overpotential during recharge of the cell after the US06 testing for all temperature conditions. Boxes show the focuses where the overvoltage conduct enunciation is first watched.¹⁷⁹

Hunt et al.¹⁸⁰ investigated the performance and aging of lithium ion batteries under three different cooling methods: cell tab cooling, cell surface cooling, and forced air convection cooling. Figure 2.26 shows the capacity fading results of 5Ah NCM cathode pouch cells tested for 1000 cycles at 20 °C and discharge rates of C/20, 1C, and 6C. Cell T, Cell S, and Cell C are referring to tab-cooled cell, surface-cooled cell, and convection-cooled cell, respectively. At lower discharge rate (C/20), capacity losses were small and approximately similar for all three cells (Figure 2.26-a). At 1C and 6C, cells were tested during run 1 and run 2, referred to as Cell C1, Cell S1, and Cell T1 during the first run, and referred to as Cell C2, Cell S2, and Cell T2 during the second run. At higher discharge rates, surface cooling resulted in higher capacity loss. Figure 2.26c shows that capacity loss for a surface-cooled cell is approximately three times higher than the capacity loss of tab-cooled and convection-cooled cells. They explained this phenomenon through two effects. The first effect was the temperature nonuniformity between the outer and central layers of the surface-cooled cell which results in nonuniform impedance and current distribution between the layers. The second effect was the localized aging caused by nonuniform temperature and current distribution.¹⁸⁰

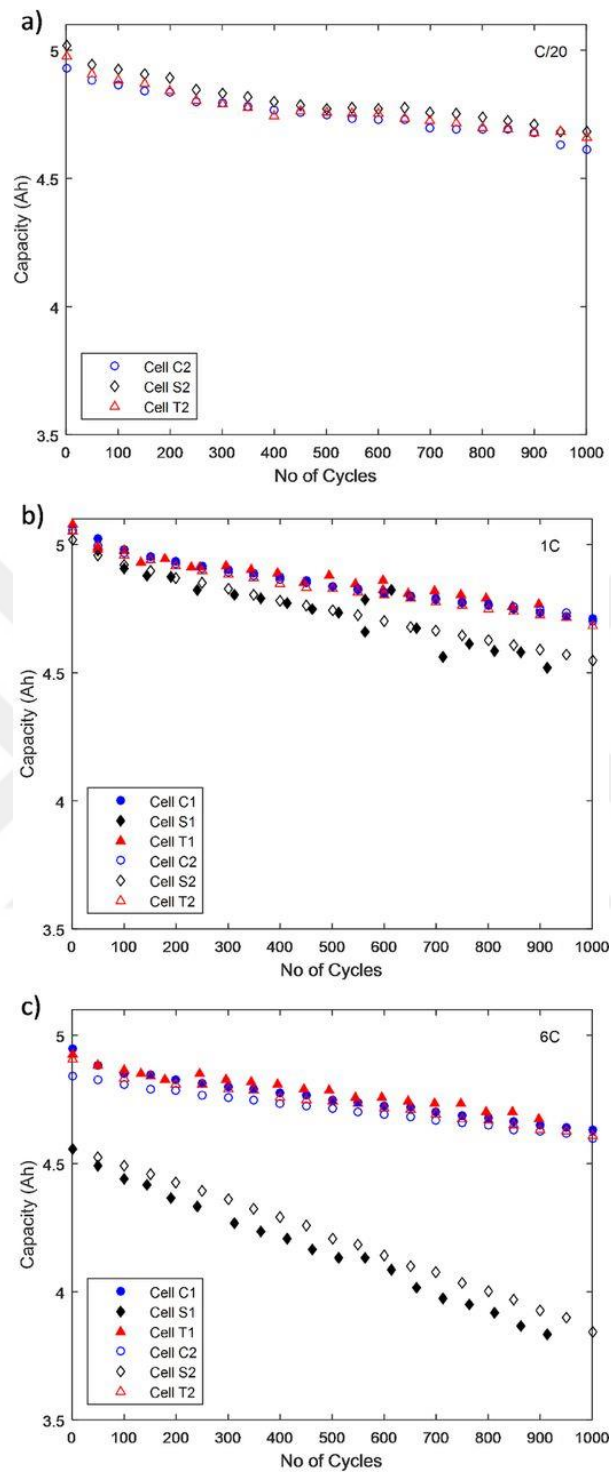


Figure 2.26. Capacities of cells over 1000 cycles, measured at discharge rate of (a) C/20, (b) 1C, (c) 6C. ¹⁸⁰

2.4 Thermal management systems

Temperature is the major parameter effecting the main aspects of the battery performance such as available power, energy, safety, and cycle life of the battery. The mentioned parameters have direct influence on battery economy. Therefore, the temperature of the battery pack needs to be controlled and be kept within an optimum range. The optimum operation temperature differs for various battery types but normally desired range for most of the batteries are between 20-40 °C¹⁸¹⁻¹⁸³. Besides the absolute temperature of the battery pack, temperature nonuniformity along the pack and between the cells cause serious problems such as electric unbalances and capacity fading. Therefore, battery thermal management system (BTMS) must be considered for high capacity battery packs and modules to ensure the safety and improve the performance¹⁸⁴⁻¹⁸⁶.

The main objectives of a BTMS are to maintain a battery pack within an optimum temperature range and to make uniform temperature distribution along the battery pack. They also need to be small and light, easy to operate, have low maintenance cost, and have less power consumption rate to apply in EVs and HEVs. Furthermore, a good BTMS must be capable of both cooling and heating of the LIB pack. At higher operation temperatures and higher charge/discharge rates, the batteries are needed to be cooled. To start and maintain sufficient and high-power output at low ambient temperatures, battery packs must be heated¹⁸⁷.

Operating at low ambient temperatures is one of the main limitations associated with the worldwide application of lithium ion batteries¹⁸⁸. These batteries show low power and capacity density at low ambient temperatures. According to Zhang et al⁶⁶, capacity of lithium ion battery at -10 °C falls 95% more than 20 °C. Figure 2.27 illustrates experimental results for capacity fall of Li-ion cell at different operating temperatures.

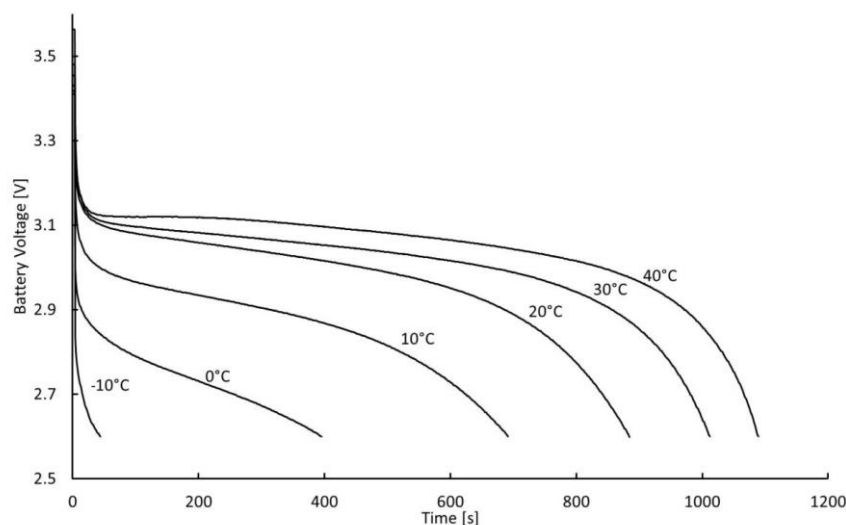


Figure 2.27. Capacity fall (discharge curves) of Li-ion battery at various ambient temperatures¹⁸⁹.

Thermal management system could be categorized as passive or active systems. In the passive system, only the ambient environment is used. However, in the active system, a built-in source is provides heating or cooling according to the operation condition¹⁹⁰. Type of the coolant medium influences the type and performance of a BTMS. A BTMS may use air, liquid, phase change material (PCM) or any combinations.

2.4.1 Air Cooling

BTMS system based on air cooling is the easiest and cheapest way of cooling battery packs. Air cooling could be classified as natural convection cooling or force convection cooling. Simple structure, easy maintenance, and low cost make air cooling a promising candidate to be used in commercial EVs and HEVs⁶³.

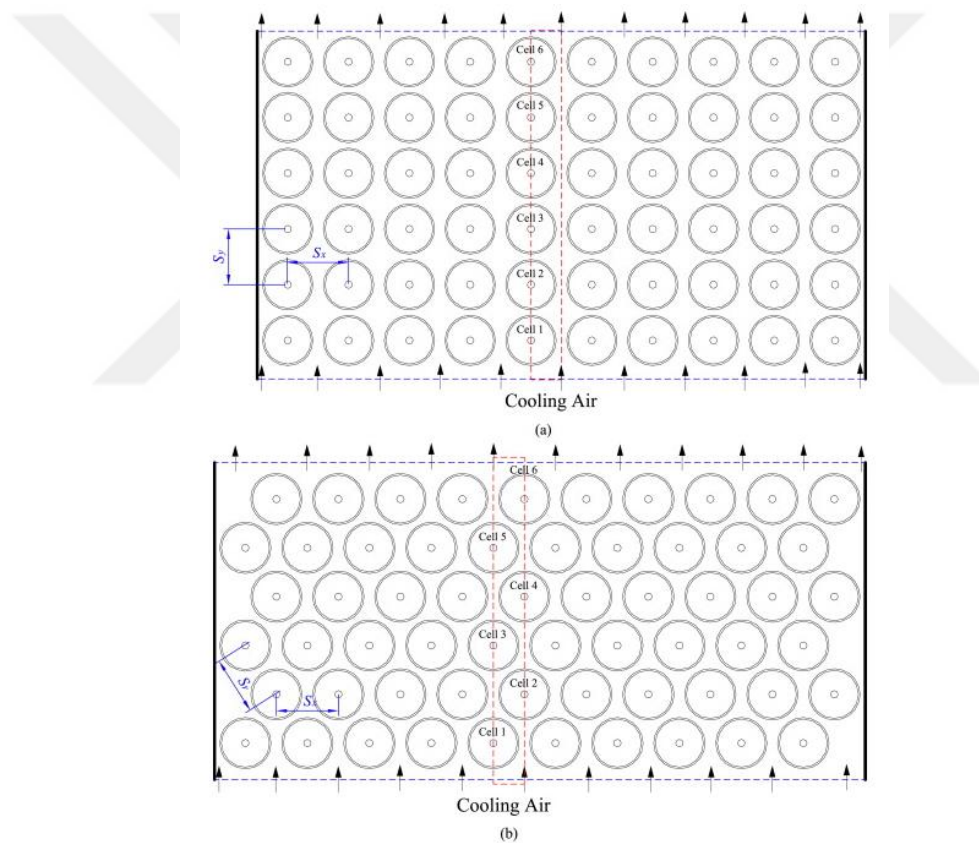


Figure 2.28. Schematic of the air cooling system for battery pack with (a) aligned arrays and (b) with staggered arrays¹⁹¹.

Design parameters of BTMS such as a connection type, array configuration, and distance between the cells and modules significantly influences the cooling performance¹⁹¹⁻¹⁹⁴. Weng et al.¹⁹⁵ examined different cell arrangement structure and inter-cell spacing on performance of air cooling system. Figure 2.28 shows two

different arrangements for battery modules; one with a longitudinal spacing (with the aligned arrays) and the other one with the transverse spacing (with the staggered arrays). Yange et al.¹⁹¹ found that maximum temperature gradient is lower in the battery pack with staggered arrays compared to the pack with aligned arrays.

In BTMS with air cooling, air flow rate is the major parameter which has a great impact in cooling/heating performance^{187, 196-200}. Giuliano et al.¹⁹⁶ showed that increasing the air inlet flow rate from 800 to 1100 ml/s makes the temperature gradient between the inlet and outlet air to rise from 10 to 14.5 °C and the total power consumed per cooling plate was 5.69 and 2.76 W at 1100 and 800 mL/s. Besides the air flow rate, the geometry of the inlet and outlet ducts has an important impact on uniformity of flow rates of cooling channel which in turn affects the temperature uniformity along the pack and the pressure drop²⁰¹.

Although air cooling system is the cheapest and simplest method of a battery thermal pack temperature control, however, it is not sufficient heat transfer medium at extreme cases such as high charge/discharge current rates and at high operating temperatures. The rate of heat transfer between the battery pack and cooling fluid relies upon the thermal conductivity, viscosity, density, and mass flow rate of the fluid. Pesaran et al.¹⁹⁰, compared air cooling with direct oil cooling for a battery pack. According to their work, under same conditions and same mass flow rate, air had a flow rate of 43 L/s and average heat transfer rate of 25 W/m²K while oil had a volumetric flow rate of 0.057 L/s with an average heat transfer rate of 57 W/m²K for indirect cooling. Figure 2.29 presents transient and steady-state comparison of cooling a battery module using oil and air based on a similar parasitic pump or fan power. Maximum temperatures at top, middle, and bottom of the cell are lower in oil cooling case and the temperature reaches to steady state faster in oil cooling.

Overall, due to the simple structure and low cost, air cooling system is proper BTMS in a mild operation condition like low current rates and moderate ambient temperatures. However, for a large-scale battery pack with higher power outputs and when the ambient temperature is too high or too low, BTMS based on air cooling may not be enough for temperature control.

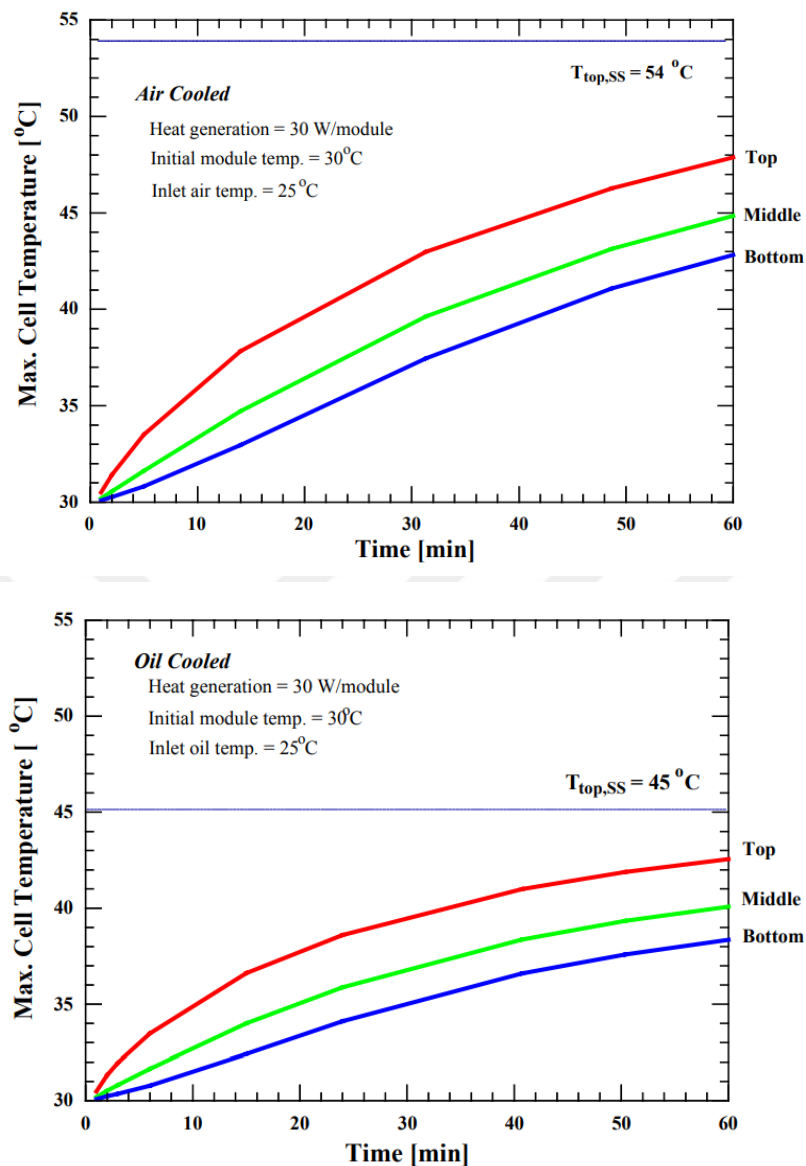


Figure 2.29. Comparison of cooling performance of air versus oil.

2.4.2 Liquid Cooling

Liquid cooling system is the most efficient cooling/heating system in terms of heat transfer rate with the wide range of applications in the industry. As mentioned in the previous section, air-based BTMS is insufficient in large-scale battery thermal

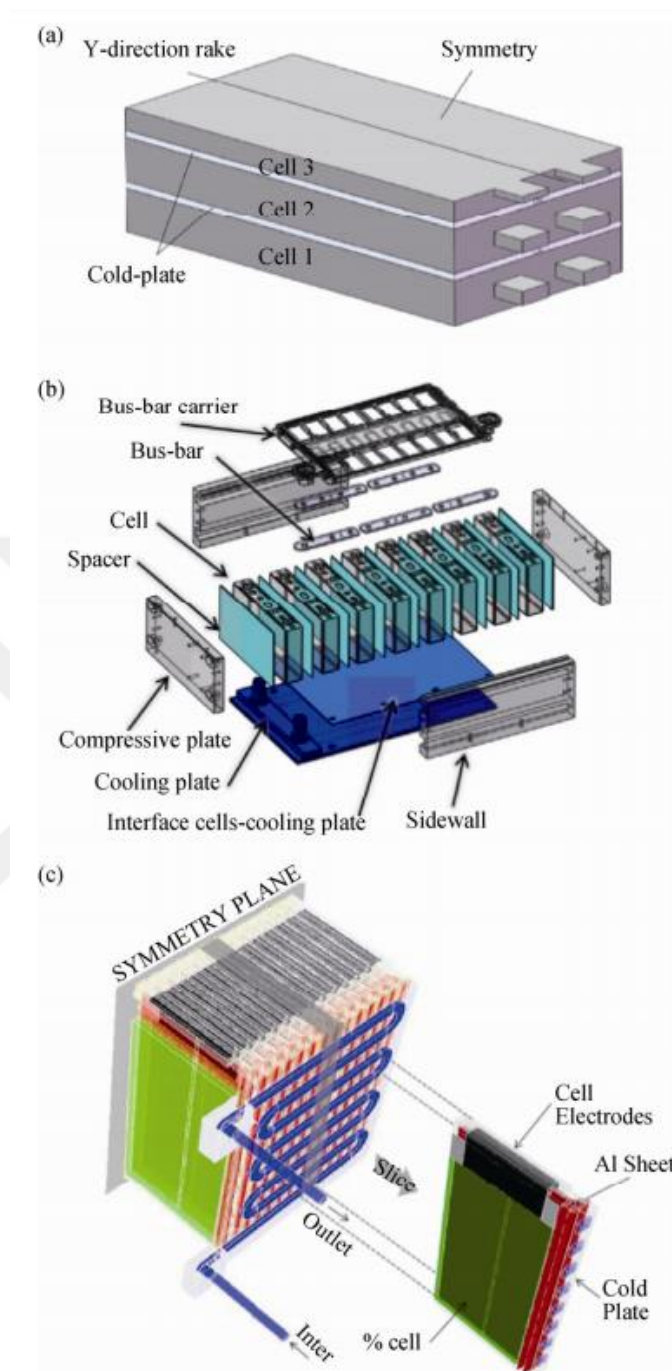


Figure 2.30. Different configuration for liquid-based BTMS with cooling plate¹⁸⁷ (a) sandwiching the batteries²⁰², (b) on the bottom of the pack²⁰³, and (c) on the side surfaces of the battery pack²⁰⁴.

management with high heat generation capabilities. Liquid-based battery thermal management systems are more efficient in terms of temperature control and high heat transfer rate due to higher specific heat of liquids^{174, 190}.

Liquid-cooling technology is classified as direct-cooling and indirect-cooling systems. In direct-cooling system, the dielectric working medium (to avoid a short circuit) such as silicon based or mineral oil, electronic cooling fluid, directly contact the battery cells and heat transfer occurs between the battery pack and the medium^{30, 171, 205}. In indirect cooling system, the heat transfer medium is passing through a cooling cold plate (heat sink) or jacket which is contact with the battery cells. The generated heat by the battery pack is transferred to the cooling plates and then to the heat transfer fluid and then removed away by the fluid. In indirect-cooling system, there is no restriction in choosing the liquid coolant. However, the seal must be considered carefully to avoid leakage¹⁸⁷. Recently, numerous researchers have designed a liquid-based cooling plate for BTMS. Generally, there are three layout arrangements for liquid cooling plates including cooling plates sandwiching the batteries, cooling plates on the bottom of the battery pack, and cooling plates on the side surfaces of the battery packs. These three layouts are shown in Figure 2.30.

2.4.3 Phase Change Material (PCM)

Low cost, low volume, and low mass are three crucial factors for an ideal BTMS that electric and hybrid car manufacturers desire. Air cooling and liquid cooling based BTMS are too bulky, complex, and expensive in terms of total power consumption, pumps, fans, compressors, pipes and other equipment²⁰⁶. a novel BTMS based on phase change material (PCM) was proposed for the first time by Al-Hallaj and Selman^{173, 207}. PCM benefit from the low melting point and high latent heat with low temperature variation. The heat dissipated from the battery packs is stored in the form of latent heat in PCM.

The PCM technology is new and numerous researchers in energy conversion and management system have focused on improving the PCM system^{184, 206, 208-210}. Moraga et al.²¹¹, used four types of pure PCM, namely: capric acid (PCM 1), eicosane (PCM 2), decahydrate sodium carbonate (PCM 3), and octadecane (PCM 4), which located in one or three layers around the battery. According to their results, the configuration with multiple PCM: PCM 1 (5 mm) + PCM 3 (2.9 mm) + PCM 2 (4.3 mm) and the configuration with a single layer of PCM 3 (14.3 mm) was the optimum configurations and respectively reduce the maximum temperature gradient of the battery about 20.9 and 23.2 K compared with the temperature reached by the battery without PCM. Paraffin is the most common PCM used in BTMS technology. However, thermal conductivity of the pure paraffin is low and recently many researches have conducted to improve the thermal conductivity of the paraffin wax. Expanded Graphite (EG) is one of the major additives used to improve the thermal conductivity of the paraffin wax²¹²⁻²¹⁷. Fathabadi²¹⁸ showed that the thermal conductivity of the paraffin wax/EG composite with the mass fraction of 10% EG increased up to 272% (Figure 2.31).

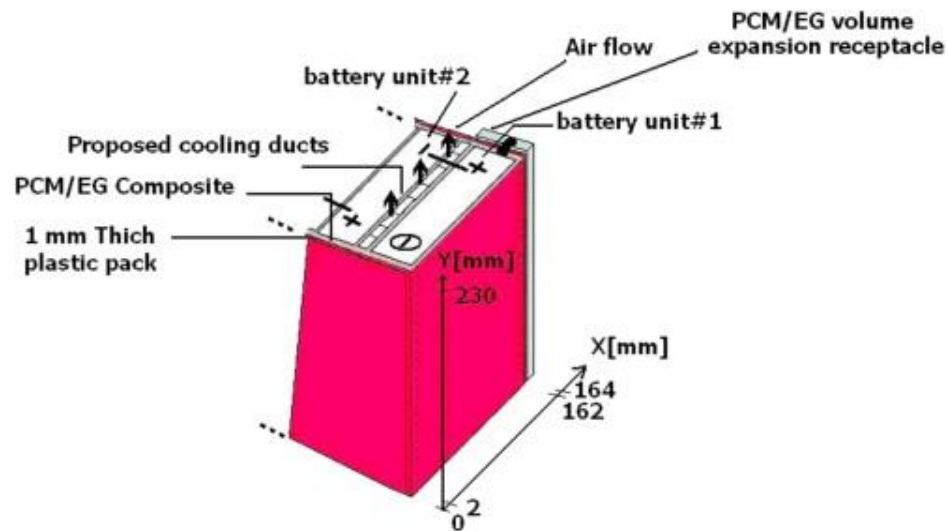


Figure 2.31. Schematic of battery pack with PCM/EG composite as BTMS ²¹⁸.

Besides thermal conductivity, one other obstacle associated with PCM as BTMS is durability of the passive PCM. Although PCM based BTMS is highly efficient in controlling the temperature rise and distribution, the system is limited by passive cooling. In other words, latent heat of the PCM is limited and in harsh operation conditions such as higher ambient temperature or at high heat dissipation density during high-current charging/discharging, the BTMS may break down if the latent heat limits of the PCM is exceeded ²¹⁹. Therefore, PCM based BTMS is required to combine with the active system to improve it. Ling et al. ²²⁰ proposed and developed a hybrid BTMS combining the PCM with forced air cooling (Figure 2.32). Using the hybrid system with force air convection, they could control the average temperature of the battery pack under 50 °C compared to passive PCM with natural convection in which the temperature of the battery pack exceeded the safety range of 60 °C.

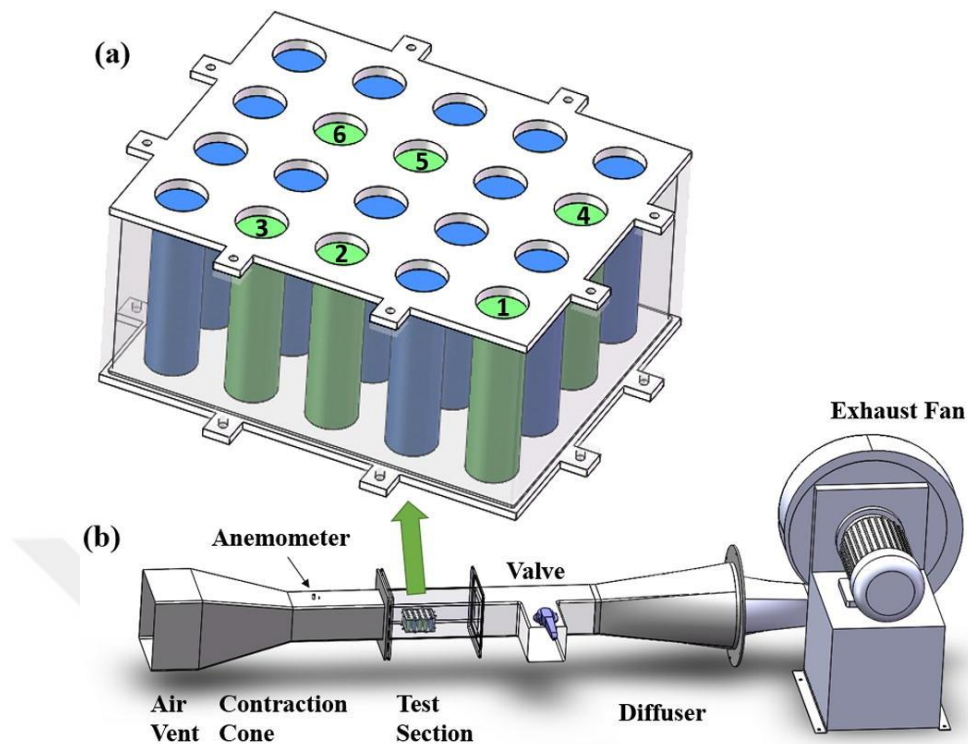


Figure 2.32. Schematic of a (a) battery pack with PCM as BTMS and (b) air cooling system ²²⁰.

2.5 Thermal models for Lithium ion batteries

There have been numerous modeling and simulation studies focusing on electrochemical-thermal behavior of the single-cells ^{108, 221, 222}. In this section, the different methods developed for thermal modeling of the lithium ion batteries will be discussed and reviewed. Most of the developed modeling approaches are being applied for EVs and HEVs, however, they can apply to other renewable energy storage applications as well. The modeling techniques, governing equations, and the physical variable inputs and assumptions are reviewed ²²³.

2.5.1 Lumped Capacitance Thermal Models

The lumped capacitance thermal model was developed by Steve Burch in the National Renewable Energy Laboratory's (NREL's) for the first time ²²⁴. This modeling approach considers the battery cell as a single solid unit with homogeneous thermal properties and therefore, the temperature profile is assumed to be spatially uniform and to be as a function of time. In other words, thermal conductivity of the solid unit is assumed to be very large with negligible temperature gradient in the system. The lumped model applies only for systems for which the ratio of thermal resistance to thermal conductivity is significantly less than convection heat transfer resistance between the solid and ambient ^{225, 226}.

$$\frac{L_c}{k} \ll \frac{1}{h} \quad (49)$$

where k is the conductive heat transfer coefficient ($\text{W.m}^{-1}.\text{K}^{-1}$), h is the convective heat transfer coefficient ($\text{W.m}^{-2}.\text{K}^{-1}$) and L_c is the characteristic length (m):

$$L_c = \frac{V}{A} \quad (50)$$

where V and A are the volume (m^3) and the surface area (m^2) of the solid respectively.

The equation (49) could be rewritten in the form of Biot (Bi) number, which represents the ratio of the conductive heat transfer resistance to convective heat transfer resistance. Therefore, in order to apply the lumped capacitance thermal model, the Bi number must be significantly less than 1.

$$Bi = \frac{hL_c}{k} \ll 1 \quad (51)$$

The energy balance for lumped model is given as equation (52) and (53) respectively:

$$\rho V C_p \frac{dT}{dt} = -hA(T - T_\infty) \quad (52)$$

$$\frac{T - T_\infty}{T_i - T_\infty} = \exp \left[-\left(\frac{hA}{\rho V C_p} \right) t \right] \quad (53)$$

where ρ is the solid density (kg.m^{-3}), V is the volume (m^3), C_p is the heat capacity ($\text{J.g}^{-1}.\text{K}^{-1}$), T is the temperature of the solid (K), T_∞ is the ambient temperature (K), T_i is the initial temperature of the solid, and t is representing the time (s).

In general, there are three major assumptions regarding the lumped capacitance thermal model ²²³:

1. The cell is considered as thermally homogenous body with effective thermo-physical characteristics.
2. The cell properties are not a function of temperature.
3. Heat generation profile throughout the cell is homogeneous.

There are numerous lumped models for investigation of electrochemical and thermal characteristics of the Li-ion cells. Pesaran et al ²²⁴ coupled the lumped capacitance thermal model in an advanced vehicle simulator (ADVISOR) with the battery performance model to characterize the battery thermal behavior according to the battery type and under air cooling conditions. The model separates the system to battery core and battery case with as two independent isothermal nodes as shown in Figure 2.33. the cell components such as anode and cathode electrodes, positive and negative current collectors, separator, and electrolyte are considered as single solid with homogeneous thermal properties. All-Hallaj et al ²²⁷ developed a simple 1-D model

with the lumped electrochemical-thermal properties to investigate the thermal behavior of the commercial SONY type Li-ion cells of 10-100 Ah.

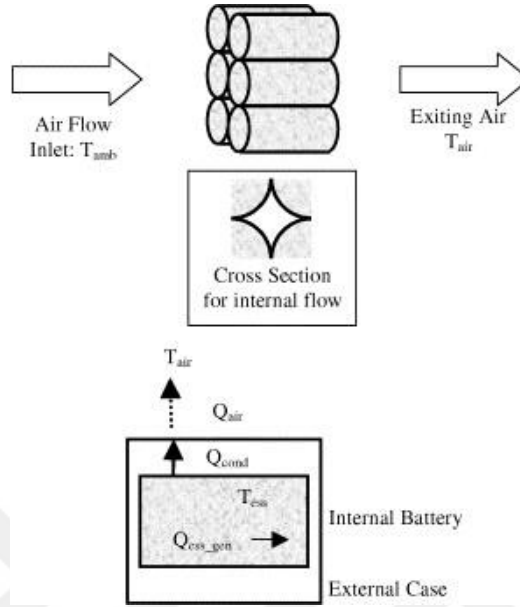


Figure 2.33. Schematic of a lumped battery model in an advanced vehicle simulator (ADVISOR)²²⁴.

2.5.2 Transient Finite Element Analysis Thermal Models

Finite Element Method (FEM) is a numerical approach that takes the total surface of a system and divides it into a finite number of elements and solve the problem by variation methods and minimizing the errors. In FEM, unlike the lumped model, the electrochemical and thermal properties of the cell elements is assumed to be unique and temperature distribution throughout the cell is not uniform. The overall energy balance in FEM is given as:

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} + \frac{\dot{q}_t}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (54)$$

where x , y , and z are the Cartesian coordinates, k is thermal conductivity ($\text{W.m}^{-1}.\text{K}^{-1}$), α is thermal diffusivity ($\text{m}^2.\text{s}^{-1}$), and $\dot{q}_t$ is the total heat generation rate.

Unlike the lumped model, in FEM, cell temperature is changing temporally and spatially, and thermal properties of the cell elements are different. Cell Internal resistance change by the operating temperature and entropy change with the state of charge (SOC) are two important data set needed in FEM. Generally, these data are not published by the manufacturing company and should be found experimentally. Table 2.2 lists the electrochemical equations used in transient FEM thermal model.

Table 2.2 Thermal equations used in FEM.¹⁷¹

Thermodynamic formulas	Variables
Heat Generation	Q_t = Total heat generation rate (W)
	Q_n = Internal resistance (R_i) heat generation (W)
$Q_t = Q_n + Q_s$	Q_s = Reversible entropic heat (W)
$Q_n = I(E_{oc} - V)$	I = Current (A)
$Q_s = -IT \frac{dE_{oc}}{dT}$	E_{oc} = Open circuit voltage (V)
$\dot{q}_t = R_i i^2 - T \Delta S \frac{i}{nF}$	V = Cell voltage (V)
$\Delta S = F \frac{dE_{oc}}{dT}$	$\dot{q}_t$ = Internal heat generation rate / unit volume (W.m^{-3})
$\frac{dE_{oc}}{dT} = \text{Temperature coefficient}$	i = Current / unit volume (A.m^{-3})
	n = number of electrons ($n = 1$)

Karimi et al.¹⁷¹ used FEM to design a thermal management system for Li-ion batteries and they studied electrochemical-thermal behaviors of the battery pack at different discharge rates. Figure 2.34 shows the schematic of the battery pack and multilayer cell structure they used in their thermal model. They used a thin film in designing a battery cell composed of various layers with heterogeneous thermal properties and heat transfer behaviors.

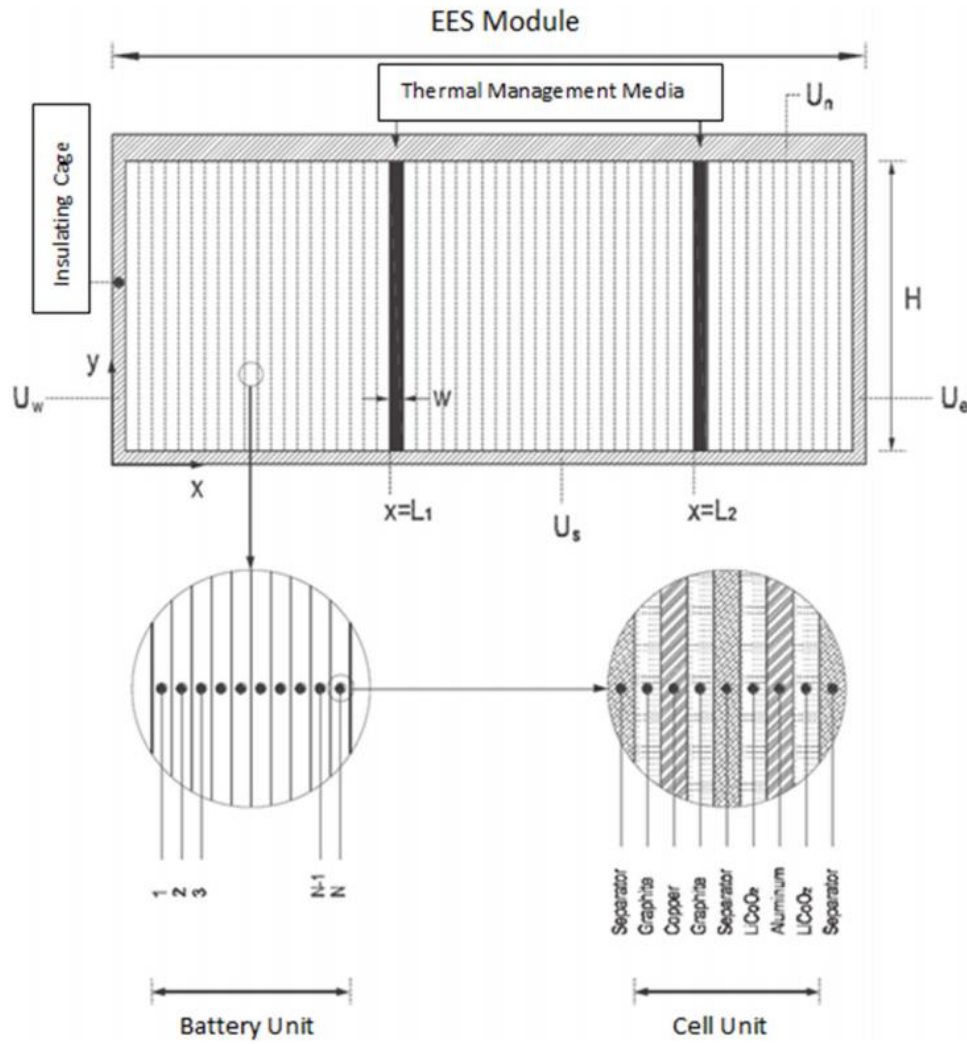


Figure 2.34. Schematic of the battery pack used in FEM thermal model. ¹⁷¹

2.5.3 Numerical model with Analytical Validations

Xun et al. ¹⁹⁸ developed both numerical and analytical model and compared the results to validate the model they developed to study the cooling performance of the TMS designed for pouch type and cylinder type lithium batteries. The general energy balance they used in their analytical model is given in equation 55:

$$\rho_{bat} C_{p,bat} A (T_{1+\Delta T} - T_1) = h_s (T_f - T_1) \Delta t + k_{bat} s (T_2 - T) + \dot{q}_t A \Delta t \quad (55)$$

where ρ_{bat} , $C_{p,bat}$, and k_{bat} are density, specific heat, and conductivity of the battery unit, A is the volume (m^3), s is the surface area (m^2), T_i is the volume average temperature ($^{\circ}C$) of each battery unit and t is the time (s). The convective heat transfer coefficient h ($W.m^{-2}.^{\circ}C^{-1}$) is given as:

$$h = \frac{Nu k_a}{L} \quad (56)$$

where Nu is the Nusselt number, k_a is the conductivity of air and L is the length (m) along the cooling channel.

2.5.4 Behavioral Model

2.5.4.1 Equivalent circuit model

Beside the electrochemical-thermal models, an equivalent circuit model is the other widely used method to model electrical and thermal response of Li-ion batteries. The parameters used in electrochemical models such as particle size and porosity, kinetic reaction parameters, electrolyte conductivity, layer thicknesses, and open circuit voltage of the anode and cathode are not provided by the manufacturing company and are measured experimentally. However, the equivalent circuit model simplifies the electrochemical model by utilizing circuit elements such as voltage sources, resistor and capacitor to represent the I–V characteristics of the battery²²⁸⁻²³⁰. In the equivalent circuit model, the thermal properties are replaced by equivalent electrical quantities. For example, temperature, heat flux, conductive resistance, convective resistance, and heat storage are represented by voltage, current, conductive conductance, convective conductance, and capacitance, respectively²²³.

Number of the resistive-capacitive (RC) block is the main parameter affecting the accuracy of the equivalent circuit model and there are numerous first-order, second-order, and third-order RC models in the literature^{231, 232}. Figure 2.35 represents the schematic of the single RC block of the equivalent circuit model. The components of the model such as a resistor ($R1$), a capacitor ($C1$), and Ohmic internal resistance ($R0$) are a function of the state of the charge (SOC) and average inner cell temperature.

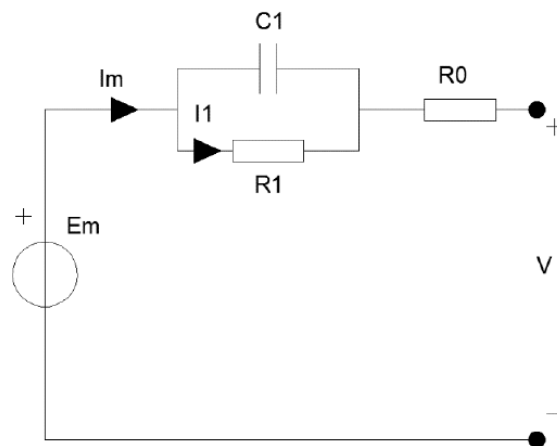


Figure 2.35. Schematic of equivalent circuit model.

The SOC is given as equation (57):

$$SOC = 1 - \frac{\int_0^t I_m dt}{C_Q} \quad (57)$$

where I_m is the main branch current (A) and C_Q is the cell capacity. The total battery voltage and total resistance are given by equations (58) and (59):

$$V_{batt} = V_{oc}(SOC, T) - I_m R_0(SOC, T) - I_m R_t(\tau_1, \tau_2, \tau_3) \quad (58)$$

$$R_t = R_1(SOC, T) e^{-\frac{1}{R_1(SOC, T)C_1(SOC, T)}t} + R_2(SOC, T) e^{-\frac{1}{R_2(SOC, T)C_2(SOC, T)}t} + R_3(SOC, T) e^{-\frac{1}{R_3(SOC, T)C_3(SOC, T)}t} \quad (59)$$

3 Chapter 3: Electrochemical-Thermal Model Development

In this section, the electrochemical behaviors of the 20Ah LiFePO₄ battery cell during charge and discharge processes is investigated using the 3D model developed by the COMSOL MULTIPHYSICS program. Solid and liquid phase potentials, solid phase and electrolyte phase concentrations, and Li ion intercalation flow on active surfaces will be determined by numerically (Transient Finite Element Method) solving the differential equations.

Model studies are composed of two parts including electrochemical characterization, and thermal characterization. In the first stage of the project, we performed electrochemical characterization tests, and using the experimental measurements, we estimated the electrochemical parameters for the model. In the second step, the thermal model equations are coupled with the electrochemical model to determine how the thermal behavior change depending on the number of layers in the cell. In this chapter, electrochemical effects were investigated, and electrochemical parameters were estimated. Table 3.2 **Conservation Equations** Table 3.3, and Table 3.4 gives the electrochemical and thermal differential equations for the active material (solid phase), electrolyte (liquid phase) and separator. The developed model couples the mass balance and charge conservation equations with the energy balance equations to study the electrochemical-thermal behavior of the cells. Later, at the last part of this work, the laminar flow CFD (Computational Fluid Dynamics) module is added to the 3D model to study the effects of cooling system.

3.1 Electrochemical characterization

In the first part of the study, Lithium ion battery model is developed to study the electrochemical behavior of the battery using the numerical simulation. Electrochemical parameters used in the model include the local current density (J_i), the solid phase potential (Φ_1), the electrolyte potential (Φ_2), the Li + ion concentration in the electrolyte phase (c), and the Li + ion concentration in the solid phase (c_s). In order to calculate these variables, the mass balance and charge balance equations are solved by the finite difference method (FDM). In battery cell components, negative and positive electrodes are defined as solid phase, while electrolytic regions are defined as liquid phase. The mass and charge balance equations for each phase were solved separately considering the diffusion and conduction parameters.

3.1.1 Liquid Phase Equations

The lithium ion concentration in the electrolyte phase (c) is defined by the following mass balance equation:

$$\varepsilon_e \frac{\partial c}{\partial t} = D_{eff} \frac{\partial^2 c}{\partial x^2} + J_i \cdot a \cdot (1 - t^+) \quad (1)$$

Where ε_e is the porosity, c (mol/m³) is the electrolyte concentration, D_{eff} (m²/s) is the effective electrolyte diffusion, J_i (mol/m²-s) is the local current density, a (m⁻¹) is the specific surface area of the active material particles, and t^+ is the transference number of the Li⁺ ions in the electrolyte.

In addition, the solution (electrolyte) phase potential (Φ_2) is defined by the following equation depending on the current:

$$\sigma_{eff,e} \frac{\partial \Phi_1}{\partial x} - \kappa_{eff,e} \frac{\partial \Phi_2}{\partial x} + \frac{2 \kappa_{eff,e} RT}{F} (1 - t^+) \frac{\partial \ln c}{\partial x} = I \quad (2)$$

where $\sigma_{eff,e}$ (S/m) is the effective electronic conductivity of the solid phase, Φ_1 is the solid phase potential, Φ_2 is the electrolyte potential, $\kappa_{eff,e}$ is the effective ionic conductivity of the electrolyte phase, R is the universal gas constant (8.314 J/mol-K), T (K) is the absolute temperature, F is the Faraday's constant (96,487 C/mol), and I is the current (A). Boundary conditions for the electrolyte phasic potential (Φ_2) is defined as continuous at the electrode-separator interface and at the electrode-current collector interface as equation (3):

$$-\kappa_{eff,e} \frac{\partial \Phi_2}{\partial x} = 0 \quad (3)$$

3.1.2 Solid Phase Equations

In the solid phase, the diffusion and conduction equations are defined where the positive and negative electrodes are present. However, the electrolyte-phase conduction and electrolyte-phase potential equations described above are solved simultaneously with the solid phase diffusion and solid-phase potential equations for the electrodes. This is because of the presence of electrolyte in porous electrodes.

Since the active material (AM) in the positive and negative electrodes is considered as spherical particles, the lithium ion concentration in the solid phase (c_s) is defined in spherical coordinates with the Fick's second Law as equation (4):

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right) \quad (4)$$

where D_s (m²/s) is the diffusion coefficient for the lithium ions inside the AM particle. Boundary conditions for the solid particles are defined as equation (5):

$$\left(\frac{\partial c_s}{\partial t} \right) \Big|_{r=0} = 0, J_i = \left(-D_{s,i} \frac{\partial c_s}{\partial r} \right) \Big|_{r=R_i} \quad (5)$$

The solid phase potential (Φ_1) for positive and negative electrodes ($i = n, p$) is defined by the following equation:

$$\sigma_{eff,i} \frac{\partial^2 \Phi_1}{\partial x^2} = j_i F a_i \quad (6)$$

Boundary conditions for the electrolyte phase potential (Φ_2) are defined for the electrode-separator interface and the electrode-current collector interface respectively as equation (7):

$$\sigma_{eff,i} \frac{\partial \Phi_1}{\partial x} = 0, \sigma_{eff,i} \frac{\partial \Phi_1}{\partial x} = 0 \quad (7)$$

The local current density (j_i) is defined by the Buttlar-Volmer equation as equation (8):

$$j = 2ki(C_{s,max} - C_s|_{r=R_i})^{0.5} (C_{s,max})^{0.5} (C_s|_{r=R})^{0.5} \sinh\left(\frac{0.5F}{RT}(\Phi_1 - \Phi_2 - U)\right) \quad (8)$$

where k_i ($\text{mol}/(\text{mol}/\text{m}^3)^{1.5}$) is the reaction rate constant of the electrode, $c_{s,max}$ (mol/m^3) is the maximum concentration of the lithium ions in the AM particle, and U (V) is the open-circuit potential of the electrode.

3.1.3 General Equations

The effective electronic solid phase conductivity ($\sigma_{eff,i}$), The effective ionic conductivity of the electrolyte phase ($K_{eff,i}$), the effective diffusion coefficient of the Li ions in the active material particles ($D_{eff,i}$), the specific surface area (a_i), and the electrode potentials (U_n and U_p) are defined in the following equations:

$$\sigma_{eff,i} = \sigma_i(1 - \varepsilon_i - \varepsilon_{f,i} - \varepsilon_{p,i}) \quad (9)$$

where σ_i (S/m) is electronic conductivity, ε_i is electrode porosity, $\varepsilon_{f,i}$ is the porosity of the additive materials in the electrode, $\varepsilon_{p,i}$ is the the porosity coefficient of the polymer (filler) used in the electrode.

The effective ionic conductivity ($K_{eff,i}$) of the electrolyte phase depends on the electrode porosity coefficient (ε_i) and the electrolyte ion conductivity (κ_i , S / m) as the following:

$$\kappa_{eff,i} = \varepsilon_i^{1.5} \kappa_i \quad (10)$$

The effective diffusion coefficient ($D_{eff,i}$) of the Li + ions in the active material particles is determined by the Li ion diffusion coefficient (D_i , m^2/s) and the electrode porosity coefficient for the negative electrode, positive electrode and separator (ε_i) as the following:

$$D_{eff,i} = D_i \varepsilon_i^{1.5} \quad (11)$$

The specific surface area is defined as equation (12):

$$a_i = 3(1 - \varepsilon_i - \varepsilon_{f,i} - \varepsilon_{p,i})/R_i \quad (12)$$

Table 3.1 lists the negative and positive electrode potentials (U_n and U_p) depend on the ratio of $C_{s,n} / C_{s,n,max}$ for the negative electrode and $C_{s,p} / C_{s,p,max}$ for the positive electrode. For the positive electrode (LiFePO₄), the $C_{s,n} / C_{s,n,max}$ values are between 0.07 and 0.95 and for the negative electrode (graphite) the $C_{s,p} / C_{s,p,max}$ values are between 0.05 and 0.95.

Table 3.1 Negative (Graphite) and Positive (LiFePO₄) electrode potentials

C/Cs_max	U _{LiPO4}	C/Cs_max	U _{Graphite}
0.01	3.538	0.05	0.976
0.02	3.431	0.1	0.818
0.03	3.425	0.15	0.682
0.04	3.425	0.2	0.564
0.05	3.425	0.25	0.464
0.1	3.425	0.3	0.377
0.2	3.425	0.35	0.302
0.3	3.425	0.4	0.238
0.4	3.425	0.45	0.182
0.5	3.425	0.5	0.135
0.6	3.425	0.55	0.094
0.7	3.425	0.6	0.058
0.8	3.424	0.65	0.028
0.81	3.424	0.7	0.002
0.82	3.424	0.8	0.001
0.83	3.424	0.9	0.0005
0.84	3.424		
0.85	3.423		
0.86	3.419		
0.87	3.407		
0.88	3.376		
0.89	3.311		
0.9	3.190		
0.91	2.950		
0.92	2.650		

3.1.4 Energy Conservation Equations

The electrochemical equations are coupled with the intracellular and cell surface thermal equations to obtain the electrochemical-thermal model for the single cell. The energy balance equation for electrodes and separator is given by equation (13):

$$\rho_k C_{p,k} \frac{\partial T}{\partial t} = \lambda_k \frac{\partial^2 T}{\partial x^2} + Q_{rxn} + Q_{rev} + Q_{ohm} \quad (13)$$

and for the current collectors, it is given by the following equation:

$$\rho_c C_p \frac{\partial T_s}{\partial t} = \lambda \frac{\partial^2 T_s}{\partial x^2} \quad (14)$$

where Q_{rxn} is the reaction heat, Q_{rev} is the reversible heat, and Q_{ohm} is the ohmic or joule heat.

All of the conservation equations and the related boundary conditions are listed in the following tables:

Table 3.2 Conservation Equations

Component	Electrochemical Reactions	Equation
Electrode	Solid Phase Potential	$\sigma_{eff,i} \frac{\partial^2 \Phi_1}{\partial x^2} = j_i F a_i$
Electrode/Separator	Electrolyte Potential	$\sigma_{eff,i} \frac{\partial \Phi_1}{\partial x} - \kappa_{eff,i} \frac{\partial \Phi_2}{\partial x} + \frac{2 \kappa_{eff,i} R T}{F} (1 - t^+) \frac{\partial \ln C}{\partial x} = I$
Electrode/Separator	Electrolyte Phase Diffusion	$\varepsilon_i \frac{\partial C}{\partial t} = D_{eff,i} \frac{\partial^2 C}{\partial x^2} + j_i a_i (1 - t^+)$
Electrode	Solid Phase Diffusion	$\frac{\partial C_s}{\partial t} = \frac{D_{s,i}}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C_s}{\partial r})_i$
Electrode	Activation Reaction	$j_i = 2k_i \left(C_{s,max,i} - C_{s,i} _{r=R_i} \right)^{0.5} (C_{s,max,i})^{0.5} (C_{s,i} _{r=R_i})^{0.5} \sinh \left(\frac{0.5F}{RT} (\Phi_1 - \Phi_2 - U_i) \right)$
	Thermal Equations	
Electrode/Separator/Current Collectors	Heat Transfer	$\rho_k C_{p,k} \frac{\partial T}{\partial t} = \lambda_k \frac{\partial^2 T}{\partial x^2} + Q_{rxn} + Q_{rev} + Q_{ohm}$
Pouch cell Surface	Heat Transfer	$\rho_c C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2}$

Table 3.3 Boundary Conditions

Boundary Conditions	Electrode/Separator Interphase	Electrode/Current Collector Interphase
Solid Phase Potential, Φ_1	$-\sigma_{eff,i} \frac{\partial \Phi_1}{\partial x} = 0$	$-\sigma_{eff,i} \frac{\partial \Phi_1}{\partial x} = I$
Electrolyte Potential, Φ_2	Continuous	$-\kappa_{eff,i} \frac{\partial \Phi_2}{\partial x} = 0$
Electrolyte Concentration, C	Continuous	$-D_{eff,i} \frac{\partial C}{\partial x} = 0$
Solid Phase Concentration, C_s	$\frac{\partial C_s}{\partial r} \Big _{r=0} = 0, -D_{s,i} \frac{\partial C_s}{\partial r} \Big _{r=0} = j_i$	$\frac{\partial C_s}{\partial t} = \frac{D_{s,i}}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C_s}{\partial r})_i$
Thermal Boundary Conditions	Current Collector Interface / Cell Protection Layer	Electrode/Current Collector Interphase
Cell inside	$-\lambda_a \frac{\partial T}{\partial x} = -\lambda_c \frac{\partial T}{\partial x}$	$-\lambda_a \frac{\partial T}{\partial x} = \lambda \frac{\partial T}{\partial x}$
	Cell Surface/Cell Protecting Layer	
Pouch Cell Surface	$-\lambda_c \frac{\partial T}{\partial x} = h(T_m - T)$	

Table 3.4 General Electrochemical Equations

$\sigma_{eff,i} = \sigma_i(1 - \varepsilon_i - \varepsilon_{f,i} - \varepsilon_{p,i})$	i= n(negative electrode), p(positive electrode) $\sigma_{eff,i}$: Effective electronic conductivity, S/m σ_i: Electronic conductivity, S/m ε_i: Electrode porosity coefficient $\varepsilon_{f,i}$: Active material porosity coefficient $\varepsilon_{p,i}$: Electrode polymer porosity coefficient
$\kappa_{eff,i} = \varepsilon_i^{1.5} \kappa_i$	i=n, p $\kappa_{eff,i}$: Effective electrolyte ionic conductivity, S/m κ_i: electrolyte ionic conductivity, S/m
$D_{eff,i} = D_i \varepsilon_i^e$	i=n, p $D_{eff,i}$: Effective diffusion coefficient, m²/s D_i: Li⁺ Diffusion coefficient, m²/s
$a_i = 3(1 - \varepsilon_i - \varepsilon_{f,i} - \varepsilon_{p,i})/R_i$	i=n, p a_i: Specific surface area, m⁻¹ R_i: Active material radius, m
ρ_i	Density (kg/m ³)

λ_k	Effective thermal conductivity, W/(m.K)
C_p	Specific heat capacity, J/(kg.K)
Q_{rxn}	Reaction heat, (W/m ³)
Q_{rev}	Reversible heat, (W/m ³)
Q_{ohm}	Ohmic heat, (W/m ³)
U_n	Negative electrode cycle voltage, V
U_p	Positive electrode cycle voltage, V
k_i	$i=n, p$ k_i : Reaction rate coefficient, mol/(sn.m ²)
t^+	Transference coefficient
F	Faraday number, 96487 C/mol
Φ_1	Solid phase potential (V)
Φ_2	Liquid phase potential (V)
C	Concentration (mol/m ³)
j_i	Local current density (A/cm ³), Butler-Volmer equation
T	Temperature (K)
I	Current Density (A/cm ²)

3.2 Experimental parameterization

The initial states of charge, the initial concentration (C_s , mol/m³), the transport number (0.363) of the electrodes, the radiuses of the particles in the positive and negative electrodes ($R_{i,n} - R_{i,p}$), the conductivities of the electrode materials, the thickness of the separator (μm) and the porosity (ϵ_e) of the separator are based on experimental measurements. These values are provided by the manufacturer. Reaction rate constants (k , mol/s.m²) and diffusion constants (D , m²/s) for electrodes and electrolytes were obtained by model fitting. The other parameters can be finding in chapter 4.

3.3 Developing the model in the COMSOL

3.3.1 Cell Geometry

The first step in developing the model is to introduce the cell geometry in COMSOL environment. COMSOL MULTIPHYSICS program uses finite element method to solve the differential equations numerically. Figure 3.1 shows the 20-layer cell geometry we use in our model. A rectangle prismatic cell containing repeating units of current collectors, anode, separator, and cathode is developed. The outermost layer is covered with a polymer film. The total electric current which is being applied to the electrode tabs is divided by the number of layers.

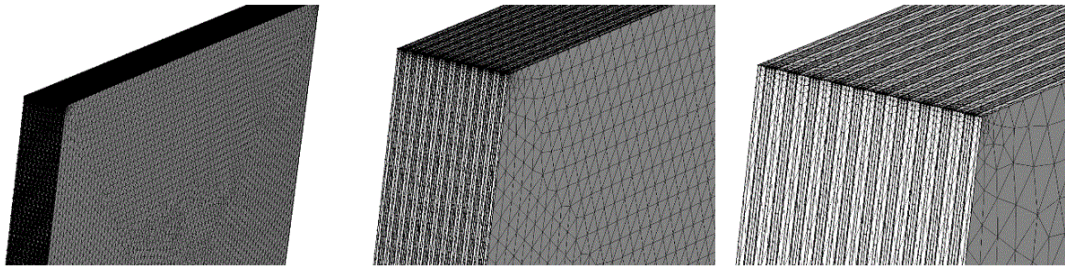


Figure 3.1. Schematic of 20-layer LiFePO₄ Geometry meshed by finite element method.

3.3.2 Defining Global Parameters and Variables

In order to solve the model equations, it is necessary to introduce the global parameters into the system. In the COMSOL environment, there are subprograms for defining parameters in the global definitions section.

3.3.3 Identification of Model Equations

The equations used in the COMSOL are listed in Table 3.2 Conservation Equations. COMSOL solves the differential equations with the finite element method (FEM). We used the COMSOL Battery and Fuel Cell module to develop our model. Figure 3.2 illustrates an example of equation introduction in the COMSOL environment.

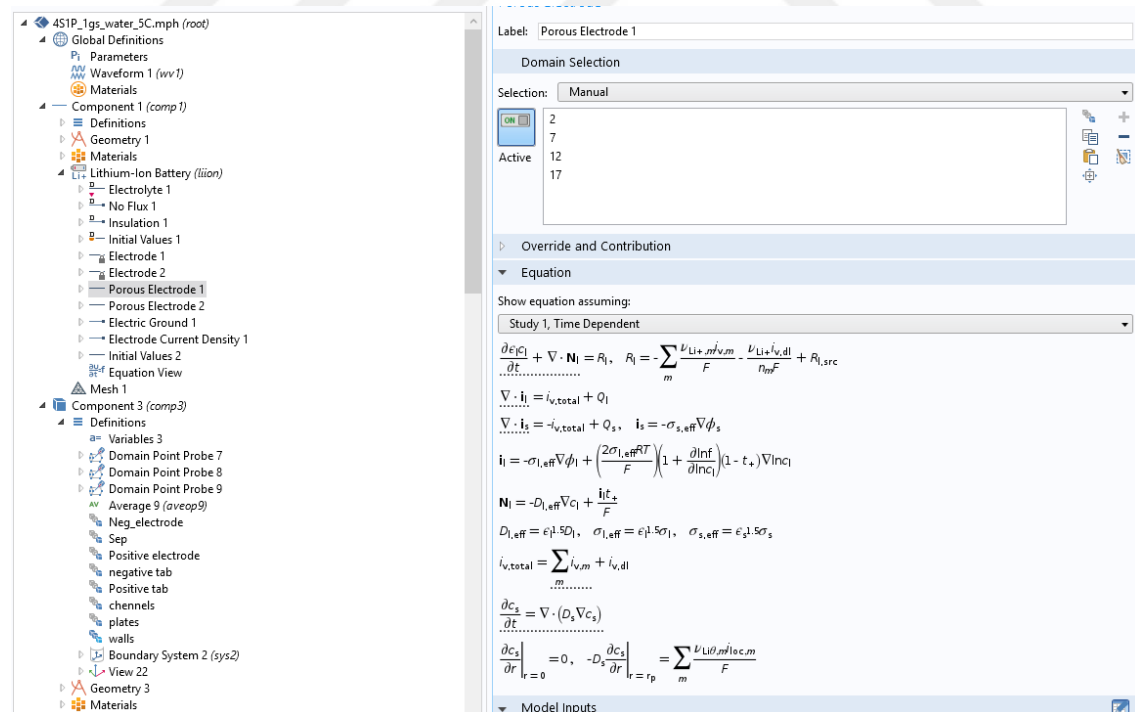


Figure 3.2. Schematic of the electrochemical equations used in the COMSOL environment.

3.4 Electrochemical Model Results

The developed model is validated using the experimental voltage-time measurements and then is used to study the electrochemical behavior of the LiFeP_4 battery cell. In this approach, cell voltage curves obtained from the model are compared with the experimental data, and the predicted parameters are corrected. The voltage-time plot at 30 °C at different discharge current rates is shown in Figure 3.3. Comparison experimental and simulated Voltage-Time graphic at different current rates. The Least square method is used to minimize the error between the model and experimental results. Standard error of estimates at different C-rates are listed in Table 3.5.

Table 3.5 Standard error of estimates.

C-rate	1C	2C	3C	4C	5C
	0.095	0.096	0.113	0.173	0.221

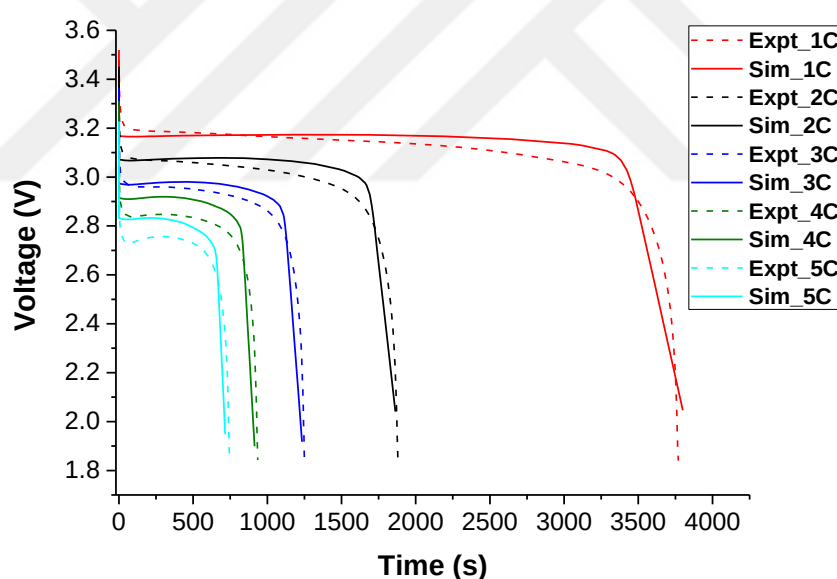


Figure 3.3. Comparison experimental and simulated Voltage-Time graphic at different current rates.

The Li ion concentration, charge/discharge capacity, electrolyte potential, and solid phase potential in the cell are determined using the estimated parameters. Li-ion concentration profile is an important outcome gotten by the model and can't be estimated experimentally. The internal resistance due to the Li ions transfer, intercalation and, deintercalation is likewise determined by the model. Figure 3.4 shows the change in Li ion concentration in the electrolyte and solid phases. Since Li ions move from the anode toward the cathode during a discharge, a rapid loss is seen in the

negative electrode. The released Li ions from the anode are transferred in to the electrolyte phase. This phenomenon explains the rising Li ion concentration in the electrolyte phase within the anode. On the cathode side, Li ions are transferred from the electrolyte phase to the solid phase leading to a linear concentration increase in the solid phase. The sudden changes observed at the end of the discharge period are because of the large voltage difference and higher power applied to achieve desired electronic and ionic fluxes.

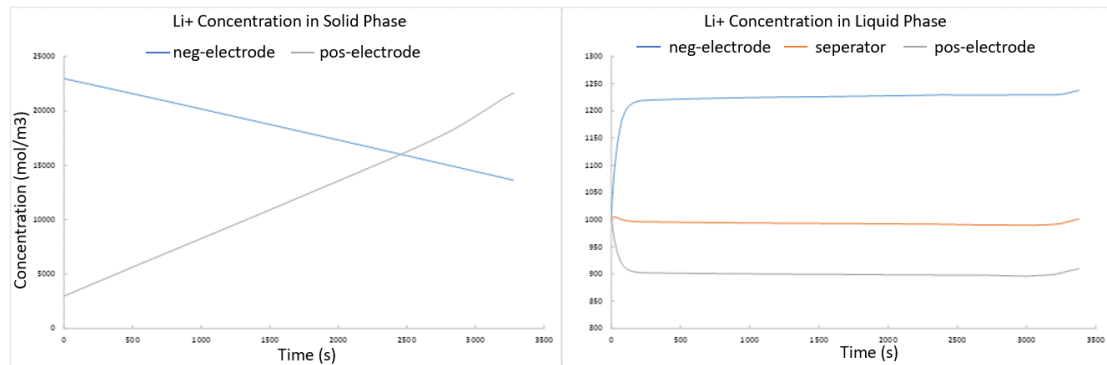
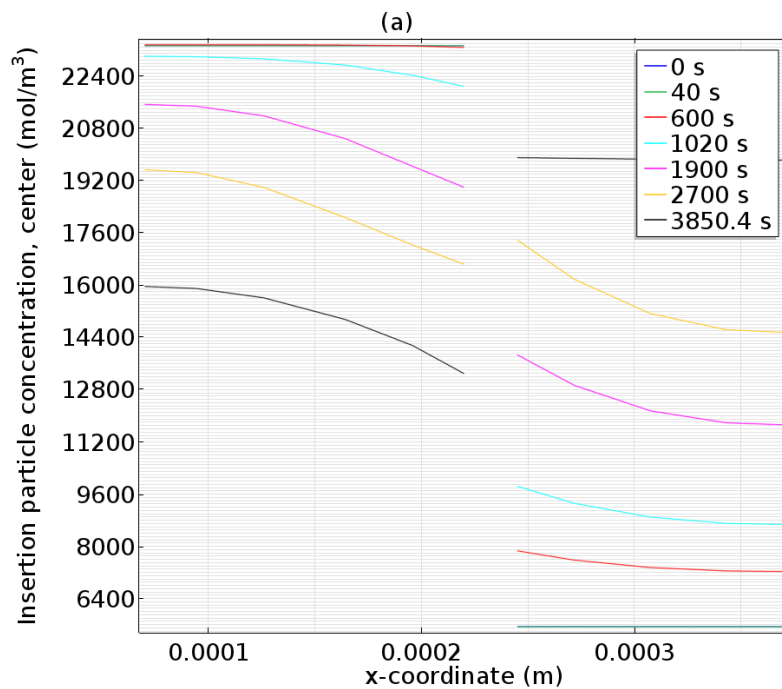


Figure 3.4. Time-dependent Li^+ ion concentration change in solid and liquid Phase.

Figure 3.5 shows the Li ion concentration change in the thickness direction within a single layer. Li ion concentration falls rapidly in the anode, keep falling till the ending boundary of the cathode. According to these results, the Li ion transfer is occurring from the solid phase to the liquid phase and vice versa in the anode and cathode, respectively.



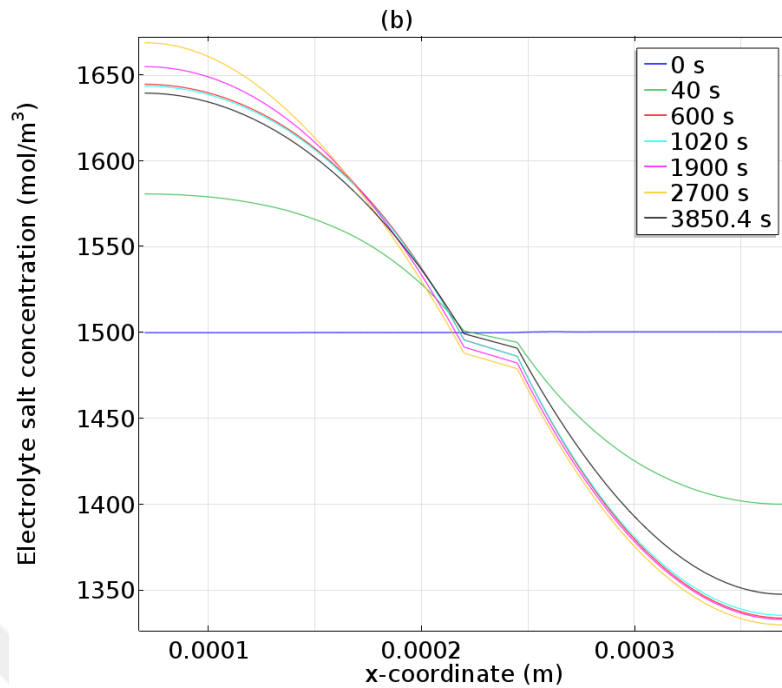


Figure 3.5. Spatial Li^+ ion concentration in (a) solid and (b) liquid phase.

The Li-ion cells could be produced in different size and configurations. Cells with a wider surface area and thinner electrodes may yield the same capacity of the cells with a narrower surface area and thicker electrodes. However, electrode thickness changes the electrochemical-thermal behavior of the cell significantly²³³. Therefore, using the developed model, we also study the effects of electrode thickness on voltage, capacity, concentration, and heat generation of the cells. Figure 3.6 shows the effect of layer thickness on voltage of the cell. As the thickness increases, the nominal voltage of the cell falls with a sharper slope. This could be clarified by the increasing internal resistance with the thickness and as a result, lower voltage output. In addition, lower nominal voltage results in lower power output. Therefore, to optimize the battery power, the electrode thickness should be optimized based on the desired capacity.

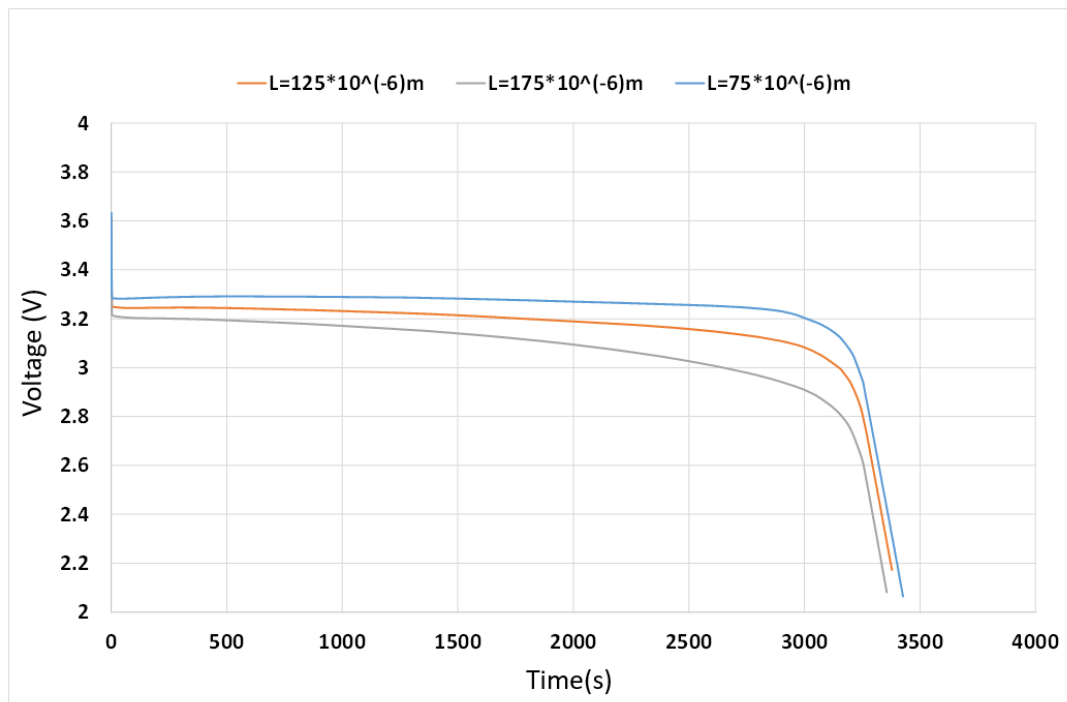


Figure 3.6. Effects of layer thickness on voltage.

In the cells with thicker electrodes, the Li ions concentration distributions in the cathode and anode electrodes are different. Figure 3.7 and Figure 3.8 show the Li^+ ion concentration change with time in the solid phase and electrolyte phase. According to the results, as the electrode thickness increases, Li ions transfer rate from the liquid phase to the cathode is increasing. In addition, as the Li ion concentration falls in the liquid phase, it rises in the solid phase. Regardless of the thickness, however, Li ion concentration is observed in equal amounts in the solid phase at the end of discharge. As a result, the capacity is reached to an equal magnitude in the cathode.

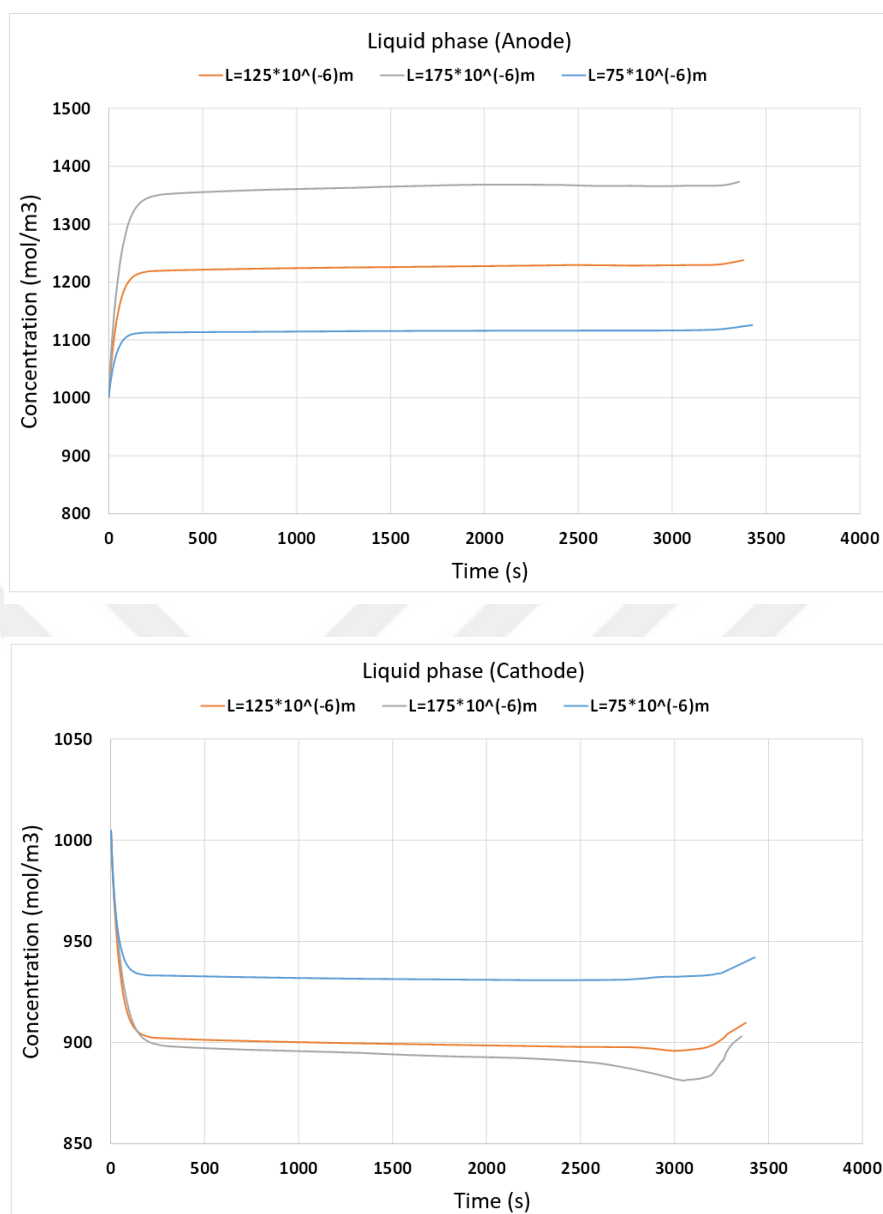


Figure 3.7. Effect of layer thickness on Li^+ ion concentration in liquid phase.

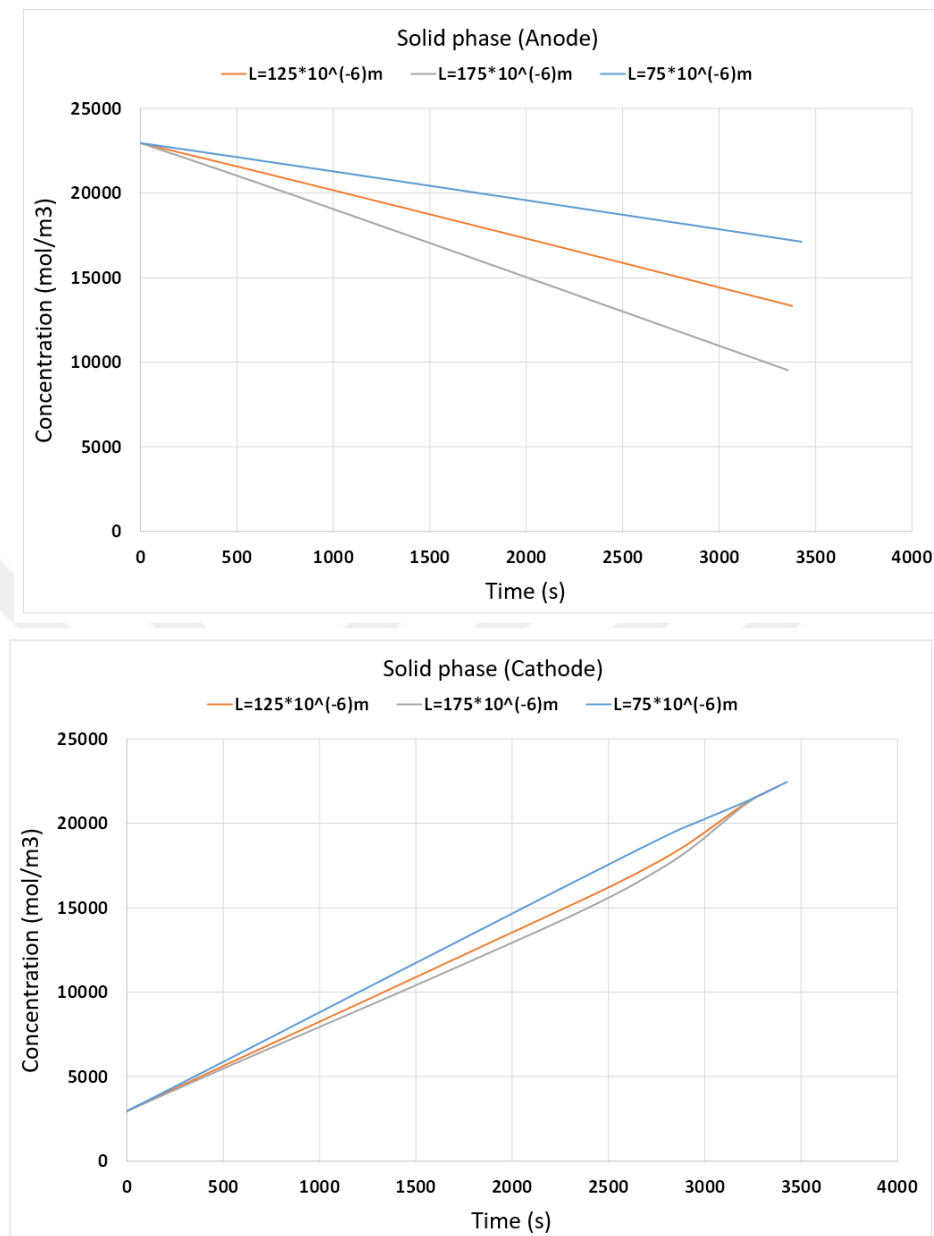


Figure 3.8. Effect of layer thickness on Li^+ ion concentration in solid phase.

Proper selection of the thermal management system is important in optimizing the cycle life and safety of the batteries. During discharge, a substantial amount of heat is released inside the cells. Among the several factors affecting the heat generation rate in the battery cells, electrode thickness impact is very significant. Based on the results (Figure 3.9), as the thickness of the electrodes increases, the heat generation rate also increases. This phenomenon can be explained by the increased internal resistance by the increasing electrode thickness.

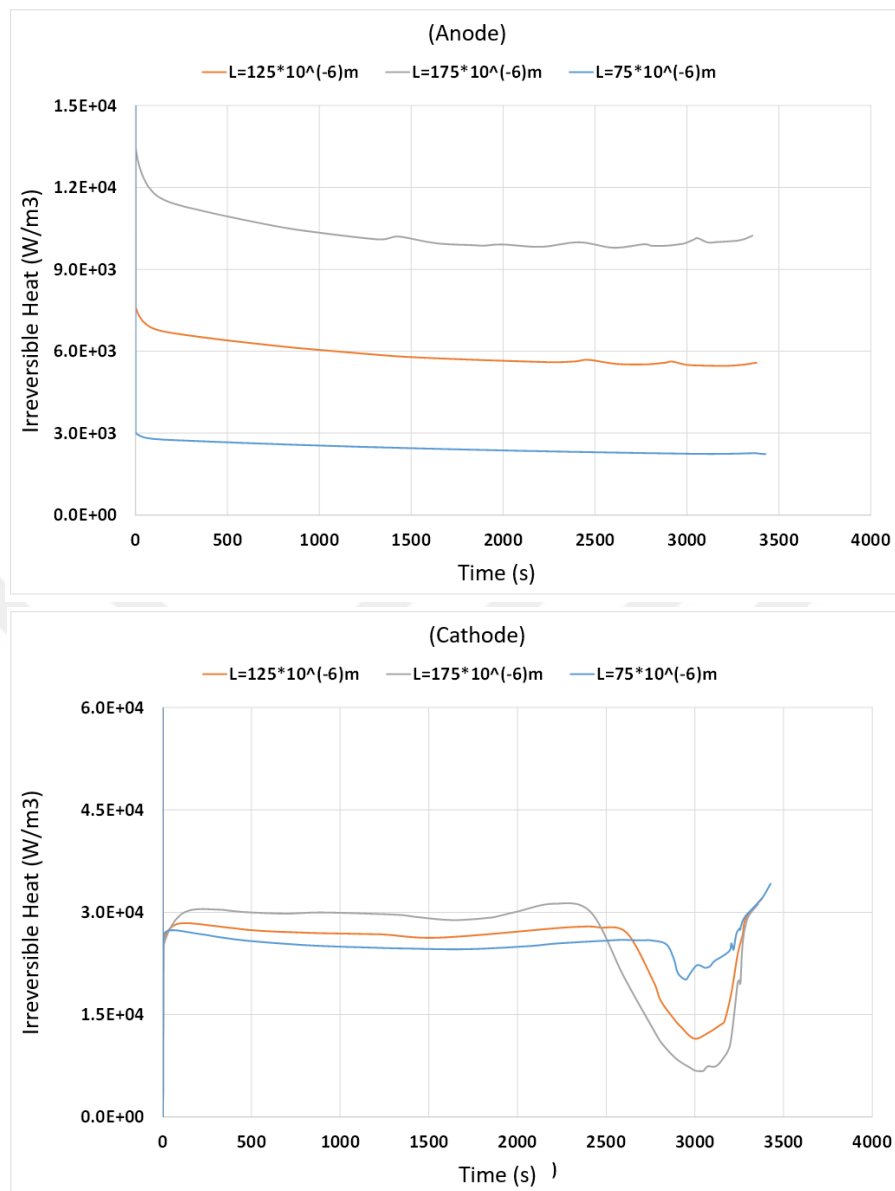


Figure 3.9. Effect of layer thickness on heat generation

4 Chapter 4: Investigation of 3-D multilayer approach in predicting the thermal behavior of 20Ah Li-ion cells

4.1 Introduction

Lithium ion batteries as rechargeable battery sources has attracted significant research attentions in last few decades due to the increasing popularity of the electrical vehicles (EVs) and hybrid electrical vehicles (HEVs)^{234, 235}. Compared to the batteries used in home electronics, the lithium ion batteries are required to provide high specific and volumetric energy, low heat dissipation, and better safety characteristics to be used as an alternative power source for EVs and other fields such as aerospace and military applications²³⁶.

During charge/discharge process, significant amount of heat is generated inside the battery cell. The main sources of heat generation are electrochemical reactions, and internal resistances¹⁸⁷. The generated heat leads to local temperature rise and temperature nonuniformity inside the cell which greatly affect the cycle life^{120, 237}, power and capacity fading²³⁸, and performance⁸⁰ of the Lithium ion batteries. In large-scale battery modules and packs, accumulation of the generated heat and temperature rise leads to accelerated exothermic reactions that cause thermal runaway to happen^{55, 239, 240}. Keeping the cell average operating temperature and local temperature gradient in an optimum range ensures cycle-life, safety, and performance of batteries²⁴¹. According to Motloch et al.²⁴², 1°C temperature rise in a range of 30-40°C results in two month decrease in the battery lifespan. Consequently, the temperature range and the cell internal temperature distribution are needed to be optimized in order to have a safe operating battery²⁴³.

Thermal behavior and power density of lithium ion cell is affected by particle size²⁴⁴, electrode porosity²⁴⁵, and electrode thickness²⁴⁶. The electrode thickness significantly affects the diffusion rate of ions and internal resistance of the cell and results in capacity fading and nonuniform local temperature distribution^{22, 243, 247-249}. Zhao et al.¹⁹ investigated the effects of electrode thickness on thermal performance and heat generation distribution. They found that a battery with thicker electrodes has more intensive and uneven temperature response and heat generation, longer diffusion distance, serious concentration polarization, higher internal resistance, and uneven distribution of electrochemical reactions. Thickness of the electrodes is directly proportional to the cell capacity, and to the number of cell layers. Therefore, thickness of the electrodes decreases as the number of layers increases, which results in a better electrochemical-thermal performance of the Li ion cell. Thus, beside the mentioned parameters, number of the electrodes is one of the main factors, which change the cell internal resistance, and temperature non-uniformity^{19, 248-251}.

Nomenclature

a	electrode specific surface area (m^{-1})	T	absolute temperature (K)
A_{tab}	cross section of the tab (m^2)	t_+	transferring number of Li^+
C_{dl}	Electrical double layer capacitance (F/m^2)	U_{eq}	open circuit potential (V)
c_e	lithium concentration in electrolyte (mol/m^3)	α_a	anodic transfer coefficient
C_p	specific heat ($\text{J}/\text{kg.K}$)	α_c	cathodic transfer coefficient
c_s	lithium concentration in solid (mol/m^3)	ε_e	volume fraction of the fillers
$c_{s,0}$	Initial lithium concentration in solid (mol/m^3)	κ_{eff}	Effective ionic conductivity of the electrolyte (S/m)
$c_{s,\text{max}}$	max li ion concentration in solid (mol/m^3)	ρ	density (kg/m^3)
$c_{s,\text{sur}}$	surface concentration of lithium in the active material (mol.m^3)	σ_s	electronic conductivity of the solid phase (S/m)
D_e	diffusion coefficient of Li ion in electrolyte (m^2/s)	σ_e	ionic conductivity of electrolyte (S/m)
D_s	diffusion coefficient of Li ion in solid (m^2/s)	λ	thermal conductivity ($\text{W}/\text{m.K}$)
f	average molar activity coefficient	φ_s	solid-phase potential (V)
F	Faraday's constant (96,487 C/mol)	φ_e	electrolyte-phase potential (V)
h	Convective heat transfer coefficient ($\text{W}/\text{m}^2.\text{K}$)	Subscripts, superscripts and acronyms	
i_0	Exchange current density (A/m^2)	0	Initial value
i_{app}	Total applied current density (A/m^2)	cc	Current collector
i_{loc}	local working current density of the cell unit (A/m^2)	eff	Efficient
i_N	Normal inward current density through the electrode/cc interface (A/m^2)	i	Indicator (i = pe, ne)
k	reaction rate constant ($\text{m}^{2.5}/\text{mol}^{0.5}.\text{s}$)	e	Electrolyte
L_{bat}	Battery cell thickness (m)	ne	Negative electrode
t			
N	Total number of cell layers	max	maximum

r	radios of electrode particle (m)	pe	Positive electrode
R	universal gas coefficient (8.314 J/mol.K)	s	Solid
t	time (s)	sep	Separator

There have been many efforts to model the thermal behavior of the batteries and to predict heat generation inside the battery cell. Non-uniform temperature distribution along a large size Li-ion battery is very common and undesired effect on designing a thermal management systems⁷⁷. Commercial Li ion cells are composed of several repeating electrochemical layers each consisting negative-current collector, negative electrode, separator, positive electrode, and positive current collector. In the case of multilayer pouch-type cells, the cell dimensions are enlarged, and the number of layers is increased to reach desired capacity. This causes the intracellular temperature distribution to become uneven, decreasing the cycle life of the cell, and even cause thermal drift. However, many researchers have adopted a single-layer cell model (with a single electrode plate pair approach) to save in computing time and to eliminate meshing effort^{252, 253}. Their hypothesis is that thermal conductivity of the layer elements is so high and heat transfer rate is so fast. In other words, they simplify the heat conduction by assuming that temperature inside the cell is uniform and the cell is a thermally uniformed body with effective thermo-physical properties²²³. Therefore, instead of several thin layers, they model the cell as one thick layer unit or they consider lumped model. In recent studies, various electrochemical and heat generation coupling numerical 1D²³⁴, 2D²⁵⁴, and 3D models has been developed to analyze the thermal characteristics of the Li-ion batteries²⁵⁵⁻²⁵⁸. Zhao et al.²⁵⁹, Al-Hallaj et al.²⁶⁰, and Fang et al.²⁶¹ developed a 3D lumped model in which the cell structure is considered as integrated and homogeneous element with the uniform thermal properties and distribution. Ping et al.²⁶² modeled the cell by a solid structure formed with homogeneous layers to study the effect of the environment or/and airflow cooling on the behavior of the cell. Jaguemont et al.²⁶³ proposed a 3D model using a single pair of layers to describe the thermal behavior of the battery at extreme temperature condition. Sun et al.²⁶⁴ predicted the temperature distribution and a thermal runaway of the battery considering layered-structure of the cells as a homogenous material. In the literature, there are also multilayer thermal models that account for heat transfer and heat generation in the individual layers. For instance, Xu et al.²⁶⁵ and Wang et al.²⁶⁶ developed a 3D electrochemical-thermal model to obtain the temperature profile of the cell. Chen et al.²⁶⁷ used a multilayer electro-chemical model to get the temperature and the current distribution during the normal discharge and the short circuit process. Goutam et al.²⁵¹ coupled a multilayer 2D-potential distribution model with a 3D-temperature distribution model and analyzed the effects of design factors on temperature distribution within the cell. However, they do not discuss how the number

of electrodes considered in the model would influence a thermal behavior of the cells such as temperature rise, and local temperature distribution.

In this work, the superiority of the multilayer approach (MLA) over the single layer approach (SLA) is investigated in predicting the thermal behavior of Li-ion batteries. In this approach, first the MLA is developed which consists of repeating units of positive current collector, positive electrode, separator, negative electrode, and negative current collector, to predict the thermal behavior of 20Ah Li-ion cell at different discharge rates using a 3D electrochemical-thermal model. Then, several arbitrary points are chosen on the surface of the cell and the predicted temperatures of these points are compared using the MLA and SLA. The number of layers in the cell is founded to greatly affect the temperature rise, and temperature non-uniformity both on the surface and inside the cell. The deviations of the model predicted temperatures from the actual recordings are discussed. The results show that the MLA leads to a better estimation of actual temperatures and promising temperature profiles. We believe that the MLA should be preferred to design an efficient thermal management system for high capacity Li-ion batteries.

4.2 Experimental setup

Commercially available pouch-type 20Ah LiFePO₄ cells (24.°m x 12.0 cm x 0.8 cm) are used to experimentally study the electrochemical and the thermal behavior of the cells under different working conditions. Neware CT-4004-20V30A-NFA and Neware CT-4008-5V60A-NFA battery testing systems are used to monitor the capacity and the cell surface temperature. VT model N type thermocouples are placed at 7 different points on the cell surface to monitor the variation of the surface temperature at different parts. All experiments are conducted in a KK 240 TOP+FIT model POL-EKO APARATURA thermal chamber to keep the ambient temperature constant. In order to determine the temperature variation along the surface, 7 thermocouples are placed on the cell surface (Figure 4.1). One other thermocouple is also used in every experiment to monitor the temperature of the environment. Electrochemical tests include constant current- constant voltage (CCCV) charging and constant current discharge schemes. Briefly, the cells are charged first in galvanotactic mode at 1C with a voltage cut-off limit of 3.6 V and then in a potentiostatic mode until the current drops to 100 mA. The cells are then kept at rest for an hour. Finally, the cells are discharged at desired rate (1C-5C) until the voltage drops to 2.0V and are kept at rest for 2 hours. The data is recorded every 5 seconds and a typical cycle can be seen on Figure 4.2.

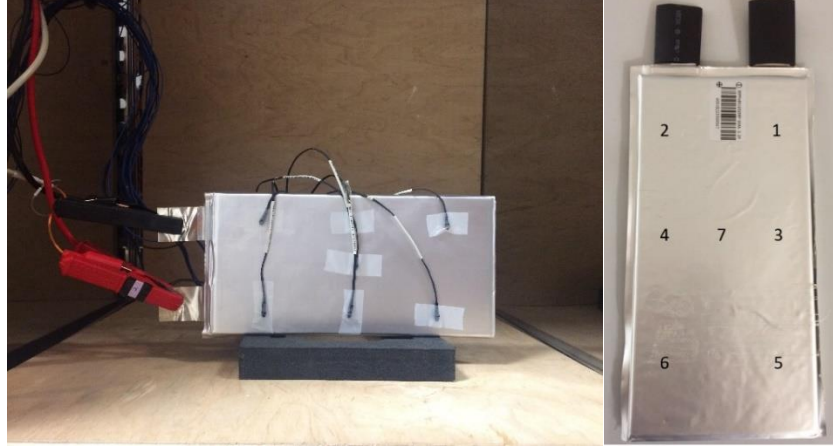


Figure 4.1. Experimental setup of measuring the cell surface temperature.

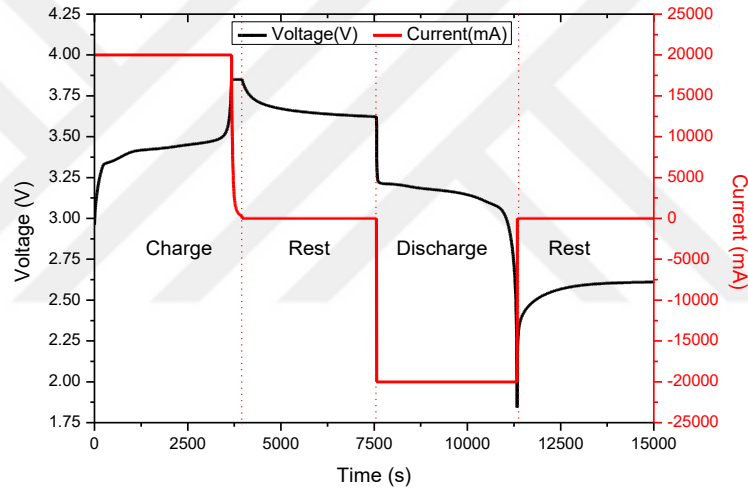


Figure 4.2. Voltage-current graphic for a cycle with 1C charge and 1C discharge rate.

4.3 Model Development

4.3.1 Electrochemical model

Figure 4.3 shows a schematic of the 2D lithium ion battery layers which consists of negative current collector (Cu), negative electrode (Graphite), separator (1:1 EC:DEC / LiPF6), positive electrode (LiFePO4), and positive current collector (Al). During the discharge process, positively charged Li ions diffuses and migrates by the electrolyte from the negative electrode through the separator to the positive electrode. The electrochemical reactions occurring during the discharge are listed in Equations (1) and (2):



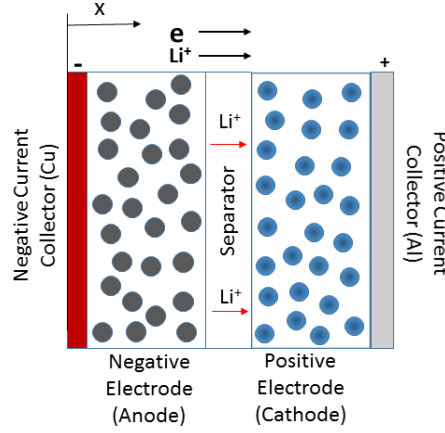
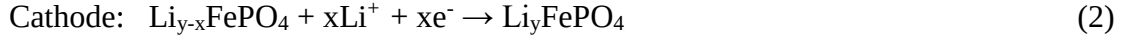


Figure 4.3. Schematic of 1D lithium ion battery layer.

Followings are the governing PDEs representing electrochemical model covering the mass balance, charge conversion (Ohm's law), and energy balance for electrochemical thermal interactions happening inside the battery²⁶⁸. The Fick's second law in spherical coordinates obtains the mass balance for lithium ions inside the solid particles (AM):

$$\frac{\partial c_{s,i}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{s,i} \frac{\partial c_{s,i}}{\partial r} \right) \quad (3)$$

The ions diffusion rate in and out of the particles are expressed as the boundary conditions at the particle surface and center as:

$$\left. \frac{\partial c_{s,i}}{\partial r} \right|_{r=0} = 0 \quad (4)$$

$$-D_{s,i} \left. \frac{\partial c_{s,i}}{\partial r} \right|_{r=R_s} = \frac{i_{loc}}{a_s F} \quad (5)$$

Mass transfer of Li-ions in the liquid phase is governed by:

$$\varepsilon_e \frac{\partial c_e}{\partial t} = \nabla \cdot (D_e^{eff} \nabla c_e) + \frac{a_s i_{loc}}{F} (1 - t_+) \quad (6)$$

where $D_{e,eff} = \varepsilon_e^{1.5} D_e$, and the boundary conditions at the interfaces are given below:

$$-\nabla \cdot \mathbf{C}_e \big|_{ne/cc^-} \&_{pe/cc^+} = 0 \quad (7)$$

$$-\nabla \cdot \mathbf{C}_e \big|_{ne/sp} = -\nabla \cdot \mathbf{C}_e \big|_{pe/sp} \quad (8)$$

The local current density, i_{loc} , for the cathode or the anode is calculated by the Butler-Volmer's equation:

$$i_{loc} = i_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right) \quad (9)$$

where η is the local surface over-potential and is defined as:

$$\eta = \phi_s - \phi_l - U_{eq} \quad (10)$$

and i_0 is the exchange current density given by Eq. (11):

$$i_0 = F(k_c)^{\alpha_a} (k_a)^{\alpha_c} (c_{s,max} - c_{s,sur})^{\alpha_a} (c_{s,sur})^{\alpha_c} \left(\frac{c}{c_{ref}} \right)^{\alpha_a} \quad (11)$$

where, $c_{s,i,sur} = c_{s,i,r=R_s}$.

The modified Ohm's law determines the electronic transport in the solid phase and the ionic transport in the electrolyte phase:

$$i_s = -\sigma_{s,eff} \nabla \phi_s \quad (12)$$

$$i_e = -\kappa_{eff} \nabla \phi_e + \left(\frac{2\kappa_{eff} RT}{F} \right) \left(1 + \frac{\partial \ln f}{\partial \ln c} \right) (1 - t^+) \nabla \ln c_e \quad (13)$$

where;

$$\sigma_{s,eff} = \mathcal{E}_s^{1.5} \sigma_s \quad (14)$$

$$\kappa_{eff} = \mathcal{E}_e^{1.5} \sigma_e \quad (15)$$

The boundary conditions at the interfaces are given by:

$$-\sigma_{s,eff} \nabla \cdot \phi_s \Big|_{ne/cc^- \& pe/cc^+} = i_{N,i} \quad (16)$$

$$-\sigma_{s,eff} \nabla \cdot \phi_s \Big|_{ne/sp \& pe/sp} = 0 \quad (17)$$

$$\nabla \cdot \phi_e \Big|_{ne/cc^- \& pe/cc^+} = 0 \quad (18)$$

The charge conversion for the transport of electrons in the solid phase and the transport of ions in the electrolyte phase are described in the following equations:

$$-\nabla \cdot i_e + a_s i_{loc} = 0 \quad (19)$$

$$-\nabla \cdot i_s - a_s (i_{loc} + C_{dl} (\frac{\partial \phi_s - \partial \phi_l}{\partial t})) = 0 \quad (20)$$

The potentials in current collectors and tabs can be expressed as:

$$\nabla \cdot (-\sigma_{cc,i} \nabla \phi_{cc,i}) \Big|_{ne/cc^- \& pe/cc^+} = -i_{N,i} \quad (21)$$

where $i_{N,i} = 0$ at the tabs. At the positive tab, the current of the cell is applied, and the negative tab is grounded during a discharge process.

$$n \cdot (-\sigma_{cc,i} \nabla \phi_{cc,i}) \Big|_{cc^- \& cc^+} = i_{app,i} = \frac{I_{app}}{N \times A_{tab}} \quad (22)$$

where, $\phi_{cc,i} = 0$ at the top of a negative tab.

4.3.2 Thermal model and heat generation

Temporal and spatial variation of the battery's inner temperature depends on the electrode's material properties and the reactions occurring inside the battery. Main sources of heat generation inside the batteries are activation reactions, ionic species transport, and ohmic heat from electronic charge transfer. Energy balance for the battery system is given by^{243, 257, 269}:

$$\rho c_p \frac{\partial T}{\partial t} - \frac{\partial}{\partial x} \left(\lambda_{\perp} \frac{\partial}{\partial x} \right) + \frac{\partial}{\partial y} \left(\lambda_{\angle} \frac{\partial}{\partial y} \right) + \frac{\partial}{\partial z} \left(\lambda_{\angle} \frac{\partial}{\partial z} \right) = Q_{rev} + Q_{irrev} + Q_{ohm} \quad (23)$$

where Q_{irrev} is the total reaction heat generation rate, Q_{rev} is the total reversible entropic heat generation rate, and Q_{ohm} is the total ohmic heat generation rate which are given by the following sets of equations:

$$Q_{rev} = a_s i_{loc} T \frac{U_{eq}}{\partial T} \quad (24)$$

$$Q_{irrev} = F a_s i_{loc} (\phi_s - \phi_e - U_{eq}) \quad (25)$$

$$Q_{ohm} = -i_s \cdot \nabla \phi_s - i_e \cdot \nabla \phi_e - i_{cc,i} \cdot \nabla \phi_{cc,i} \quad (26)$$

Convective heat dissipation on the boundaries are also considered and defined as:

$$(i = x) : -\lambda_{\perp} \frac{\partial T}{\partial i} \Big|_{x=0 \& x=L_{batt}} = h_i (T_s - T_{\infty}) \quad (27)$$

$$(i = y, z) : -\lambda_{\angle} \frac{\partial T}{\partial i} \Big|_{y=0 \& y=w \& z=0 \& z=h} = h_i (T_s - T_{\infty}) \quad (28)$$

$$(i = x, y, z) : -\lambda_{tab} \frac{\partial T}{\partial i} \Big|_{tabs \& ambient} = h(T_{s,tab} - T_{\infty}) \quad (29)$$

where x is the thickness direction, y is the width direction, z is the length direction, and T_{∞} is the ambient temperature. The cross-plane thermal conductivity ($\lambda_{\perp}$) corresponds to the thickness direction, whereas, the in plane thermal conductivity ($\lambda_{\angle}$) corresponds to the width and length directions. The convective heat transfer coefficient (h_i) is assumed equal in all directions for the natural convection condition.

4.3.3 Model parameterization

Model parameterization and parameters evaluation is necessary for a model validation. Table 4.1 lists the battery geometrical and design parameters used in the coupled electrochemical-thermal model. Some of the electrochemical parameters used in the model are not constant and their values change as a function of the temperature and concentration. The temperature and SOC-dependent diffusion coefficients in the solid and electrolyte phase are expressed as follow:

$$D_{s,ne} = 3.9 \times 10^{-14} (1.5 - SOC)^{3.5} \exp \left[\frac{E_{aR}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (30)$$

$$D_{s,pe} = 1.25 \times 10^{-15} \exp \left[\frac{E_{aR}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (31)$$

$$D_e = 10^{\left(-4.43 - \left(\frac{54}{T - 229 - 0.005c_e} \right) - 0.0022c_e \right) - 4} \quad (32)$$

Arrhenius equation was used to formulate the temperature dependency of reaction rate constants and electrolyte phase conductivity as follow:

$$k_{0,ne} = 3 \times 10^{-11} \exp \left[\frac{E_{aR}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (33)$$

$$k_{0,pe} = 1.2 \times 10^{-14} \exp \left[\frac{E_{aR}}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (34)$$

$$\sigma_e = \exp \left[\frac{1100}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \quad (35)$$

Table 4.1. Parameters and material properties

Parameter	Cu foil	Anode	Separator	Cathode	Al foil
$L(\mu m)^{[a]}$	70	150	25	125	75
$\varepsilon_{s\ 118}$	—	0.56	—	0.435	—
$\varepsilon_e\ 118$	—	0.3	0.4	0.28	—
$R_s(\mu m)^{118}$	—	14.75	—	1.15	—
$\rho\ (kg.m^{-3})^{118, 256, 270}$	8900	2660	1009	1500	2700
$D_s\ (m^2.s^{-1})^{118,[b]}$	—	Eq. (30)	—	Eq. (31)	—
$D_e\ (m^2.s^{-1})^{271,[b]}$	—		Eq. (32)		—
$k\ (m^{2.5}.mol^{-0.5}/s)^{[b]}$	—	Eq. (33)	—	Eq. (34)	—
$\sigma_s\ (S.m^{-1})^{19}$	6e7	100	0	11.8	3.77e7

σ_e (S.m ⁻¹) ^[b]	—		Eq. (35)		—
$c_{s,max}$ (mol. ⁻³) ^[b]	—	31,540	—	26,390	—
$c_{s,0}$ (mol.m ⁻³) ^[b]	—	16,361	—	3900	—
c_p (J.kg ⁻¹ .K ⁻¹) ^{118, 256, 272}	385	1437.4	1978	1260.2	903
$\lambda_{\perp}$ (W.m ⁻¹ .K ⁻¹) ^{118, 256, 270-274}	398	1.06 ± 0.16	0.334	1.79 ± 0.18	238
$\lambda_{\parallel}$ (W.m ⁻¹ .K ⁻¹) ^{273, 275}	398	31	0.334	23	238
E_{aD} (J.mol ⁻¹) ¹	—	4000	—	20,000	—
E_{aR} (J.mol ⁻¹) ²⁷¹	—	20,000	—	30,000	—
α_a ²⁵⁶		0.5		0.5	
α_c ²⁵⁶		0.5		0.5	
T_{ref} (K)	298.15				
h (W/m ² .K) ^[b]	8				
[a] from company	[b]				
	fitting				

4.3.4 Single vs Multilayer Approach

The commercial pouch-type cells consist of many layers. However, the effects of the multilayer structure on thermal behavior of the Li-ion cell has not been fully investigated. In this approach, using the finite element simulation software (COMSOL Multiphysics), 3D models of single-layer cell and multilayer cell are developed. All the electrochemical and thermal equations are solved using the COMSOL, and a two-way approach is used for coupling the electrochemical and thermal modules. In this approach, the heat generation rates due to electrochemical reactions, entropy change, and joule heating are calculated locally with the multiphase electrochemical model. Then, the 3D thermal solver uses the heat generation to find the temperature field in the battery cell. The temperature field is used in 3D solver while the average of temperature is used to update temperature dependent physiochemical properties in the 1D electrochemical solver. The multilayer cells consist repeating units of positive current collector, positive electrode, separator, negative electrode, and negative current collector. Figure 4.4 represents the schematic of the single-layer and multilayer cells. The dimensions of the modeled cells in this study are the same as the purchased commercial 20Ah LiFePO₄ batteries (24.5 cm x 12.0 cm x 0.8 cm).

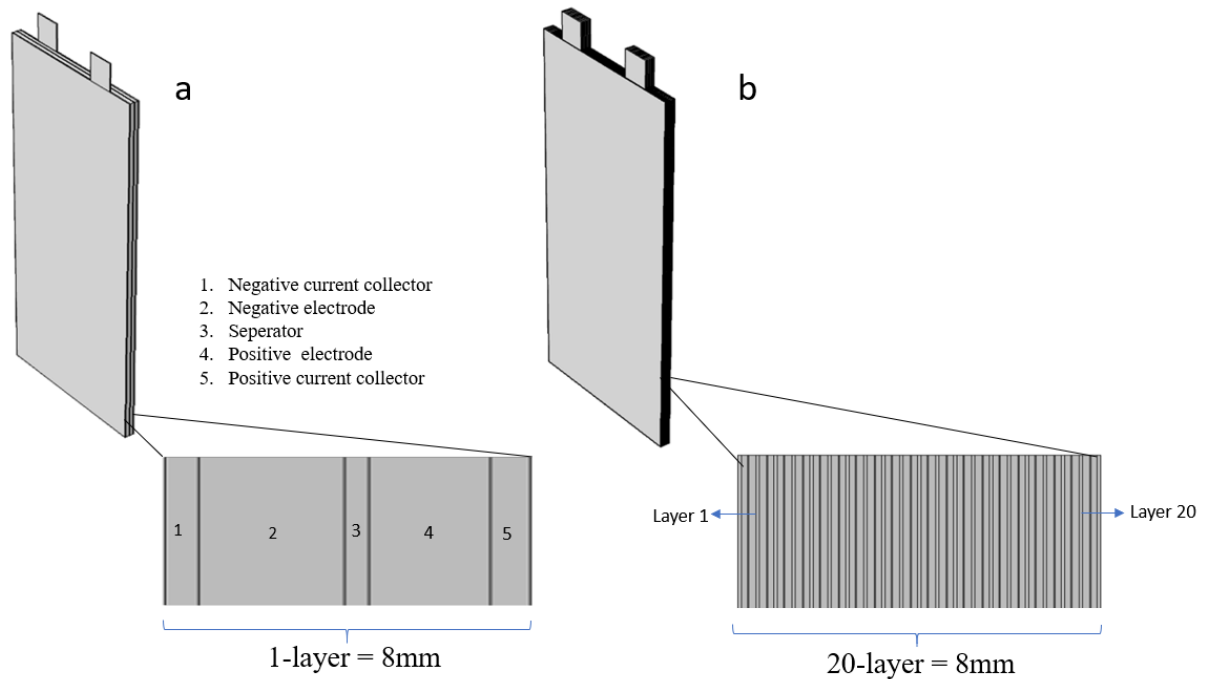


Figure 4.4. Schematic of (a) the single-layer cell and (b) the multilayer cell with the thickness of real pouch cells.

To investigate the thermal characteristics of the multilayer cells, we developed cells of the same type and size with different number of layers. To see the effects of the multilayer structure on thermal behavior of the cells, the thickness of the cells is kept constant and number of the layers were used as the controlling parameters. As the number of layer increases, the thickness of each layer decreases. Consequently, the total amount of active material remains same in all of the developed cells. For instance, Figure 4.5 illustrates schematic of a single-layer cell versus an 8-layer cell. In the single-layer cell, there is one layer with the thickness of x (mm) while in the 8-layer cell there are 8 repeating layers with the thicknesses of $x/8$ (mm).

Table 4.2 summarizes the number of layers and related thicknesses for different multilayer cells.

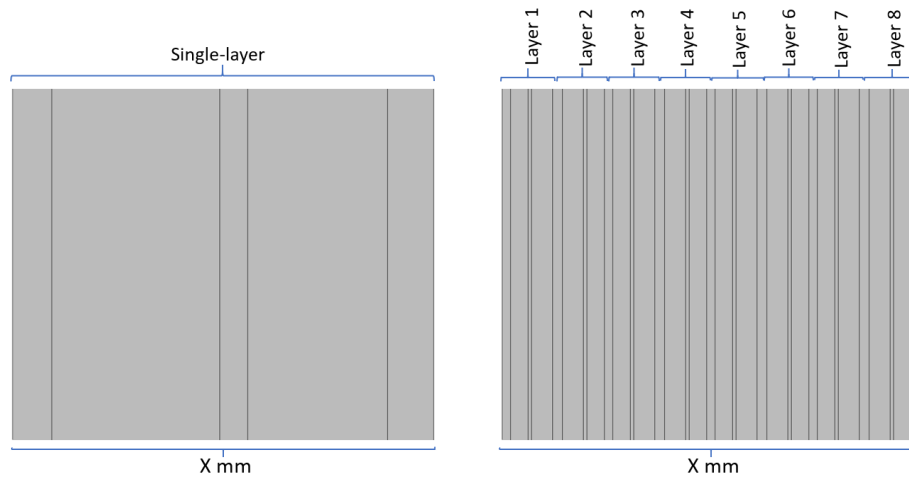


Figure 4.5. Schematic of single-layer (left) and 8-layer (right) approaches.

Table 4.2 Number of layers and thicknesses of single-layer cell and multilayer cell.

	Negative_cc	Anode	Separator	Cathode	Positive_cc
20-layer					
# of	10	20	20	20	11
component					
thickness	$1 \cdot L_{neg_cc}$	$1 \cdot L_{neg}$	$1 \cdot L_{sep}$	$1 \cdot L_{pos}$	$1 \cdot L_{pos_cc}$
16-layer					
# of	8	16	16	16	9
component					
thickness	$(10/8) \cdot L_{neg_cc}$	$(20/16) \cdot L_{neg}$	$(20/16) \cdot L_{sep}$	$(20/16) \cdot L_{pos}$	$(11/9) \cdot L_{pos_cc}$
8-layer					
# of	4	8	8	8	5
component					
thickness	$(10/4) \cdot L_{pos_cc}$	$(20/8) \cdot L_{neg}$	$(20/8) \cdot L_{sep}$	$(20/8) \cdot L_{pos}$	$(11/5) \cdot L_{pos_cc}$
4-layer					
# of	2	4	4	4	3
component					
thickness	$(10/2) \cdot L_{neg_cc}$	$(20/4) \cdot L_{neg}$	$(20/4) \cdot L_{sep}$	$(20/4) \cdot L_{pos}$	$(11/3) \cdot L_{pos_cc}$
Single-layer					
# of	1	1	1	1	1
component					
thickness	$10 \cdot L_{neg_cc}$	$20 \cdot L_{neg}$	$20 \cdot L_{sep}$	$20 \cdot L_{pos}$	$11 \cdot L_{pos_cc}$

4.4 Results and Discussion

4.4.1 Experimental Observations

Li-ion cells with the dimensions of 24.5 cm x 12.0 cm x 0.8 cm has two large surface areas which resulted in non-uniform temperature distribution along these surfaces. However, it is crucial to keep the temperature of Li cells uniform and, if possible, at an optimum level in order to obtain highest performance for a longer period. Figure 4.6 shows temperature distribution of Li-ion cell discharged at 5C and 30°C. It is clearly seen that the temperature of the cell decreases from top to bottom and from positive tab side to negative tab side. The highest temperature readings are observed towards positive tab due to the irreversible ohmic heat produced during discharge. Temperature non-uniformity along the surface is high and the maximum temperature difference is about 8°C. While a surface shows noticeable temperature gradient, temperature behavior of the front and back surfaces is similar with each other and show symmetric temperature profiles. For example, temperature readings of point 2 on the front and back surfaces differ only by 0.2K.



Figure 4.6. Observation of temperature distribution at 5C and 30°C

4.4.2 Model validation

To validate the developed multilayer model, electrochemical and thermal results obtained from the experimental measurements and the model were compared at five discharge current rates (1C, 2C, 3C, 4C, and 5C). The parameters used in the model are obtained either from fitting the model data to the experimental measurements or from the literature. Table 4.1 shows the list of the parameters and their references.

4.4.3 Electrochemical validation

Electrochemical validation is done by comparing the simulated and experimental cell voltages at different current rates (1C, 2C, 3C, 4C, and 5C). Figure

4.7 represents the cell working voltage at 5 different C-rates at constant ambient temperature of 30°C. The results show that voltage curves obtained from the simulation results agree with the experimental measurements. Table 4.3 shows the corresponding standard error of estimates for each discharge rates. It is worth noting that as the discharge current decreases, the differences between the experimental observations and modeling results decrease as well.

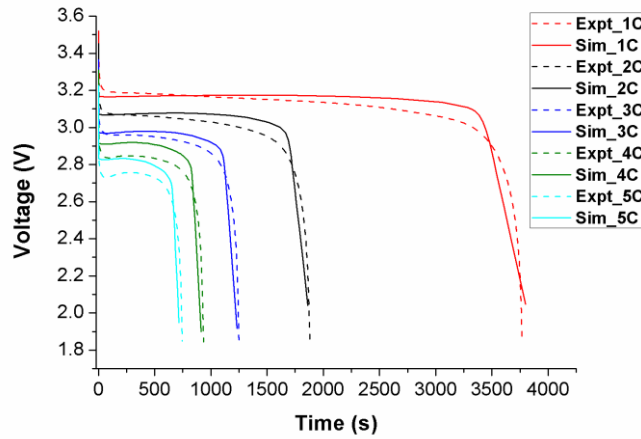


Figure 4.7. Comparisons of simulated and experimental cell voltage values at different current rates.

Table 4.3 Standard error of estimates at different C-rates

C-rate	1C	2C	3C	4C	5C
	0.095	0.096	0.113	0.173	0.221

4.4.4 Thermal validation

In the literature, thermal validation has been presented mostly at the lower current rates^{265, 267}. Nevertheless, presenting and validating the thermal behavior of the lithium ion batteries at C-rates greater than 1C is critical. In this study, an arbitrarily selected point, which is point 7 shown in Figure 4.1, is used to thermally validate the single-layer (SLA) and multilayer (MLA) approaches at different C-rates (1C, 2C, 3C, 4C, and 5C) by using reported and estimated modeling parameters listed in Table 4.4. It should be noted that same parameters are used in the SLA and MLA and parameter estimation for unknowns is done by minimizing the error of estimates for the SLA and MLA at the same time. Figure 4.8 shows the comparisons of the simulated and experimental temperature elevations for the SLA (Figure 4.8-a) and MLA (Figure 4.8-b). It can be easily seen that the temperature elevation from the simulated results are in good agreement with the experimental data at each C-rate for both cases, but the figures demonstrate that the MLA predicts the temperature rise slightly better than the SLA for point 7, and Table 4.4 presents the error analysis for each discharge rate. However, pouch cells for automotive industry and grid energy storage are produced in large sizes. As a consequence, the large-format of Li-ion battery brings a number of limiting factors

for operation with it, such as battery operation temperature²⁷⁶ or non-uniform temperature distribution²⁷⁷. Moreover, non-uniform temperature distribution on large-format Li-ion cells greatly affect the performance of Li-ion batteries. Therefore, it is important to determine how well the modeling approaches predict the temperature at any point on the surface of the cell. In the following section, the SLA and MLA are compared using specifically selected 4 points on the front and back surfaces of the cell in order to find out if any model predicts the actual temperature reliably and/or one model is superior to the other in predicting the temperature.

Table 4.4 Minimized Error of Estimates for point 7

C-rate	1C	2C	3C	4C	5C
Single-layer	0.816	0.912	1.089	1.341	1.587
20-layer	0.787	0.897	0.933	1.319	1.539

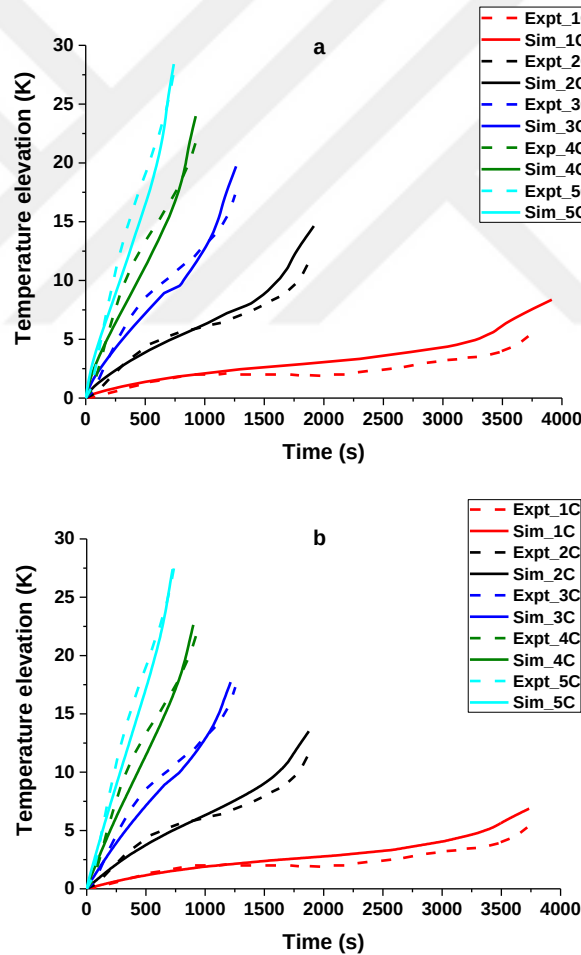


Figure 4.8. Comparisons of the experimental and simulated (a) Single-layer cell and (b) 20-layer cell surface temperature elevations on point 7 at different C-rates.

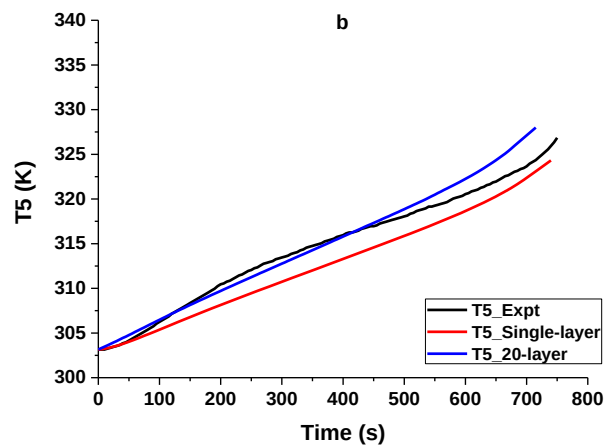
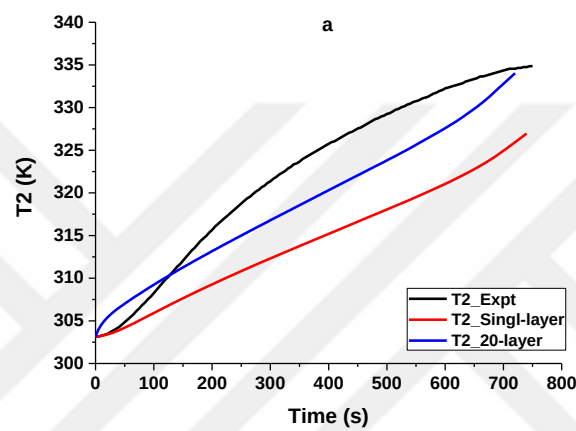
4.4.5 Comparison of single-layer approach (SLA) and multilayer approach (MLA)

Besides point 7, two extreme points on both front and back surfaces are selected to compare the effectiveness of the SLA and MLA. Point 2, which is closer to the tab, is selected purposely to observe the effect of ohmic heating during 5C discharge rate because the temperature of the tab increases considerably with increasing current (Figure 4.1). Point 5, on the other hand, is far from the tab and minimally affected by the temperature increase on the tab (Figure 4.1). It is also important to select points on the front and back surfaces of the cell because single layer has anode on one side and cathode on the other side whereas multilayer shows recurring positive and negative electrodes and ends with the starting electrode, i.e if it starts with a cathode, then it ends with the cathode. Points 2 and 5 on each side of the cell are referred as 2f, 2b, 5f, and 5b for point 2 on the front side, point 2 on the back side, point 5 on the front side and point 5 on the back side, respectively. Figure 4.9 show the simulated and experimental temperature profiles of points 2f, 2b, 5f and 5b. It should be noted that point 2 and 5 are two opposite extreme points in temperature. Among selected 4 points, points 2f and 2b are significantly under the influence of the heat generated by high current during discharge and measured temperature were as high as 334.85 K at the end of the discharge on the front side (Figure 4.9-a). This was the highest recorded temperature of all. Temperature on the back side was very close to the maximum temperature with a slight difference and recorded as 334.65K (Figure 4.9-c). Similarly, small temperature deviation was observed between 5f and 5b. Maximum observed temperatures are 326.85K and 326.80K for 5f and 5b, respectively. Temperature measurements on points 2 and 5 imply that there is a significant temperature non-uniformity along a surface but reasonably similar temperature profiles among counter points, i.e 2f and 2b or 5f and 5b.

Temperature profiles predicted from the MLA and SLA are also shown in Figure 4.9. Comparison of temperature estimation from these two approaches are made based on their error of estimates (EoE) from experimental measurements. Total of 145 data points are considered in estimating the deviation from experimental observations. On the front side, the calculated EoEs on point 2 for the MLA and SLA are 3.81 and 8.78, respectively, whereas they were 1.23 and 2.05 on point 5 for the MLA and SLA, respectively. On the back surface, the EoEs are again lower when the MLA is used, and corresponding results are tabulated in Table 4.5. The results show that the EoEs are doubled with the SLA as compared to the MLA. Moreover, estimated temperatures are lower than the measured ones if the front surface is considered, whereas they are considerably higher if the back surface is considered (Figure 4.9). This behavior indicates that estimated temperatures using the SLA deviate from the actual readings depending on the type of electrode. The results indicate that the ohmic effect cause larger EoE in predicting the temperatures regardless of the approach. As the point to be predicted moves away from the tab, the temperature predictions become closer.

Table 4.5 Error of estimates on the back and front sides.

	T2		T5	
	front	back	front	back
Single-layer	8.78	3.75	2.05	1.57
20-layer	3.81	3.83	1.23	1.22



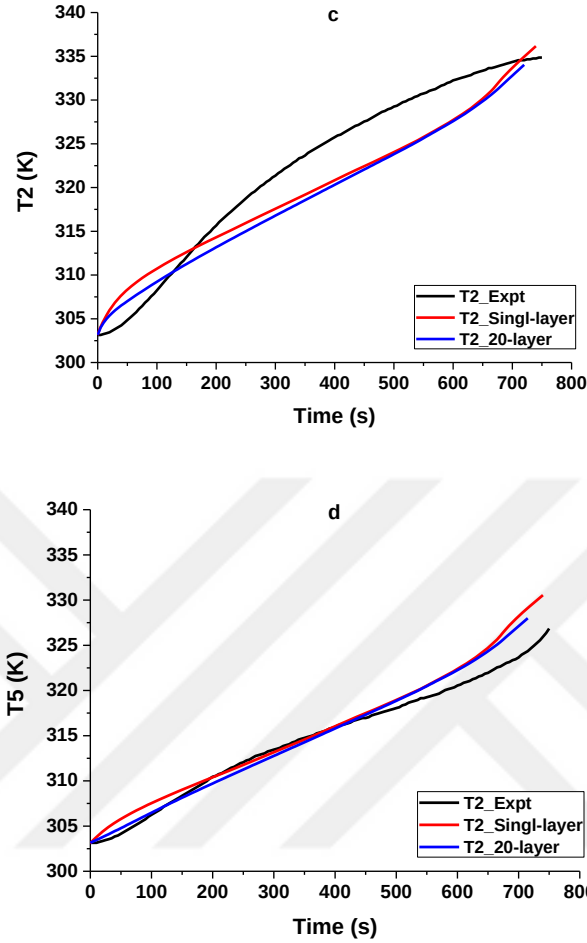


Figure 4.9. Comparison of the experimental and simulated surface temperature rise on the front side (a) point 2 and (b) point 5 and the back side (c) point 2 and (d) point 5 of the cells.

4.4.5.1 Prediction of symmetric thermal behavior of opposite surfaces

As discussed before, symmetric temperature behavior was observed on either side of the cell. Figure 4.10 shows the temperature difference between two sides of the SLA and the MLA (20-layer). The SLA predicts huge temperature difference between the front and back surfaces while the MLA shows totally symmetric profile. Unsymmetrical temperature profile from SLA is related to significant heat generation difference between the cathode and the anode during the discharge process. Figure 4.11 shows the total heat dissipation density in the different layer components of the cell at 5C. The heat dissipated from the positive electrode and positive current collector is much greater than the heat dissipated from the negative electrode and negative current collector during the discharge process. Therefore, the SLA predicts a difference of approximately 12°C between the two surfaces (Figure 4.10-a). On the other hand, when MLA is used (Figure 4.10-b), repeating units of positive and negative electrodes and

current collectors are considered, and therefore the cell component starts and ends with positive current collector. As a result, symmetrical temperature profile on either side of the cell is observed which is consistent with the experimental results.

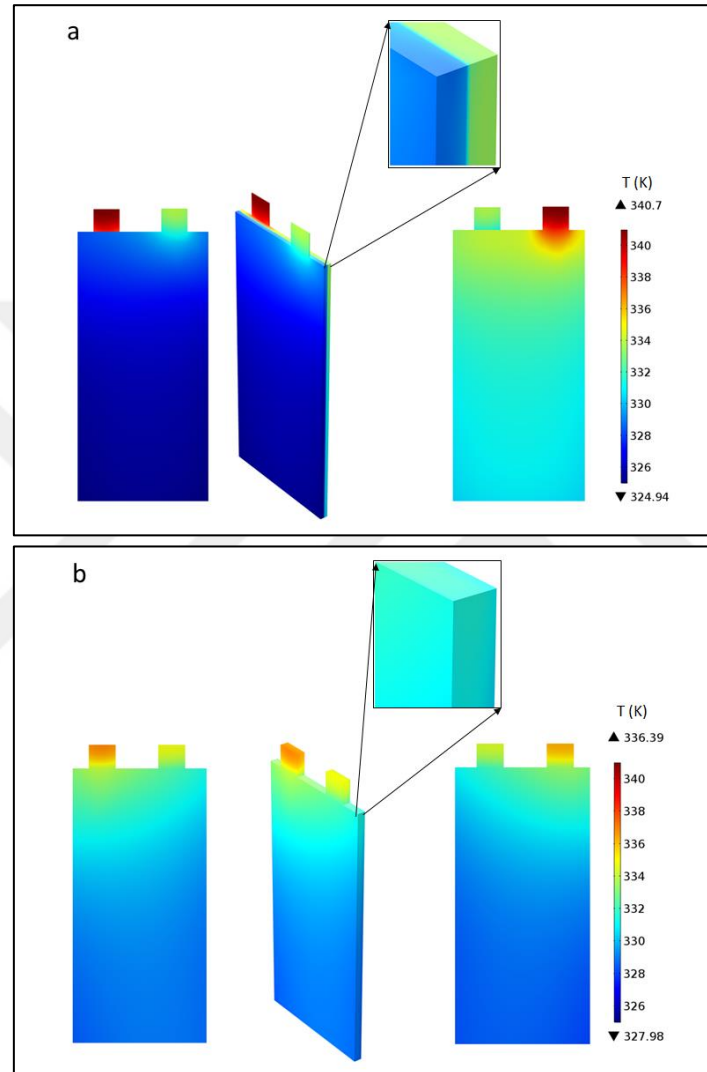


Figure 4.10. 3D profiles of the surface temperature on two side of (a) a single-layer cell and (b) a multilayer cell during 5C discharge and 30°C.

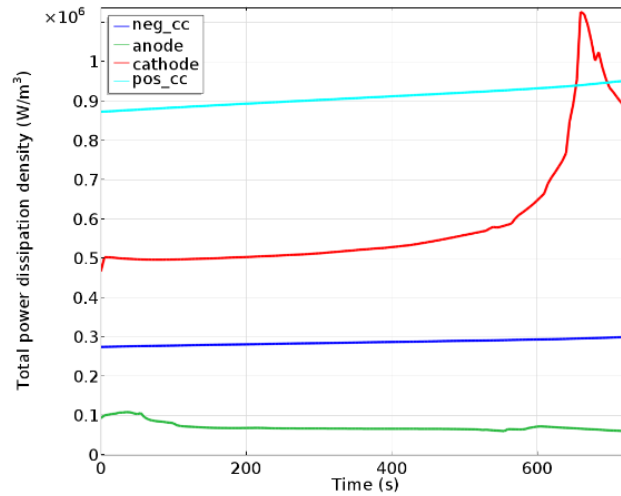


Figure 4.11. Total power dissipation density in the various cell layer components at 5C and 30 °C.

4.4.5.2 3D prediction of temperature non-uniformity

Temperature rise and nonuniformity along the cell significantly affects the electrochemical reactions, performance and cycle life of the Li-ion batteries²⁷⁸. Therefore, the thermal behavior of the Li ion batteries needs to be modeled and simulated accurately to get more reliable temperature profile along the cells. Table 4.6 lists the experimental temperature recordings of different points on the surface for the different C-rates (5C, 3C, and 1C). The experimental data clearly shows that the temperature profile of the cell is not uniform regardless of discharge rates. At 5C, temperature difference between two points is as high as 8°C while the maximum temperature differences are 3.5°C and 1.1°C at 3C and 1C, respectively. At higher C-rates, joule-heating rate is quite high that warms up the regions near to the positive tab. Thus, higher temperature rises on points 1 and 2 and lower temperature rises on points 5 and 6 is observed at 5C. At lower C-rates, the hot regions shift to the center of the cell. This can be explained by the comparable contributions of joule heating, reversible and irreversible heats. Figure 4.12 shows the simulated temperature profiles of the MLA and SLA at different C-rates. The MLA shows non-uniform temperature profile and follows similar thermal behavior as seen in the experimental results. At 5C, points 1 and 2 get warmer than points 3 to 7 (Figure 4.12-a) because immense heat is dissipated by joule heating from tabs, especially from the positive tab. Any point closer to the tabs is highly affected by this behavior. Point 2, which is located closer to the positive tab, warms up slightly more than point 1. This phenomenon can be clarified by the result shown in Figure 4.11, which indicates that joule heating is the main source of the heat dissipation at 5C. The maximum temperature difference on the surfaces is 6.24 °C. Similarly, when the cell is discharged at 3C, points 1 and 2 still warm up more and modeling results are again in agreement with the experimental observations (Figure 4.12-b and Table 4.6). Further decrease in discharge current results in less heat

dissipation from the tabs and consequently heat loss from the tabs becomes considerable. Therefore, slightly different thermal behavior is observed experimentally and numerically, such that points 4 and 7 becomes warmer than the rest of the surface of the cell (Figure 4.12-c and Table 4.6). On the other hand, temperature non-uniformity in the SLA varies with the type of the electrode. Cathode shows a difference of 5.61°C on the cell surface and reflects a close value to the actual readings. However, non-uniformity disappears on the anode and the maximum temperature difference is predicted as 2.63°C . This depicts a significant difference from the experimental observations, which is about 8°C . For instance, at 5C, maximum temperature difference on the surface of the SLA is 2.63°C , while it is 6.24°C and 8°C in the case of the MLA and experimental measurement respectively. After all, single-layer approach does not draw a good picture for a 3D thermal modeling.

Table 4.6 Experimental surface temperatures (K) for various C-rates at 30°C .

Experimental	T1	T2	T3	T4	T5	T6	T7
5C	334.65	334.85	328.25	332.65	326.85	329.05	331.45
3C	320.45	321.95	318.45	320.05	318.75	319.85	320.2
1C	308.35	308.45	308.55	309.45	308.15	308.8	309.2

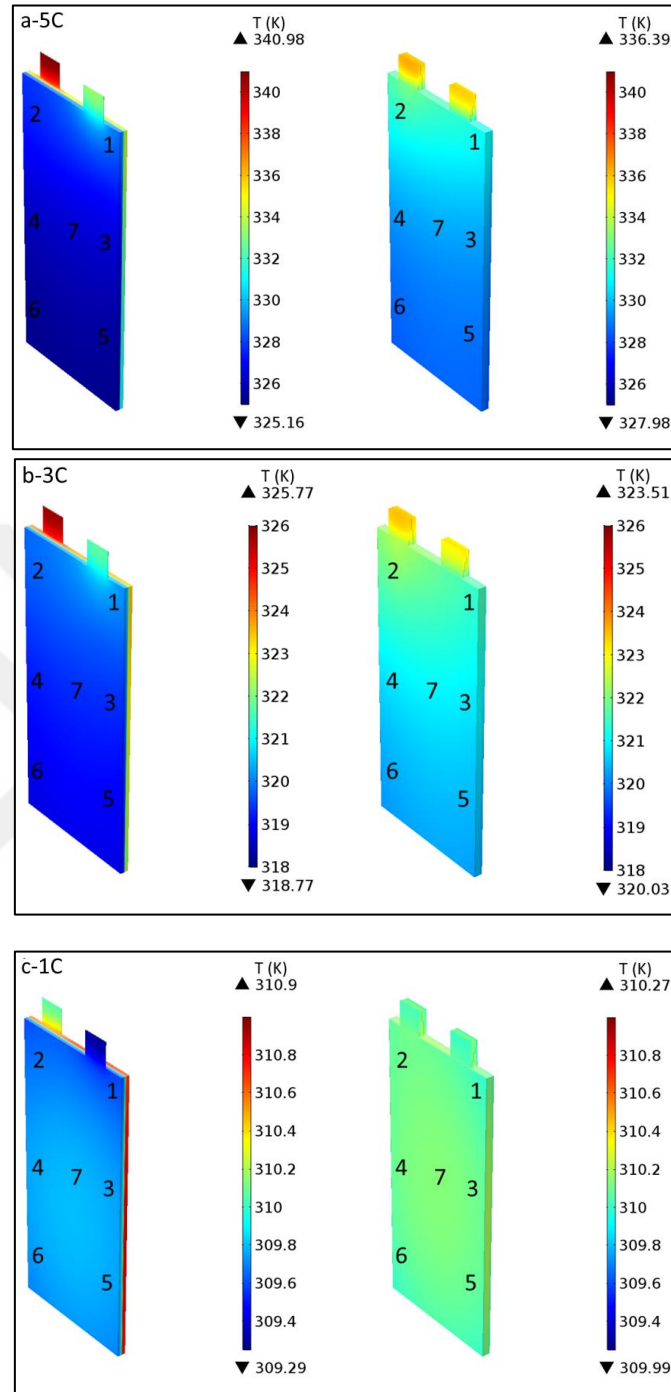
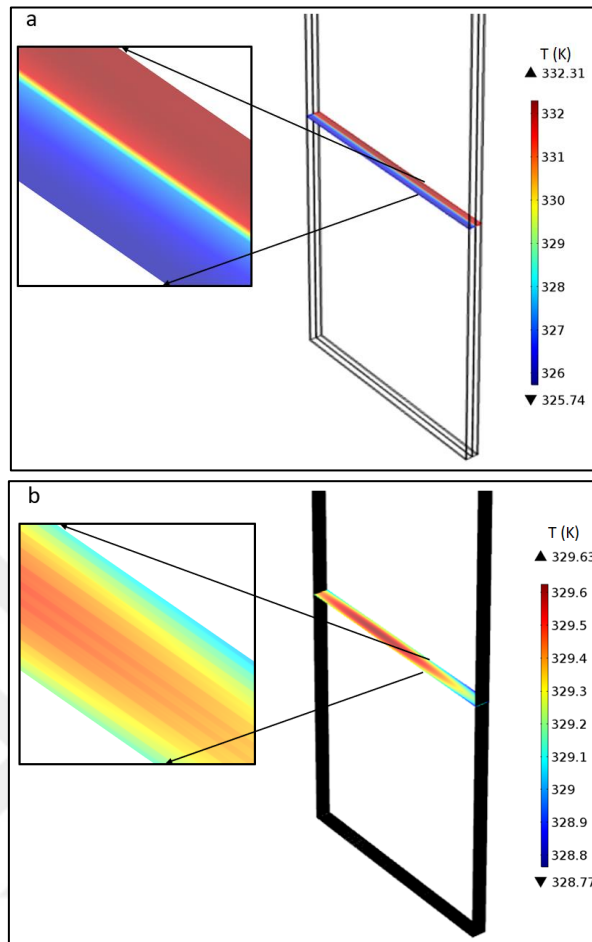


Figure 4.12. Comparison of the 3D temperature profiles of the simulated SLA (left) and the MLA (right) during (a) 5C, (b) 3C, and (c) 1C discharge at 30°C.

4.4.5.3 Internal temperature profile

Lastly, the insufficiency of the SLA in determining the internal temperature distribution was investigated. Many researchers have been interested in measuring the cell internal temperature distribution²⁷⁹⁻²⁸². For instance, Zhang et al.²⁸¹ reported in situ

measurement of the radial temperature distribution inside a cylindrical Li-ion battery cell and studied the effects of various operating conditions including temperature, C-rate, and cooling conditions on internal temperature distribution. Anthony et al.²⁸⁰ developed a new theoretical technique for non-invasive measurements of the core temperature of a cylindrical Li ion cell. Zhe Li et al.²⁸³ measured the temporal and spatial variation of the internal temperature for the LiMn_2O_4 cell. They found that the internal layers temperature could differ from the surface for as large as $1.1\text{ }^\circ\text{C}$ even for a thin laminated cell. Figure 4.13 represents comparison of the internal temperature profiles of the MLA versus the SLA at 5C discharge. The SLA (Figure 4.13-a, c) presents a unidirectional temperature gradient between the anode and the cathode. In other words, the internal temperature increases as we move from the negative side (the negative electrode and the negative current collector) towards the positive side (the positive electrode and the positive current collector). Furthermore, the temperature difference between the two surfaces of the cell is $6.57\text{ }^\circ\text{C}$, which is not supported by the experimental observations. The experimental temperature difference was only $0.3\text{ }^\circ\text{C}$ (Figure 4.6). However, in the MLA (Figure 4.13-b, d), the inner temperature distribution along the layers is nonlinear; with relatively lower temperature in outer layers and higher temperature in inner layers. In addition, maximum internal and surface temperature gradient is almost $1\text{ }^\circ\text{C}$ degree which is completely in agreement with the experimental results that Zhe Li et al.²⁸³ proposed.



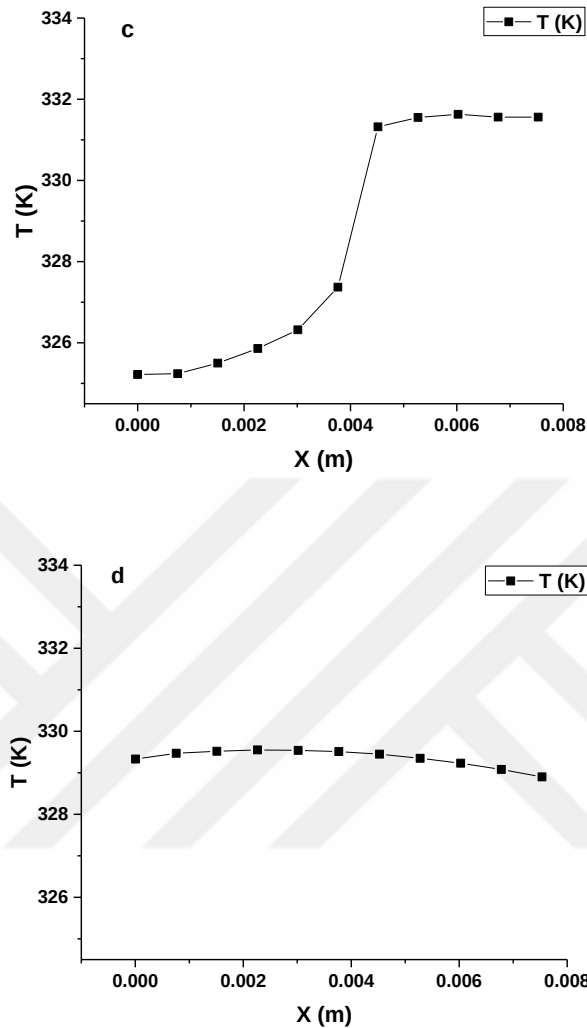


Figure 4.13. Comparison of the inner temperature profiles of (a) the single-layer cell versus (b) the 20-layer cell, and curves of the temperature variation in the thickness direction for (c) the single-layer cell versus (d) the 20-layer cell.

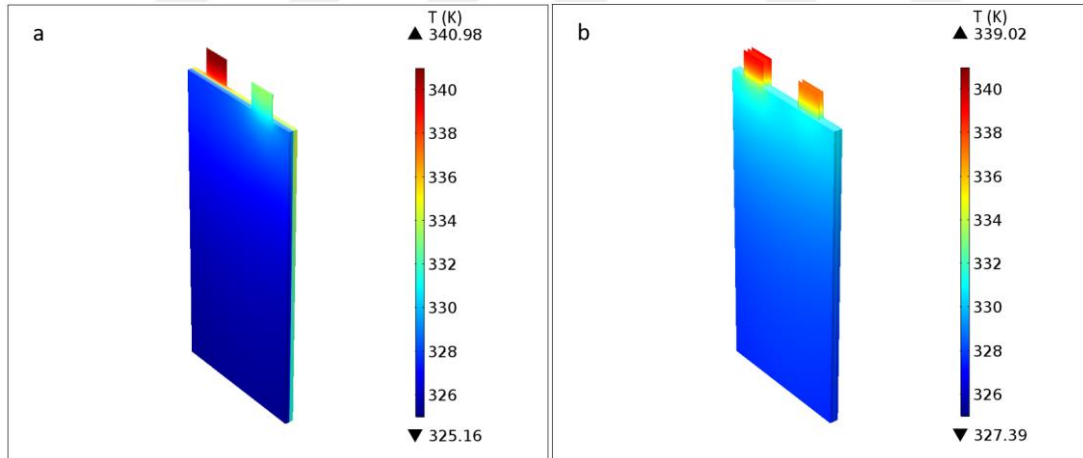
4.4.6 Effects of the number of layers on thermal behavior of the cell

In this section, the effects of number of layers on thermal behavior and temperature non-uniformity of the cells are discussed. According to experimental results, temperature non-uniformity on cell surfaces increases as the current rate increases (Table 4.6). Therefore, the 5C discharge rate is chosen to study the effects of number of layers. Figure 4.14 represents the 3D temperature profiles of the single-layer, 4-layer, 8-layer, 16-layer, and the 20-layer cells at 5C discharge. As expected, uniformity of the surface temperature distribution and temperature gradient between tabs and bottom of the cells depends on the number of layers. In the SLA, temperature gradient between the positive tab and cell bottom is 15.82 °C. Similarly, it is 11.63 °C, 10.06 °C, 8.76 °C, and 8.41 °C for cells with 4-layer, 8-layer, 16-layer, and 20-layer, respectively. This could be clarified by the faster heat transfer rate between the tabs and

cell bottom and lower heat generation rate as the layers get thinner¹⁹. Therefore, temperature gradient (ΔT) on the surface of the cells increases as the layer number increases. In other words, as the layer number increases, simulated cells represent the temperature non-uniformity of the real cells more exactly. The surface temperature non-uniformity factor which is defined based on the following formula²⁶⁷, are calculated for the single-layer and multilayer cells:

$$\phi = \frac{T_{cen,max} - T_{cen,min}}{T_{cen,max} + T_{cen,min}} \quad (21)$$

where $T_{cen,max}$ and $T_{cen,min}$ are the maximum and minimum temperature on the cell surface, respectively. Table 4.7 presents ϕ values for the single-layer cell and multi-layer cells. According to the ϕ values, the 20-layer cell predicts the temperature nonuniformity of the LiFePO₄ more accurately. The ϕ value is 6.93, and 5.38 for the experimental measurements, and for the 20-layer model, respectively. With decreasing the number of layers, the ϕ value decreases and diverges from the experimental value (Table 4.7). The SLA shows different ϕ values on the front surface (2.51) and on the back surface (4.62) because of the variant temperature profile between two surfaces. This thermal behavior is totally far from the experimental results since almost symmetrical temperature behavior is observed on either side of the cell.



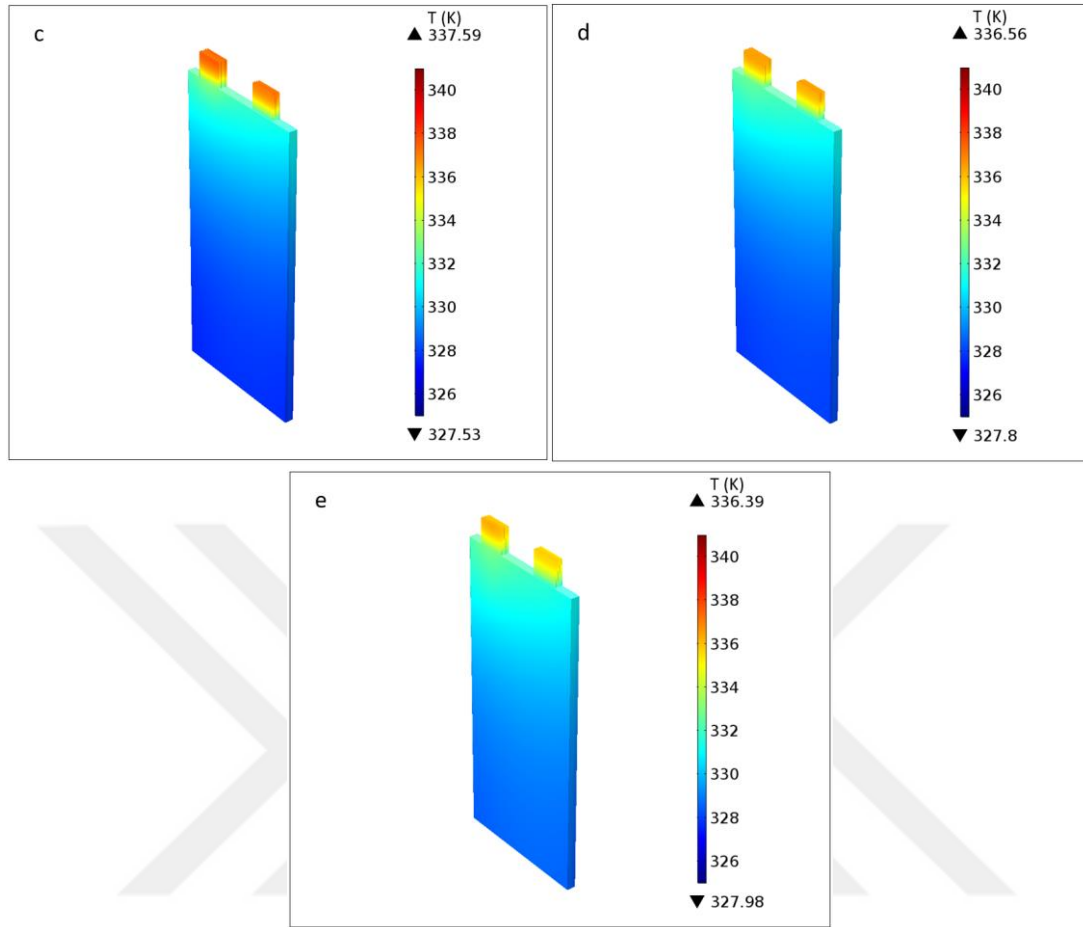


Figure 4.14. Comparisons of the 3D cell temperature distribution for (a) the single-layer, (b) 4-layer, (c) 8-layer, (d) 16-layer, and (e) 20-layer 20Ah LiFePO₄ cell.

Table 4.7 Temperature gradient and non-uniformity factors

30 °C_5C	ΔT (K)	ϕ (%)
Experimental (front)	8	6.93
Experimental (back)	7.85	6.81
20-layer (front)	6.24	5.38
20-layer (back)	6.11	5.28
16-Layers (front)	6.03	5.22
16-Layers (back)	5.88	5.10
8-Layers (front)	4.32	3.82
8-Layers (back)	4.07	3.60
4-Layers (front)	3.89	3.48
4-Layers (back)	3.50	3.12
Single-layer (front)	2.63	2.51
Single-layer (back)	5.61	4.62

4.5 Conclusion

Extensive modeling and simulation approaches including 1D models, lumped models, 3D single-layer models, and 3D multilayer models have been developed to investigate the electrochemical and thermal behaviors of pouch type Li ion batteries. Although multilayer structure of the Li ion cells and heterogenous physiochemical properties of the cell components have been considered in many 3D thermal models, however, the effects of number of cell layers on the thermal behavior of the large sized, and high capacity cells have not been fully investigated to the best of our knowledge. Therefore, in this study, a 3D coupled electrochemical-thermal models are developed to simulate and study the effects of number of layers on thermal behavior of the Li-ion batteries. According to the results, cells with different number of layers show different thermal behavior in terms of local temperature rise, and temperature nonuniformity. The 3D single-layer approach represented insufficient results to model the thermal behavior of the cells. In addition, the SLA showed unsymmetrical temperature distribution on two opposite surfaces. Inconveniences caused by the SLA, are corrected by developing the multilayer cells. The temperature nonuniformity factor was calculated for the single-layer, and multilayer cells and was compared with the experimental value. It was found that the MLA predicts the spatial temperature profile of the Li ion cell more exactly, and the temperature nonuniformity factor gets closer to the experimental value as the number of layers increases. Results obtained with the 20-layer cell were in better agreement with the experimental results. Overall, with a better precision of thermal behavior and heat generation analysis, this study is useful in development of an efficient thermal management system for high capacity battery packs in electric vehicles.

5 Chapter 5: Numerical investigation of design parameters effects on performance of cooling system designed for a Lithium ion cell

5.1 Introduction

The environmental issues associated with fossil fuels and nuclear energy necessitate usage of renewable energy sources. The main advantages of renewable technologies as clean energy sources are minimized environmental impacts and minimum secondary waste production. However, renewable energy sources are limited, and they are not sustainable in most regions. Therefore, high efficiency energy storage systems are needed to store the produced energies.^{8, 284}

The popularity of Lithium ion batteries as rechargeable devices is growing due to their applications in electrochemical energy storage (EES) and electrical vehicles (EVs). However, these batteries suffer from some thermal issues. The temperature of a cell greatly affects the performance efficiency and cycle-life of lithium ion batteries.^{69, 77} High internal resistance at low temperatures as well as active material and electrolyte decomposition at high temperatures result in capacity fade.^{22, 243, 247} Uncontrolled temperature elevation inside the battery due to self-accelerated exothermic side reactions results in thermal runaway.^{243, 285} In addition, small non-uniformity of temperature significantly affects performance and the cycle-life of the batteries.²⁶⁷ Therefore, an appropriate thermal management system is necessary for Li-ion battery packs and modules especially within high power energy storage devices and systems.^{286, 287}

Thermal management of batteries include either cooling the battery packs at higher operating temperatures or heating them at lower operating temperatures.²⁴¹ Choosing a proper cooling method to keep the temperature at an optimal range is essential for increasing safety, extending the battery life, and reducing costs.¹⁹ The thermal management can be broadly classified as air-cooling, liquid-cooling, and phase change material-based (PCM) cooling.¹⁸⁷ There has been much research done with regard to thermal management of lithium batteries, both on the numerical and experimental front. However, most researchers use a single-layer cell or lumped model in designing a thermal management system to save computing time.^{263, 288} In the lumped model, the battery cell is considered as a single solid with a spatially uniform temperature distribution, and the temperature is assumed to be only as a function of time (t). In other words, thermal conductivity (k) of the solid is assumed to be infinite and negligible temperature gradient is observed.²²³ For instance, Ping et al.²⁶² modeled the cell by a solid structure formed with homogeneous layers to study the effect of the environment or/and airflow cooling on the behavior of the cell. Liu et al.²⁸⁹ developed a 3D lumped model in which the cell structure is considered as an integrated and homogeneous element with the uniform thermal properties and distribution. Chen et al.¹⁷⁴ used a single-layer cell model to compare different cooling methods for lithium ion battery

cells. The Above methods, however, neglect the effects of cell multilayer structure on temperature distribution along the battery cell as the thermal properties of different layers would differ and would significantly influence the conductive heat transfer within the cell. Moreover, total internal impedance of the cell is affected by electrodes thickness.¹⁸⁷ Therefore, in this work, a multilayer cell model instead of lumped model or single-layer model is used for designing a thermal management system. Mini-channel cold plates are used as the thermal management system. Then, the effects of design parameters on cooling performance of the cooling plates are investigated. Cooling performance of passive water-cooling system (WCS) and air-cooling system (ACS) are compared using the optimized parameters. Based on the results, the WCS shows better cooling performance in terms of decreasing temperature rise, temperature uniformity, and total power consumption.

5.2 Model and methodology

5.2.1 Governing equations

The model includes the mathematical equations used for both the cell and the cooling plates. The electrochemical-thermal equations which are used for the Li-ion cell are listed in Table 5.1. These equations consist the transient conservation of the energy, charges, and ions in the solid and liquid phase.

Table 5.1 Electrochemical equations.

Process	Equation	
Material balance, solid phase	$\frac{\partial c_{s,i}}{\partial t} = \frac{D_{s,i}}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{s,i}}{\partial r} \right)$	(1)
Material balance, liquid phase	$\varepsilon_i \frac{\partial c}{\partial t} = D_{l,i}^{eff} \frac{\partial^2 c}{\partial x^2} + a_i \frac{1+t_+}{F} i_{loc}$	(2)
Electron transport, solid phase	$i_s = -\sigma_{s,eff} \nabla \phi_s$	(3)
Ionic transport, liquid phase	$i_l = -\kappa_{eff} \nabla \phi_l + \left(\frac{2\kappa_{eff} RT}{F} \right) \left(1 + \frac{\partial \ln f}{\partial \ln c} \right) (1-t_+) \nabla \ln c$	(4)
Charge conservation, solid phase	$\nabla \cdot i_s = a_s i_{loc}$	(5)
Charge conservation, liquid phase	$\nabla \cdot i_l = a_s (i_{loc} + C_{dl} \left(\frac{\partial (\phi_s - \phi_l)}{\partial t} \right))$	(6)
Local current density (Butler - Volmer equation)	$i_{loc} = i_0 \left(\exp \left(\frac{\alpha_a F \eta}{RT} \right) - \exp \left(\frac{-\alpha_c F \eta}{RT} \right) \right)$	(7)

Exchange current density
$$i_0 = F(k_c)^{\alpha_a}(k_a)^{\alpha_c}(c_{s,max} - c_{s,sur})^{\alpha_a}(c_{s,sur})^{\alpha_c}\left(\frac{c}{c_{ref}}\right)^{\alpha_a} \quad (8)$$

Over-potential
$$\eta = \phi_1 - \phi_2 - U_{eq} \quad (9)$$

Effective solid electrical conductivity
$$\sigma_{s,eff} = \varepsilon_s^{1.5} \sigma_s \quad (10)$$

Effective electrolyte ionic conductivity
$$\kappa_{eff} = \varepsilon_l^{1.5} \sigma_l \quad (11)$$

Effective electrolyte ionic diffusivity
$$D_{l,eff} = \varepsilon_l^{1.5} D_l \quad (12)$$

Energy balance
$$\rho c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = Q_{revv} + Q_{irrev} + Q_{ohm} \quad (13)$$

Reversible entropic heat
$$Q_{revv} = a_s i_{loc} T \frac{U_{eq}}{\partial T} \quad (14)$$

Irreversible reaction heat (polarization heat)
$$Q_{irrev} = F a_s i_{loc} (\phi_1 - \phi_2 - U) \quad (15)$$

Ohmic heat
$$Q_{ohm} = -i_s \cdot \nabla \phi_1 - i_l \cdot \nabla \phi_2 \quad (16)$$

We further add the equations used for the cooling plates. These equations consist the conservation of mass, momentum, and energy in the cooling system. The equation of continuity and momentum conversion of cooling fluid are as follows:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 \quad (17)$$

$$\frac{\partial}{\partial t} (\rho \vec{v}) + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla p \quad (18)$$

The energy conversion equations of fluid and the cold plate are as follows:

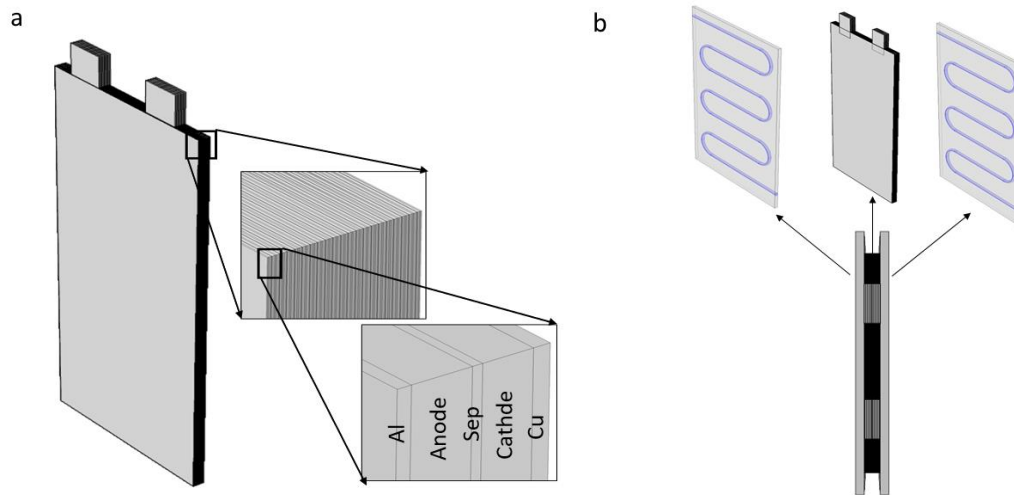
$$\frac{\partial}{\partial t} (\rho c T) + \nabla \cdot (\rho c \vec{v} T) = \nabla \cdot (k \nabla T) \quad (19)$$

$$\frac{\partial}{\partial t} (\rho_p c_p T_p) = \nabla \cdot (k_p \nabla T_p) \quad (20)$$

Where ρ , c , k , T , $\vec{v}$ are the density, heat capacity, thermal conductivity, temperature and velocity vector of fluid and ρ_p , c_p , k_p , T_p are the density, heat capacity, thermal conductivity and temperature of the plate respectively.

5.3 Numerical 3D modeling

The heat transfer, laminar flow, and electrochemical equations are coupled and solved using the COMSOL program. Heat transfer in solids and battery electrochemical-thermal equations are solved using time-dependent study, and laminar flow equations are solved using the stationary study. The setup consists of a commercially available 20 Ah LiFePO₄ cell surrounded by aluminum mini-channel cooling plates. The schematic of the set up as well as the cell and cooling plate dimensions are shown in Figure 5.1. Each plate has one inlet and one outlet, and all the surfaces and boundaries are open to convective heat fluxes with the heat transfer coefficient of 8 W/(mK). The battery cell is discharged at 30 °C and extreme current rate of 5C, and inlet coolant temperature is set to ambient temperature. Laminar flow with no shear slip condition on channel wall was applied to the cooling plates. The thermal and electrochemical validation of the model is provided as supplementary material.



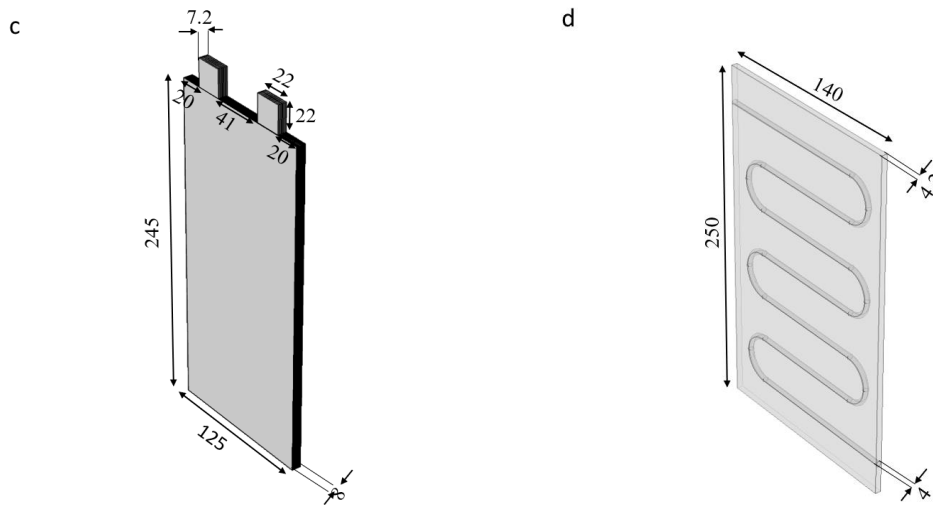


Figure 5.1. Schematic of (a) the multilayer cell and (b) the cooling system, and dimensions of (c) the cell and (d) the cooling system.

5.4 Results and Discussion

Nonuniform temperature profile greatly affects the cell cycle life and leads to the accelerated power and capacity fade⁷⁷. Figure 5.2 illustrates the temperature profile of the cathode electrode of the first layer (Figure 5.2-a) and the central layer where the temperature is maximum (Figure 5.2-b) at the end of 5C discharge without using cooling plates. The temperature on the electrode is as low as 53°C and as high as 63°C. However, olivine systems have major issues with high temperature cycling. If LiFePO_4 cell is discharged above 50°C, chemical degradation reactions in cathode increases.¹³³ As a result LiFePO_4 electrode forms Fe^{+2} ions and catalyze the side reactions on anode, causing SEI film to get thicker.^{53, 133, 290} This limits Li^+ diffusion through the thicker SEI layer and increases the bulk and SEI resistances. Consequently, power and capacity losses at high temperatures (>50°C) are unavoidable. Moreover, temperature non-uniformity is more harmful for the anode and the cathode electrodes which contain active material. When the cell is discharged at 5C, ohmic heat becomes dominant and the regions close to the tab heat faster.¹¹⁸ The temperature gradients on the first and central cathode electrodes are 8.59 °C and 9.60 °C, respectively, and result in localized aging. If the cells are used in a battery pack, the capacity of each cell will differ from one another.

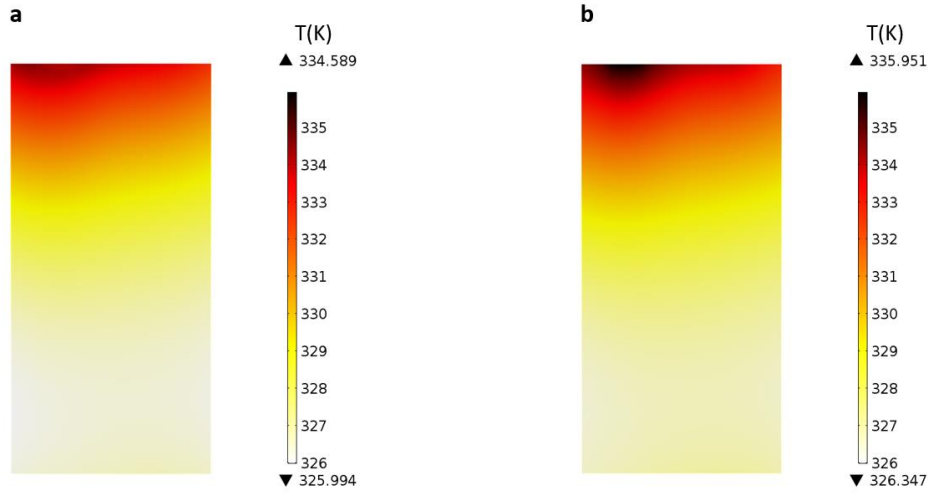


Figure 5.2. Temperature profile of the cathode electrode of the (a) first layer and (b) the central layer without cooling system at 5C.

In this work a series of simulation conducted to investigate the effects of design parameters such as cooling fluid, number of channel passes, channel width, and inlet mass flow rate on cooling performance of the cooling system. All the simulations are done at ambient temperature of 30 °C and 5C discharge. As cooling performance, we consider three parameters; maximum temperature rise (T_{max}) on cell surface, maximum temperature difference (ΔT) on cell surface, and pressure difference between the inlet and outlet of the cooling plate. We measure the cell surface temperature on 7 different points (Figure 5.3-a). In our previous work²⁹¹, we showed that point 2 which is near to positive tab, is under joule heating and gets the maximum temperature at 5C discharge. Similarly, we showed that point 5 at the bottom of the cell gets the minimum temperature. In other words, regions close to tab show maximum temperature whereas the bottom of the cell presents the minimum temperature. Therefore, Figure 5.3-a represents a maximum and minimum temperature on the cell surface and Figure 5.3-b represents the locations where pressure difference is calculated.

Our aim is to get uniform temperature profile by minimizing the temperature gradient (ΔT). However, we need to consider pressure difference (ΔP) while minimizing ΔT . Because higher ΔP results in higher power consumption which is not favorable from economical viewpoint. The ideal power consumption used for the coolant driving force can be calculated using equation 21:

$$Power = \sum_i^n \Delta P_i V_i \quad (21)$$

Where, ΔP_i is the pressure drop from the coolant inlet to the coolant outlet of the channels, V_i is the volume flow rate of in the coolant channel, i and represents the

coolant channel number. Overall, the lower the ΔT and the ΔP , the better the cooling performance is.

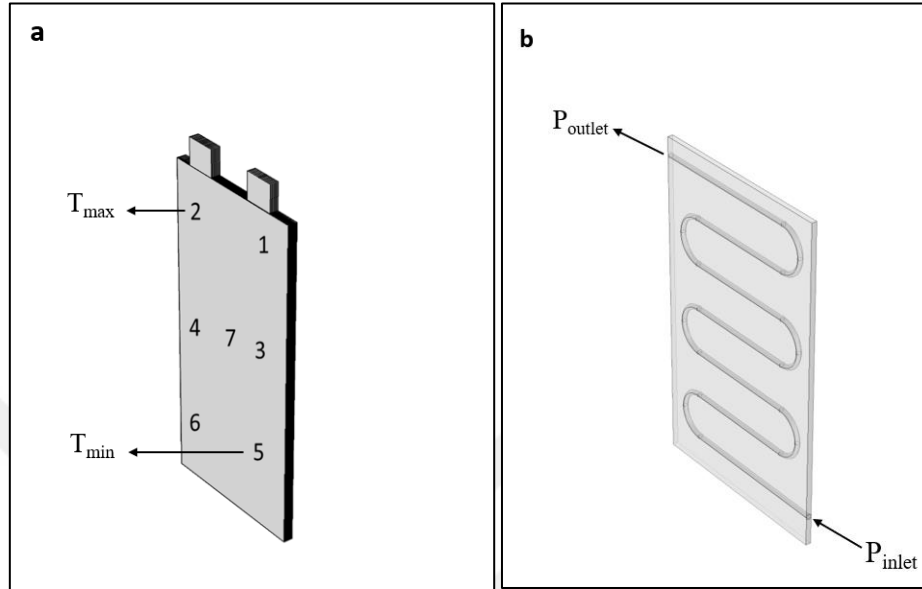


Figure 5.3. Schematic representation of maximum and minimum (a) temperature and (b) pressure.

5.4.1 Effects of inlet flow rate

In the first section, we studied the effects of inlet mass flow rate on cooling performance. In this approach, the coolant type, channel width, and a number of passes are kept as fixed parameters while the inlet mass flow rate is chosen as a variable parameter. The inlet mass flow rate is changed from 0.1 g/s to 10 g/s. Figure 5.4 shows the maximum temperature rise on the surface of the cells with and without a cooling system under different inlet mass flow rates. Without any cooling plates, the maximum temperature rises approximately 33°C. High convective heat transfer coefficient of water in conjunction with the high thermal conductivity of the aluminum plates results in significant heat flux and make the maximum temperature to fall from 33 °C to 13.64 °C when the inlet mass flow rate is set to 0.1 g/s. If the inlet mass flow rate increases, cooling performance gets better. The maximum temperature rises are calculated as 10.18 °C, 8.58, 6.21 °C, and 5.89 °C when the inlet mass flow rates are set to 0.5 g/s, 1 g/s, 5 g/s, and 10 g/s respectively (Figure 5.4). However, higher inlet mass flow rate will result in a higher pressure drop and consequently higher pump power consumption. Therefore, cost of the power needed to pump the coolant through the channels should also be considered in optimization of the battery temperature. Table 5.2 lists the temperature gradient (ΔT) and pressure drop (ΔP) under different flow rates. Higher flow rate results in a lower temperature gradient and higher pressure drop. Thermal performance for $\dot{m} = 5$ g/s and $\dot{m} = 10$ g/s is quite close while pressure drop for $\dot{m} =$

5 g/s is significantly lower than $\dot{m} = 10$ g/s. Therefore, inlet mass flow rate of 5 g/s seems to be a best case at 5C discharge.

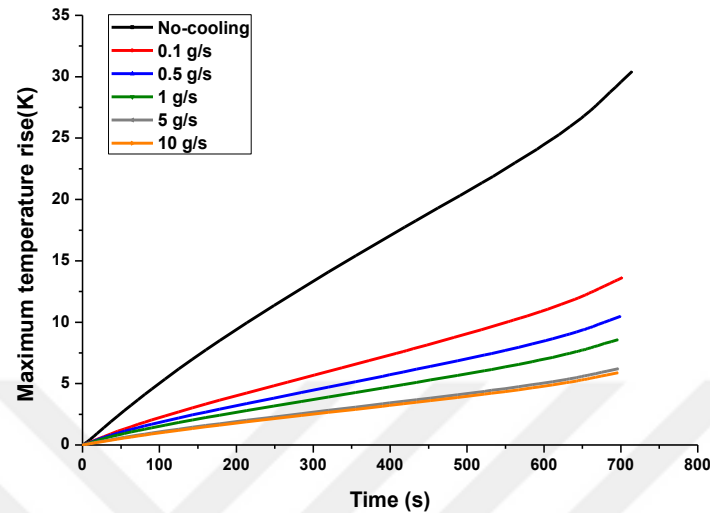


Figure 5.4. Maximum temperature rise (K) under different flow rates at 5C and 30 °C.

Table 5.2. ΔT and ΔP values at different mass flow rates.

Mass Flow Rate (g/s)	ΔT (K)	ΔP (KPa)
No cooling	7.26	-
0.1	1.43	0.011
0.5	1.18	0.06
1	1.01	0.12
5	0.72	1.75
10	0.62	2.5

5.4.2 Effects of channel width

In the second section, we investigated the effects of channel width on cooling performance. In this approach three types of channels with the radius of 1 mm, 1.5 mm, and 2 mm were considered. The inlet mass flow rate is set to 1 g/s and a plate with seven channel passes was chosen. As coolant medium, water is passed through the channels. Figure 5.5 illustrates the maximum temperature rise on the cell surface considering the cooling plates with different channel width. The maximum temperature rise decreases from 9.84 °C to 8.58 °C when the channel width was changed from 1 mm to 2mm. This can be explained by the increased heat transfer area and increased coolant residence time as channel width increases. When the inlet mass flow rate is kept constant, the fluid velocity decreases by the increased channel width resulting in higher

residence time. Consequently, more heat is dissipated using the plate with wider channels. Furthermore, wider channel width results in a more uniform temperature distribution and lower pressure drop and therefore lower cost. Table 5.3 lists the temperature gradients (ΔT) on the cell surface and the pressure drops (ΔP) for different channel widths. ΔT decreases from 1.93 °C to 1.01 °C and ΔP deduces from 2.13 KPa to 0.12 KPa as channel width enlarges from 1 mm to 2 mm, respectively. Overall, wider channel leads to better cooling performance. However, wider channels need to be carved in thicker plates which adds extra mass to battery modules and packs.

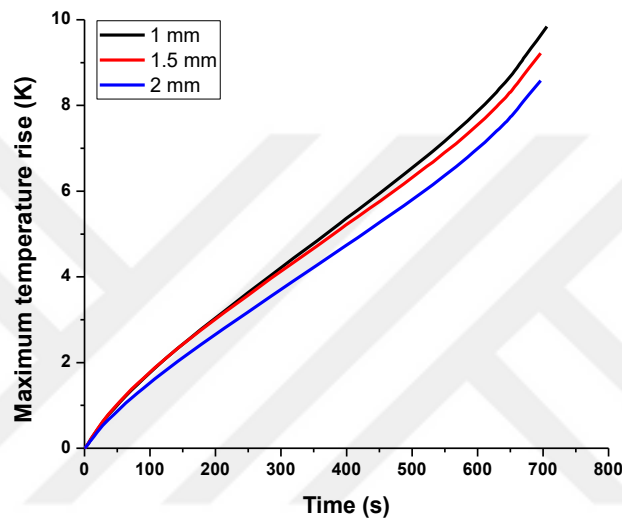


Figure 5.5. Maximum temperature rise (K) for plates with different channel width at 5C.

Table 5.3. ΔT and ΔP values at different channel widths.

Channel radius (mm)	ΔT (K)	ΔP (KPa)
1	1.93	2.13
1.5	1.58	0.91
2	1.01	0.12

5.4.3 Effects of number of channel passes

Number of the channel passes influences the cooling performance and pressure drop of thermal management system. Figure 5.6 shows the schematic of cooling plates with three channel passes (Figure 5.6-a) and eleven channel passes (Figure 5.6-b). It is clear that heat transfer area and fluid residence time inside the channels increases as the number of passes increases which results in more heat dissipation. However, increasing the number of passes results in fabrication complexity, higher cost, and higher pressure drop. Figure 5.6-c shows a maximum temperature rises on cell surface using plates with a different number of channel passes. Water with a mass flow rate of 1 g/s is pumped through the channels with a radius of 2mm. Maximum temperature on cell surface rises

to 14.35, 11.98, 9.28, 8.89, and 8.58 °C as plates with 3, 5, 7, 9, and 11 channel passes are used, respectively. It can be observed that as a number of passes increases, the impact on maximum temperature rise decreases. In other words, plates with 7, 9, and 11 channels passes show almost same impact on maximum temperature rise.

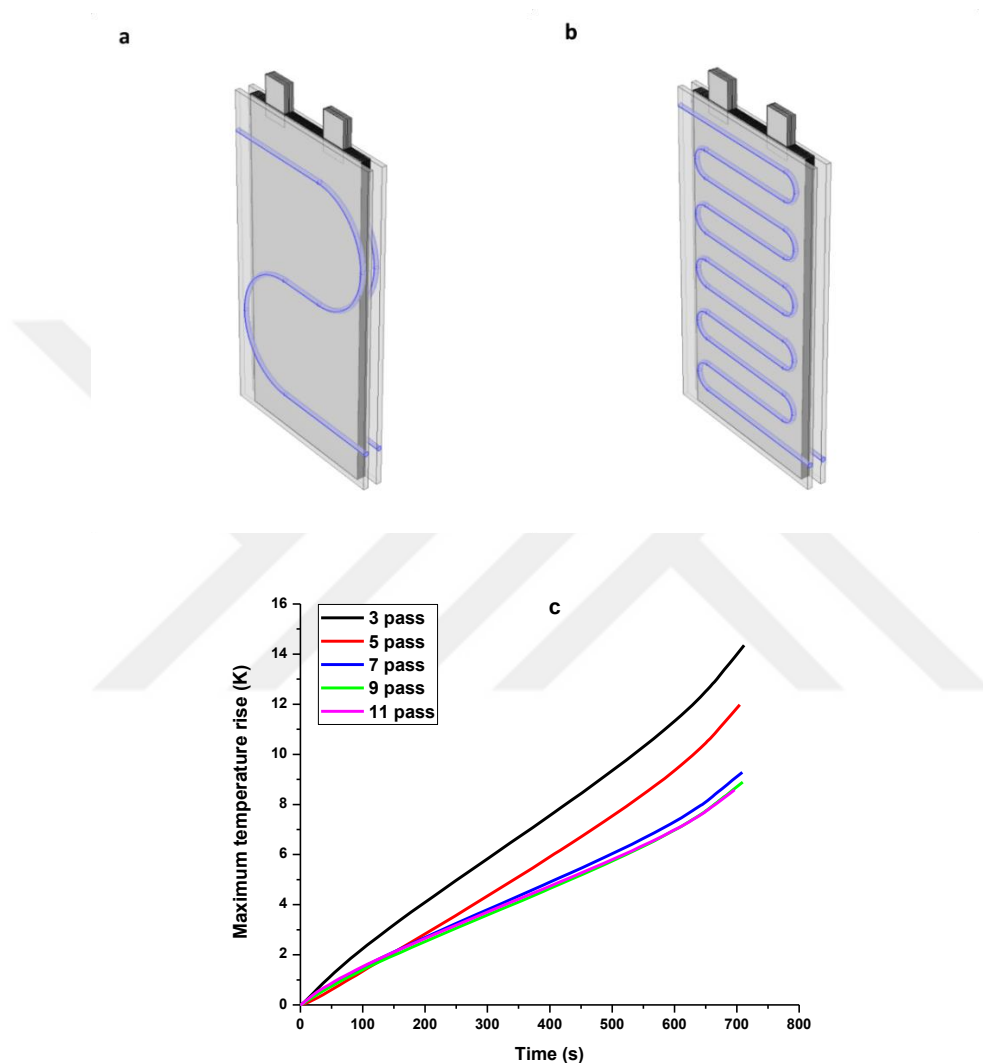


Figure 5.6. Schematic of cooling system with (a) 3 channel pass and (b) 11 channel passes and (c) maximum temperature rises for plate with different channel passes.

Temperature differences (ΔT) on cell surface and pressure drops (ΔP) are listed in Table 5.4. Plates with a greater number of channel passes show better cooling performance. However, ΔT get less influenced as a number of passes increases. In the other hand, ΔP values get highly influenced by the number of passes. When the inlet flow rate is set to 1 g/s, the difference of ΔP values between 3 and 11 passes become 0.173 KPa. The difference even further increases at higher flow rates. According to equation 21, even a small pressure drops results in a big difference in power

consumption. Therefore, choosing the optimum case is necessary. Overall, plate with 7 number of passes show optimum results considering the $T_{\max}$, ΔT , and ΔP values.

Table 5.4. ΔT and ΔP values for plat with different channel passes.

# of channel passes	ΔT (K)	ΔP (KPa)
3	1.63	0.057
5	1.30	0.083
7	1.01	0.12
9	0.86	0.17
11	0.75	0.23

5.4.4 Effects of cooling medium

Type of cooling medium greatly affects the performance and cost of the thermal management system¹⁷⁴. Heat transfer rate between the cooling plates and medium highly depends on the physical and thermal properties of the medium such as viscosity, thermal conductivity, and density. The heat transfer medium could be chosen according to the type of coolant system. We compared cooling performance of a water-cooling system (WCS) and air-cooling system (ACS) in our model. In this approach, plates with a channel width of 2 mm and 7 passes were used in this section. Figure 5.7 shows a comparison of WCS and ACS at three inlet mass flow rates. The maximum temperature rises to 14.85 °C for ACS and 13.64 °C for WCS at the end of the discharge when the inlet mass flow rate is set to 0.1 g/s (Figure 5.7-a). By increasing the mass flow rate, the difference between cooling performances of systems become more distinctive. At $\dot{m} = 1$ g/s, the maximum temperature drops 5.30 °C more when the WCS is considered (Figure 5.7-b). Similarly, at $\dot{m} = 10$ g/s WCS shows 4.1 °C better cooling than ACS (Figure 5.7-c). Furthermore, Furthermore, the cooling performance of the WCS with $\dot{m} = 1$ g/s is better than cooling performance of the ACS with $\dot{m} = 10$ g/s (Figure 5.7-b, c). This is due to higher heat thermal conductivity of water with respect to air.

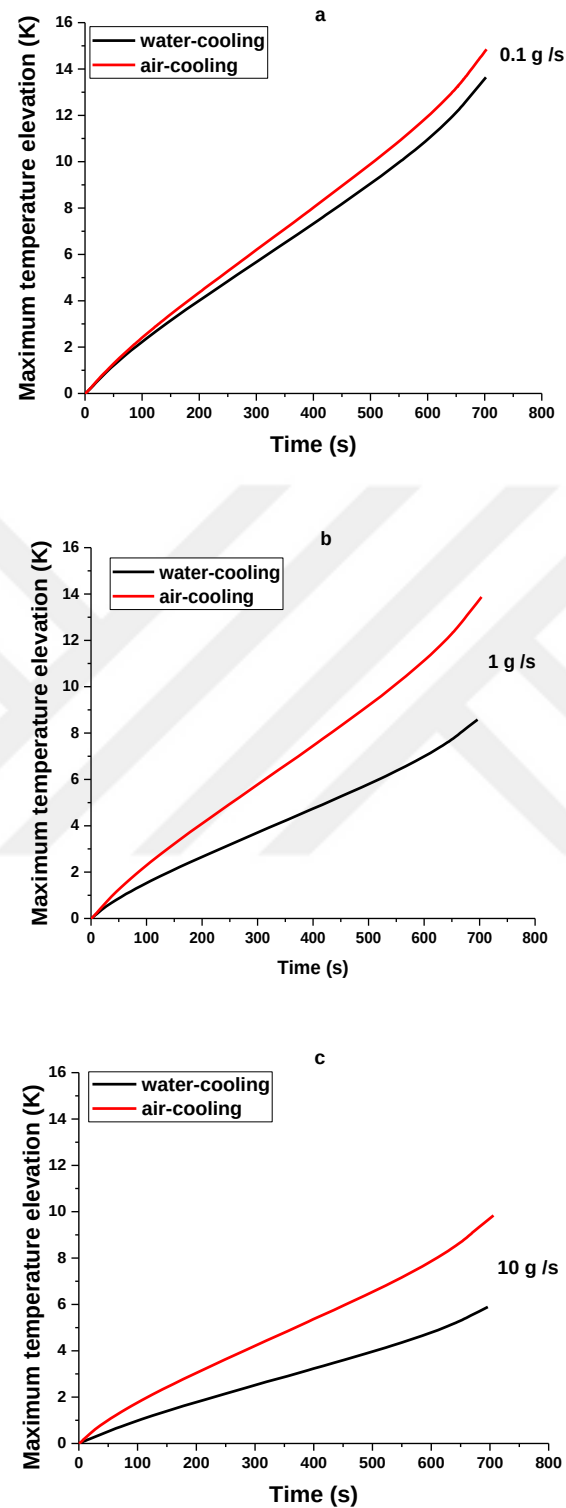
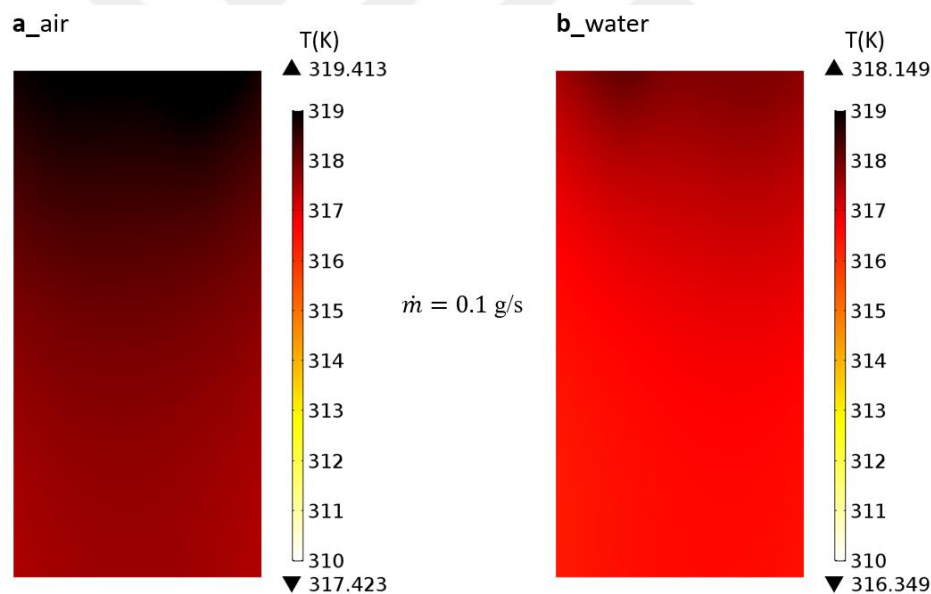


Figure 5.7. Comparison of maximum temperature elevations (k) on the surface of cells with air cooling versus water cooling system at (a) 0.1 g/s, (b) 1 g/s, and (c) 10 g/s.

Temperature profile of the cathode from the center of the cell using water cooling and air-cooling systems is shown in Figure 5.8. Mass flow rate significantly affects the thermal performance of the air-cooling and water-cooling systems. Therefore, two extreme cases were selected; the minimum flow rate ($\dot{m} = 0.1$ g/s) and the maximum flow rate ($\dot{m} = 10$ g/s). At $\dot{m} = 0.1$ g/s, the $T_{\max}$ and ΔT are 319.413 K and 1.99 K when ACS is used, and they are 318.149 K and 1.8 K when WCS is used, respectively. Similarly, at $\dot{m} = 10$ g/s $T_{\max}$ and ΔT are 313.997 K and 1.323 K for ACS and 311.198 K and 1.172 K for WCS. Considering the thermal behavior of the cell without a cooling system, ACS offers 26.33 % and 79.9% efficiency on dropping the $T_{\max}$ and ΔT when $\dot{m} = 0.1$ g/s and 34.95 % and 86.21 % efficiency when $\dot{m} = 10$ g/s. Similarly, WCS offers 28.34 % and 81.25 % efficiency on dropping the $T_{\max}$ and ΔT when $\dot{m} = 0.1$ g/s and 39.41 % and 87.8 % efficiency when $\dot{m} = 10$ g/s. Overall, water cooling shows better performance compared to air cooling system at same mass flow rates.



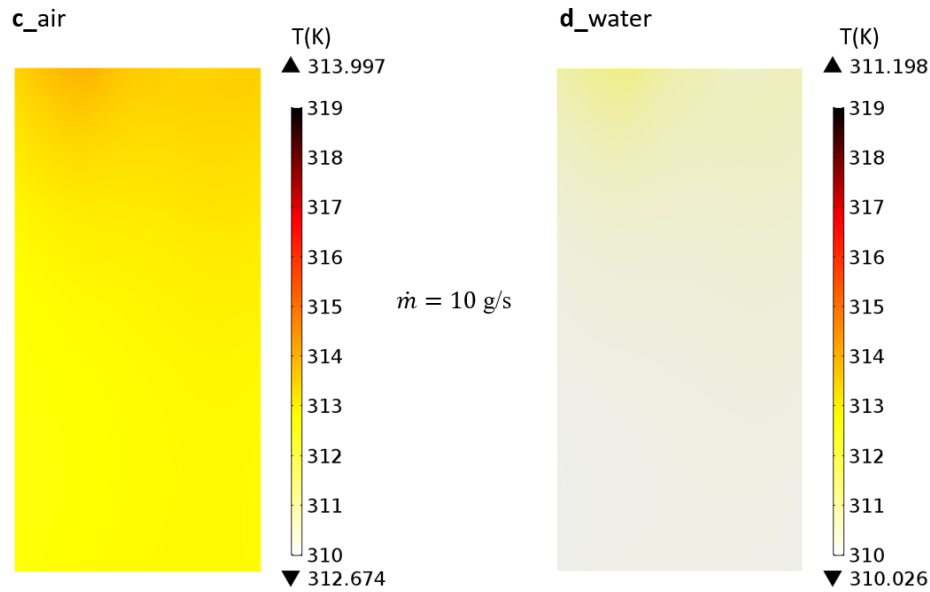


Figure 5.8. Comparison of the 3D cell internal (cathode from layer 10) temperature (K) profiles of the air cooling (a, c) and the water cooling (b,d) systems at $\dot{m} = 0.1 \text{ g/s}$ (a,b) and $\dot{m} = 10 \text{ g/s}$ (c,d).

We also evaluated temperature nonuniformity on cell surface using different heat transfer mediums. $T_{\max}$ graphics on surface were shown in Figure 5.7 where superior cooling performance of WCS is observed. Figure 5.9 shows temperature nonuniformity on cell surfaces using the air cooling and water cooling at two different mass flow rates. At $\dot{m} = 0.1 \text{ g/s}$, ΔT gets 1.43 K for water cooling and 1.46 K for air cooling system. Similarly, at $\dot{m} = 10 \text{ g/s}$, ΔT becomes 0.62 K for water cooling and 0.70 for air cooling. According to above results, considering the $T_{\max}$ on cell surface, WCS shows better cooling performance than ACS while they show almost similar impact on ΔT at same inlet mass flow rates. However, looking at the power consumption values (Table 5.5 and Table 5.6), WCA system shows superior performance.

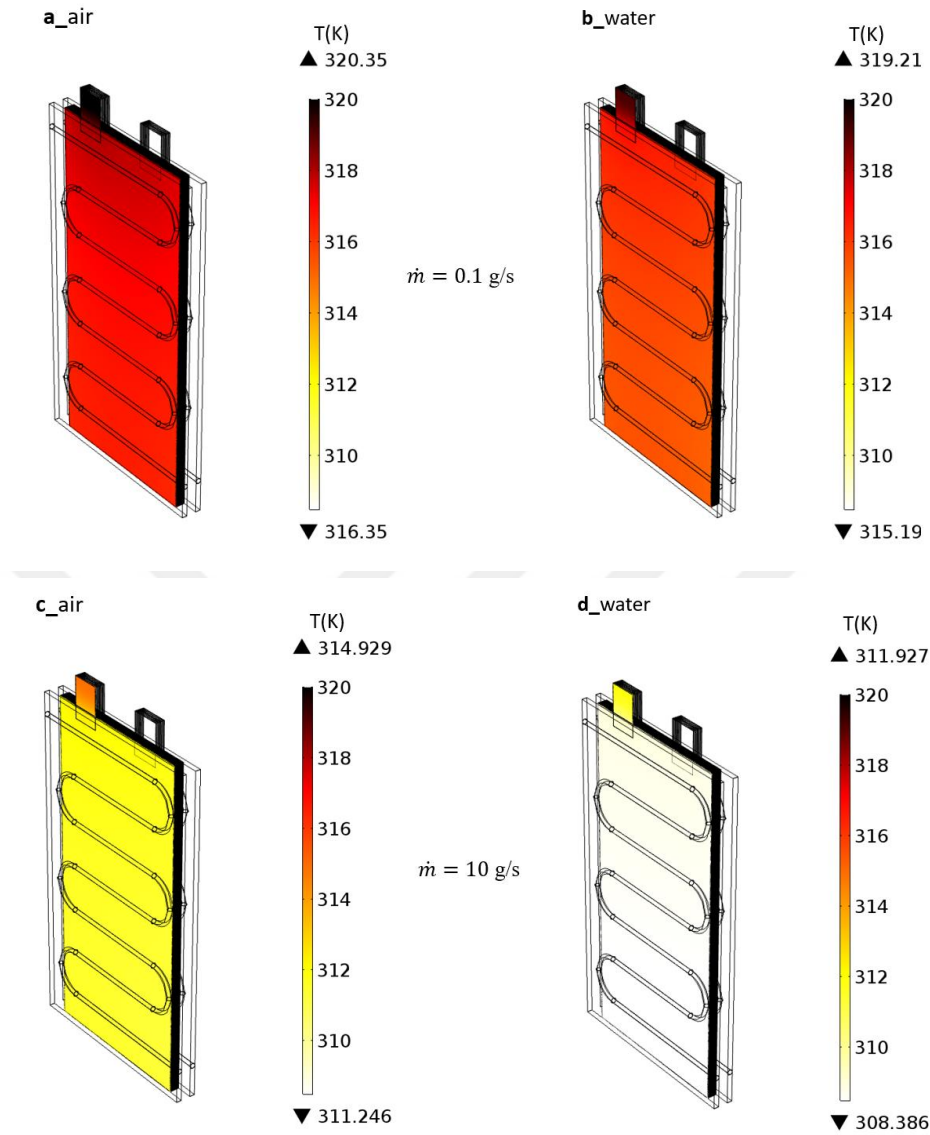


Figure 5.9. Comparison of the 3D cell surface temperature (K) profiles of the air cooling (a, c) and the water cooling (b,d) systems at $\dot{m} = 0.1 \text{ g/s}$ (a,b) and $\dot{m} = 10 \text{ g/s}$ (c,d).

By increasing the mass flow rate of the cooling medium, average temperature of the cell can be dropped further. Also, increased mass flow rate will result in a more uniform temperature profile which is the main aim of this study. However, with increasing the coolant flow rate, the power used to blow or pump the coolant increases dramatically (equation 21). Table 5.5 and Table 5.6 lists the volumetric flow rates ($\dot{V}$), pressure drop (ΔP), and total power consumption values for WCA and ACS at different inlet mass flow rates, respectively. Volumetric flow rate ($\dot{V}$) is obtained by dividing the mass flow rate ($\dot{m}$) by the density (ρ). At 30°C, density of water and air²⁹² are considered as 995.6 and 1.164 Kg/m³. It means that at same mass flow rates, $\dot{V}$ of air

becomes approximately 885 times $\dot{V}$ of water leading to a great pressure drop in the air-cooling system. As listed in Table 5.5 and Table 5.6, a pressure drop of air cooling system is 40.9, 267.5, and 474.9 times pressure drop of water cooling system at $\dot{m} = 0.1$, $\dot{m} = 1$, and $\dot{m} = 10$ g/s. Higher volumetric flow rates and pressure drop values in air cooling system leads to huge power loss since it is obtained by multiplying $\dot{V}$ and ΔP (equation 21). As an instance, at $\dot{m} = 10$ g/s, the power loss of WCS is 0.025 W compared to the power loss of ACS which is 10,180 W.

Table 5.5 ΔP , $\dot{V}$, and Power Loss values for water cooling system.

Mass Flow Rate (g/s)	ΔP (KPa)	$\dot{V}$ (mL/s)	Power Loss (W)
0.1	0.011	0.1005	1.11e-6
1	0.120	1.005	1.21e-4
10	2.495	10.05	0.025

Table 5.6 ΔP , $\dot{V}$, and Power Loss values for air cooling system.

Mass Flow Rate (g/s)	ΔP (KPa)	$\dot{V}$ (mL/s)	Power Loss (W)
0.1	0.450	85.91	0.038
1	32.11	859.1	27.586
10	1185	8591	10180

5.5 Conclusions

By using proper thermal management system, thermal issues of Li-ion battery could be controlled. Temperature profile of the Li-ion cells has a significant role on the performance, safety, and cycle life of the battery. That explains why little temperature gradient can lead to a great loss in the performances of the battery packs. In this work we studied the effects of a cooling design parameters on thermal behavior of the multilayer LiFePO₄ cell. Both surface and internal temperature profiles of a single cell is investigated with and without cooling systems. The main conclusions of this study are summarized as follows:

1. Inlet mass flow rate is the main effective parameter in cooling performance.
2. Channel width has more influence on pressure drop than temperature drop.
3. Plate with seven channel passes show superior cooling performance considering both ΔT and ΔP .
4. At higher current rate, air cooling system leads to great power consumption and water-cooling system is recommended.

6 Chapter 6: Developing Thermal Management System for Battery Modules

In the previous chapters, the effects of design parameters are analyzed on the electrochemical-thermal behavior of a single cell. This chapter covers developing a cooling system for battery modules. In this approach, first, the parameters optimized by the model were used to develop and fabricate the mini-channel cooling system. Then, the model experimental and simulation results were compared. Finally, after validating the model with the experimental results, it is used to specify the needed flow rates and power losses for WCS and ACS at different current rates.

6.1 Battery Modules and Cooling System Development

Using many lithium-ion batteries in electric vehicles requires many safety measures for the Li-ion batteries (LIB). The capacity loss due to the nonuniform temperature distribution of the cells in the battery unit and the thermal runaway are two important points to take precautions. As the number of layers increases, the increase of hot spots in some areas of the battery will increase the capacity loss. For this reason, the temperature difference at different points in the cell should be kept at the desired low values during charging and discharging. Therefore, it is necessary to apply a suitable thermal management in order to remove the heat from the hot regions, and to homogenize the surface temperature.

In the last section of our project, battery modules were prepared by using 20Ah cells which showed an optimum performance. At this stage, the 2016 model Nissan LEAF batteries with a total capacity of 24kWh, a nominal voltage of 360V, and 48 modules each consisting of 4 cells was taken. Therefore, two types of battery modules, 2S1P and 4S1P, were prepared, and their thermal and electrochemical properties were investigated under different operating conditions. For creating battery modules, the poles of the batteries are connected by brazing or riveting. Battery modules can be prepared by coupling the cells in a series or parallel way. The process of connecting the positive pole of a cell to the negative pole of the other cell is defined as a series connection, while the process of connecting the same pole of a cell to each other is defined as parallel linking. Battery cells used for creating battery packs may have a same or different capacity. However, the optimum performance cannot be achieved by connection the batteries in different capacities. This can be explained by fast filling the cell with a low capacity than other cells. Therefore, ignoring the aforementioned fact can result in the overvoltage of the low capacity cell.

When the batteries of the same capacity are connected in series, the total capacity of the generated battery pack does not change and is equal to the capacity of a battery cells that generate the package, and the voltage of the battery pack is equal to the sum of the voltages of all the cells that make up the package. However, when the batteries of the same capacity are connected in parallel, the total voltage of the battery pack is equal to the voltage of a battery cells forming the package, and the total capacity of the package is equal to the sum of the capacities of all the batteries that make up the

package. Figure 6.1 shows the schematic of the parallel and series connected battery modules.

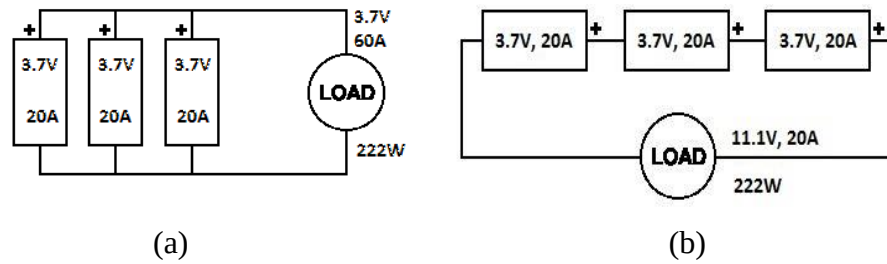


Figure 6.1. Schematic of (a) a parallel and (b) series connected battery modules.

The higher the battery capacity, the higher the price of the batteries. Therefore, it is preferred to connect low-capacity (more affordable) batteries in parallel instead of connecting high-capacity (expensive) batteries in series. However, this will increase the whole battery pack weight. In addition, as more batteries will need to be connected to each other, it will lead to increased electronic resistance and thus to a reduction in capacity. For identifying battery packs, the letter 'S' represents series-connected batteries, while the letter 'P' represents parallel-connected batteries. For example, a battery module represented by 2S1P comprises 2 cells connected in series, and a battery module represented by 2S2P indicates that 2 separate series-connected battery groups that are connected in parallel. The formats of the 2S1P and 2S2P packages are shown in Figure 6.2.

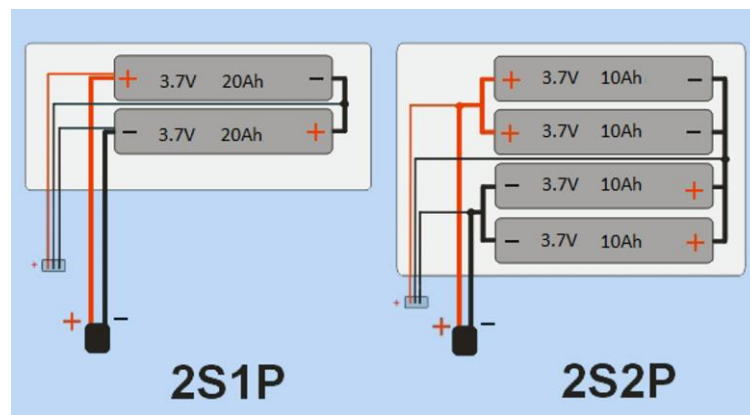


Figure 6.2. Schematic of 2S1P and 2S2P battery modules.

we developed 4S1P (4 series and 1 parallel) battery modules, and we applied a cooling system to improve their thermal behavior. Figure 6.3 shows a schematic of a single cell and a 4S1P module which is composed of 4 cells coupled in series.

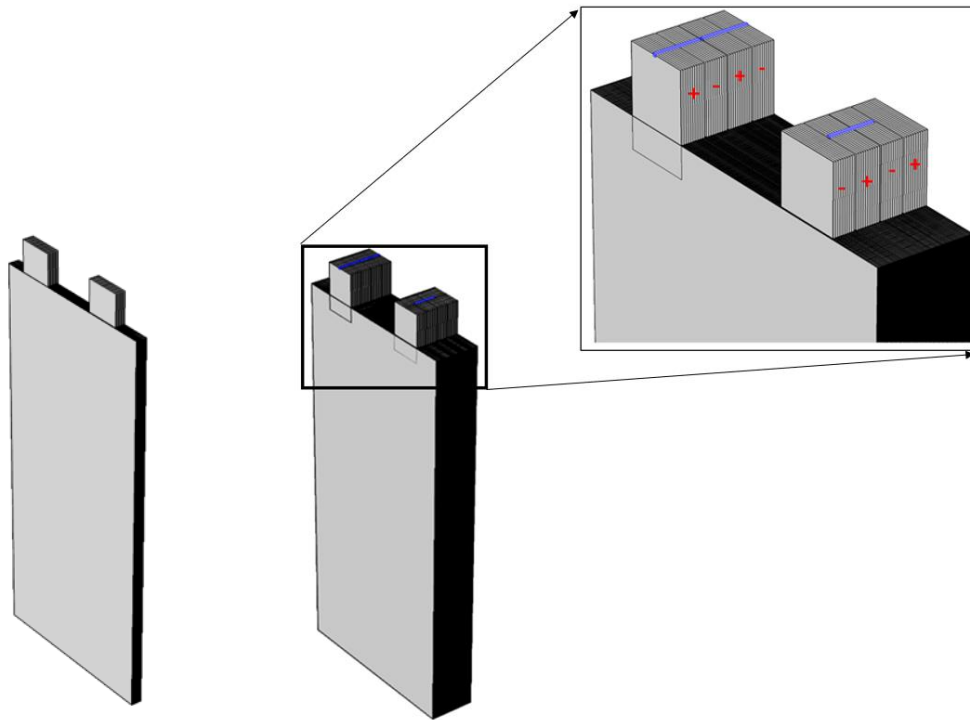


Figure 6.3. Schematic of (left) single cell and (right) 4S1P cell module.

Figure 6.4 shows a schematic of a cooling system for a single cell and a battery module. Each battery cell is sandwiched between two cooling plates. There are 4 cells in the model which are coupled in series. There is only one inlet and outlet in every cooling plate. Considering the higher joule heat generation in tab regions, the last channel pass is considered very near to tabs. The distance between the channel passes is considered uniform to make even temperature profile on cell surfaces. The cold plate is made of aluminum. As a cooling medium, air and water are considered in the model, and only air is considered for the experimental part.

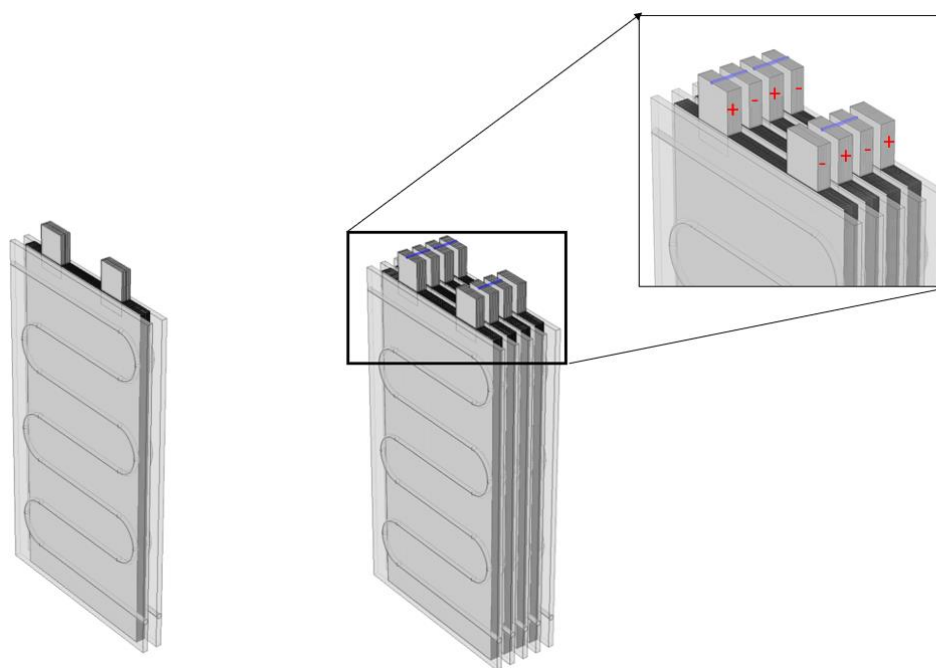


Figure 6.4. Schematic of cooling system for a (left) single cell and (right) 4S1P cell module.

Based on the optimized simulation results, we developed a thermal management system for 4S1P battery packs experimentally. The developed thermal management system consists of mini-channels carved on aluminum plates with a high thermal conductivity. The shape and depth of the channels were determined according to the results obtained in the simulation part. The channel system was drawn using the SolidWorks program and carved on the 6000 series aluminum plates with the help of Computer Numerical Control (CNC) machine. Then, two aluminum plates with symmetrical half channels were assembled using 20 screws. In order to prevent air leakage, a liquid seal was applied between the plates and after the plates were joined, air was vented to ensure that there was no air leakage. Figure 6.5, illustrates the schematic of the sample design drawn using SolidWorks program and the developed Aluminum mini-channel plates.

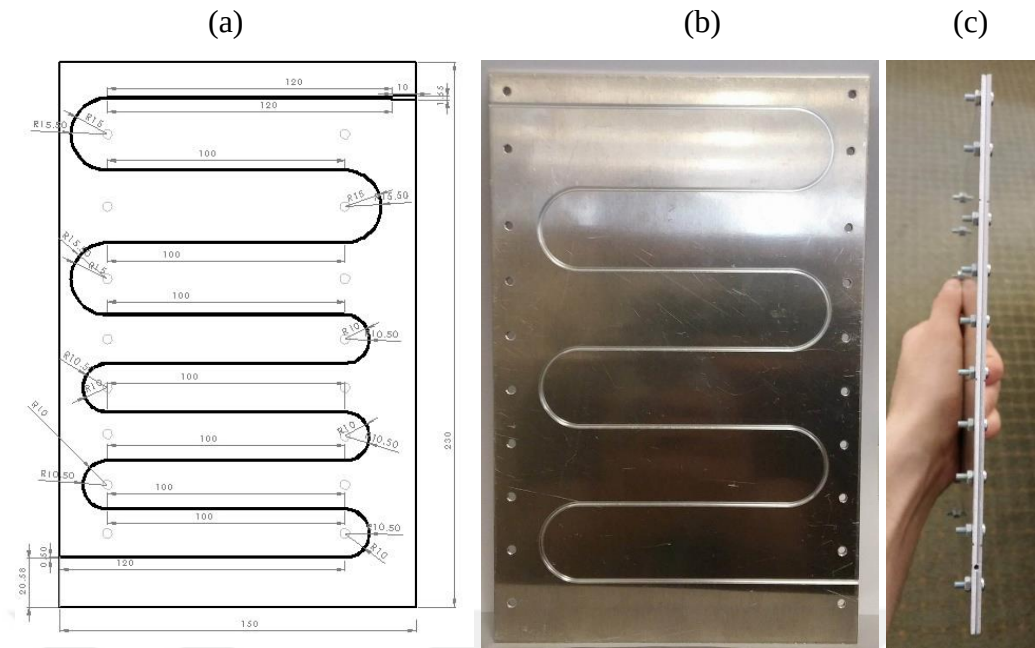


Figure 6.5. Plates used in the thermal management system (a) drawing example prepared in SolidWorks program (b) mini-channels carved by CNC machine on aluminum plate (c) mini-channel cooling plate.

Cavities with a diameter of 1 mm were opened on the outer surface of the aluminum plates as shown in Figure 6.6, and thermocouples with a diameter of 1 mm were embedded in these cavities, and the plates were placed between the battery cells. In this way, surface temperatures can be measured without any gap between the plates and the battery cells surfaces. The cooling plates with the coupled thermocouples were placed between the 4S1P module cells. In order to create 4S1P battery modules, 4 batteries in the same size and same capacity are connected to each other in series (Figure 6.6).



Figure 6.6. Schematic of the thermocouple placed on the outer surface of the cooling plate (Left) 4S1P battery module with cooling system

For temperature measurement, three thermocouples are placed on the surface of each cell; One on the top, one on the center, and the last one is placed on the bottom of

the cell. The setup for measuring surface temperature on each cell of 4S1P module is shown in Figure 6.7.

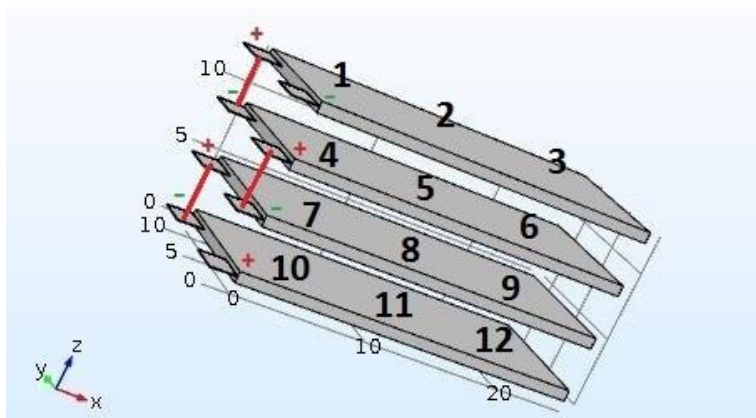


Figure 6.7. Set up for measuring the surface temperature of the 4S1P module.

Figure 6.8 illustrates the experimental set up for a battery module thermal management. All experiments were repeated at 6 different ambient temperatures (50 °C, 40 °C, 30 °C, 20 °C, 10 °C, 0 °C). Discharging the batteries at high current rates at negative temperatures may result in a permanent damage to the battery components and the swelling of the batteries. Therefore, experimental tests are not carried out at -10 °C and -20 °C.



Figure 6.8. Schematic of experimental set up for battery module thermal management.

6.2 Results and discussion

6.2.1 Experimental observation

The prepared 14.4V 4S1P modules were discharged with a 3C current-rate (60 A/h) in the range of 50 °C - 0 °C, and the temperature changes of the three points at the outer and interface surfaces were recorded during the discharge. The reason for the discharge current-rate to be determined as 3C is that this value is the rate recommended by the manufacturer. The charging current is set at 0.4C in all experiments in order to

reach the maximum capacity of the modules. The set up for temperature recording is shown in Figure 6.7. All thermocouples are spaced at equal intervals. The temperature changes in the external and interfaced of 4S1P modules discharged at 3C are shown in Figure 6.9-14. As shown in Figure 6.9, when the modules are discharged without BTMS at 3C, regardless of the ambient temperature, the maximum temperature rise is measured on point 7, which is placed at the center of the module near to the tabs. Without BTMS, the maximum measured temperature is 32.7 °C, and the maximum temperature difference between the surfaces becomes 12.9 °C. This situation increases the risk of thermal drift and decreases the life of the batteries as it makes the use of active material in the cell's irregular. With the BTMS, the maximum temperature rise is 19.8 °C, and the maximum temperature difference drops (from 12.9 °C) to 4.1 °C when the air flow rate is set to 0.3 g/s.

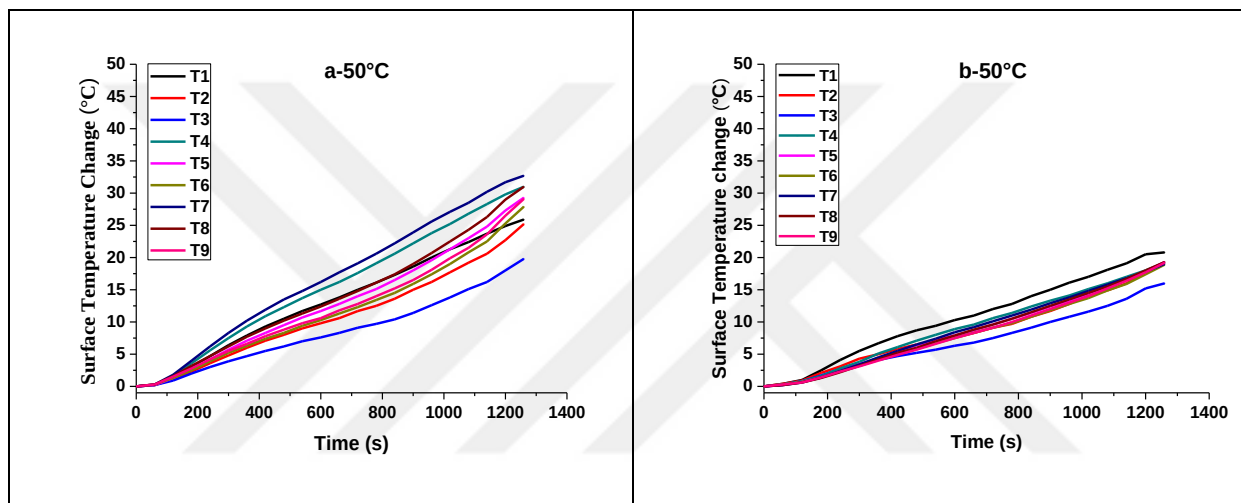


Figure 6.9. Surface temperature of 4S1P battery module at 50 °C (a) without BTMS, and (b) with BTMS.

Similarly, at 3C and 40 °C, the maximum measured temperature rise becomes 37.4 °C without the BTMS, and it becomes 21.9 °C with the BTMS (Figure 6.10).

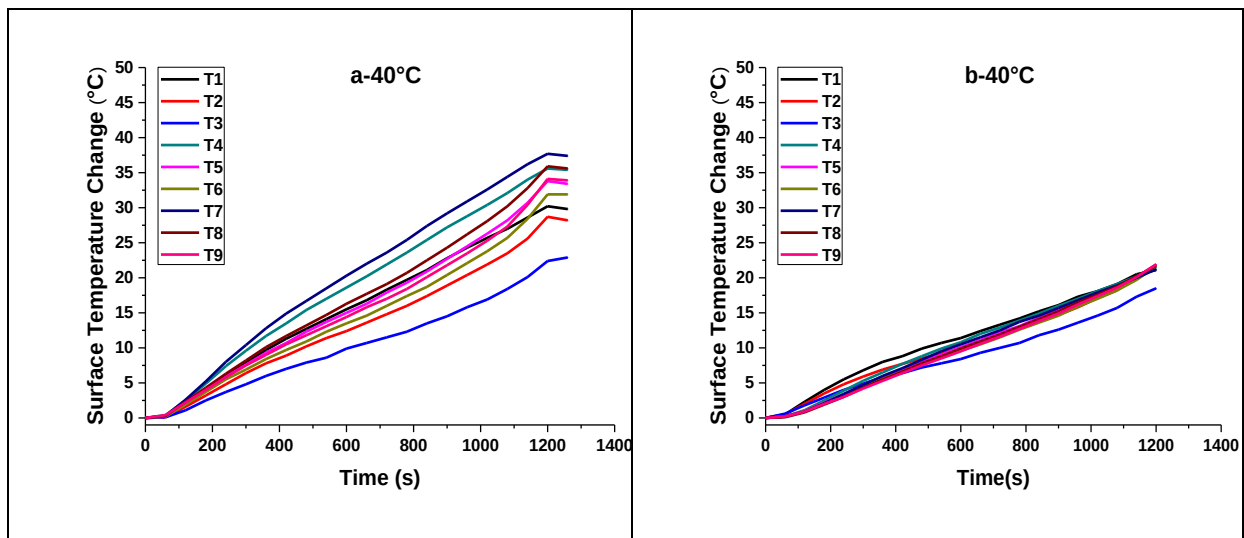


Figure 6.10. Surface temperature of 4S1P battery module at 40 °C (a) without BTMS, and (b) with BTMS

According to results, utilizing the BTMS at lower temperatures is progressively compelling in homogenizing the temperature dispersion along the module than bringing down the most extreme temperature rise. Figure 6.11 shows that at 3C and 10 °C, the maximum measured temperature rises are 49.8 °C and 34.3 °C without and with BTMS, respectively. Furthermore, the maximum temperature difference between the surfaces fall from 17.7 °C to 3.8 °C when the air-based BTMS is used with the inlet mass flow rate of 0.3 g/s.

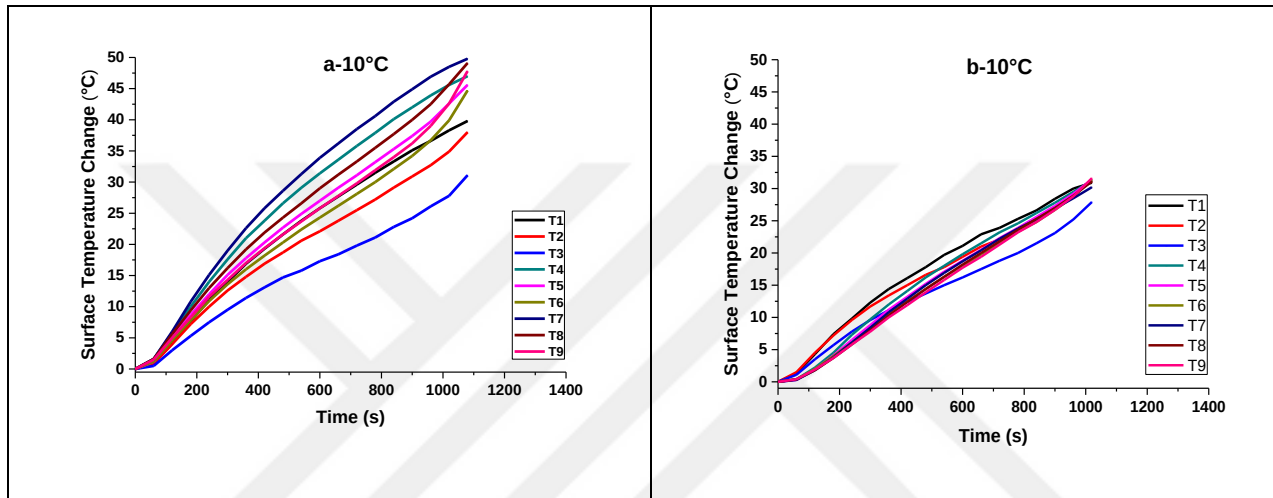


Figure 6.11. Surface temperature of 4S1P battery module at 10 °C (a) without BTMS, and (b) with BTMS

It is shown that BTMS has significant impacts on controlling the maximum temperature and temperature uniformity along the battery module's cells. However, Figure 6.12 shows that using the BTMS causes in decrees in power and capacity outputs. This decrease is more explicit at lower ambient temperatures (0 °C and 10°C). These phenomena can be explained by the increasing battery resistances as the average battery temperature decreases. The temperature dependency of the battery resistances is explained in detail in chapter 2. Therefore, with using the BTMS, average battery temperature decreases leading to increased resistances and slightly decreased battery power and capacity outputs.

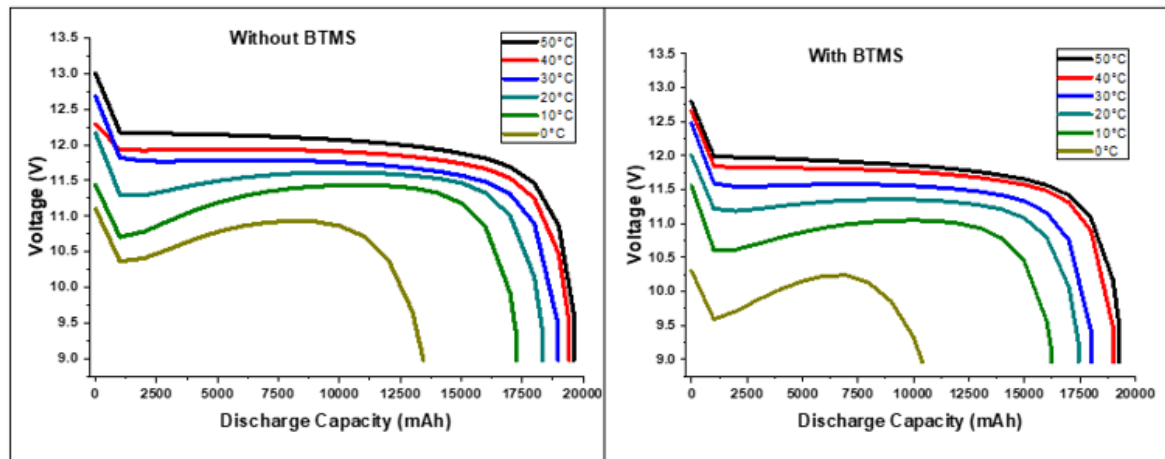


Figure 6.12. Effect of thermal management system on module capacity

6.2.2 Model Validation

The developed model is validated both for a single cell and 4S1P module using experimental measurements. Figure 6.13 shows a temperature profile for a simulated cell and the cells which temperature were measured experimentally. The temperature distributions for the simulated and experimental cell matches greatly. Furthermore, the temperature validation for a single cell at different current rates were shown in chapter 2.

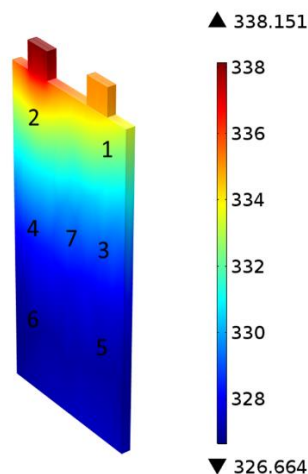


Figure 6.13. Temperature profile of a single cell; model result (left) and experimental result (right).

In addition to a single cell, we also validated temperature profile of the developed 4S1P module using the experimental measurements.

The temperature of the 4S1P module is measured at twelve points as shown in Figure 6.7, however, only nine of them plotted to avoid overlapping. Figure 6.14 shows the experimental (Figure 6.14-a) and simulated (Figure 6.14-b) results obtained from

4S1P module at 3C discharge and 30 °C. There is good agreement between the experimental and model results considering the maximum temperature rise and temperature gradients on cell surfaces. The $T_{\max}$ value gets 344.8 K in experiment and 343.9 K in simulation. Similarly, the difference between $T_{\max}$ and $T_{\min}$ values are 15 K and 14.6 K according to experimental and model measurements, respectively.

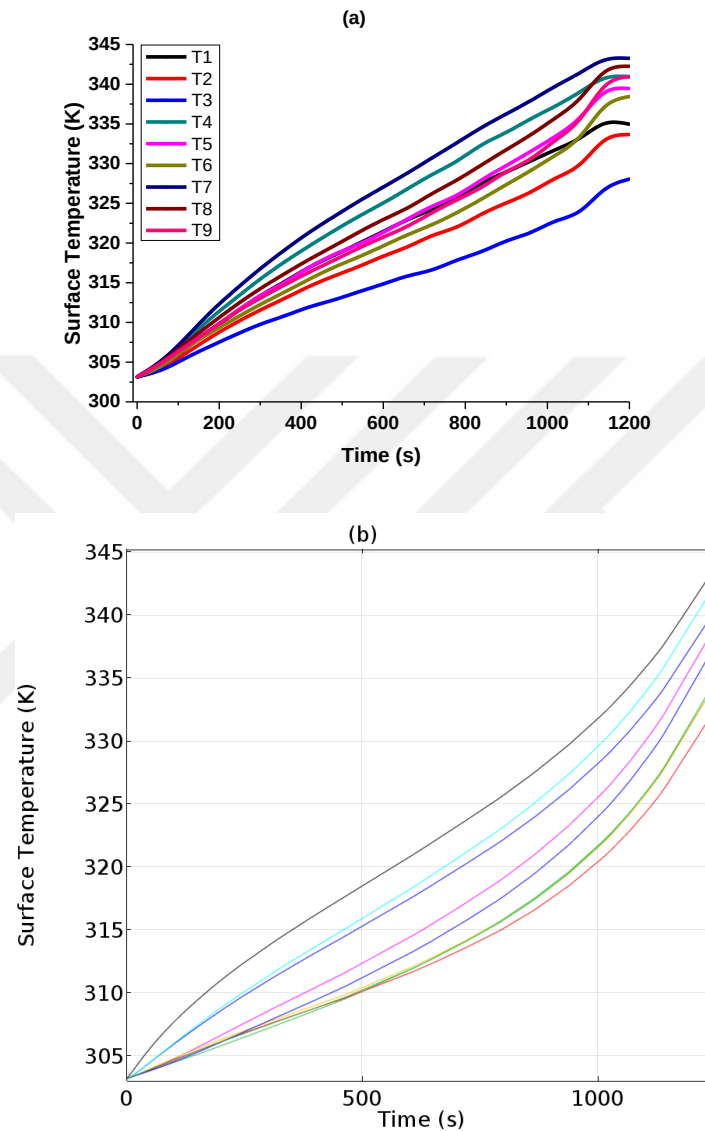


Figure 6.14. Surface temperature graphics of the 4S1P module without cooling system measured (a) experimentally and (b) by the model.

We also validated the temperature distribution along the 4S1P module using the air-cooling system (ACS). In the experimental part, we used a type of air compressor providing 0.4 g/s inlet mass flow rate. Consequently, we set the same inlet mass flow rate in the model to compare the cooling results obtained experimentally and by the model. Figure 6.15 represents the surface temperature profiles of the 4S1P module with the air-cooling system measured experimentally and from the model. According to the experimental results, $T_{\max}$ gets 328 K and ΔT gets 2.8 K with the aforementioned inlet flow rate. At the same conditions, $T_{\max}$ gets 329 K and ΔT gets 2.1 K based on the

simulation results. Thus, a good accordance is seen between the experimental and simulation results.

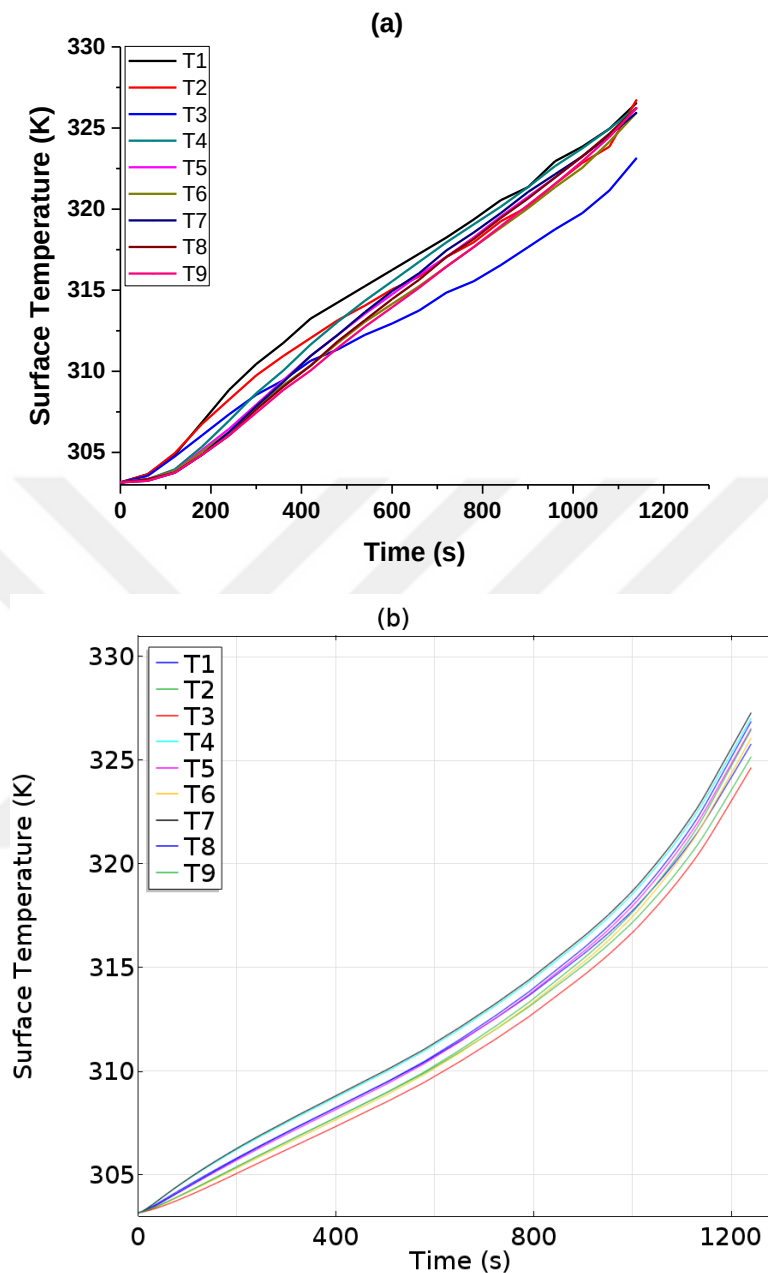


Figure 6.15. Surface temperature graphics of the 4S1P module with cooling system ($\dot{m} = 0.4$ g/s.) measured (a) experimentally and (b) by the model.

6.2.3 Cooling performance at different C-rates

Choosing a proper cooling medium has great impacts on overall performance and cost of the BTMS. Each heat transfer medium has advantages and drawbacks, and the cooling medium should be selected based on the operating conditions. However, the heat transfer mechanism using the cooling plates is same. The generated heat in the cells is transferred to the cooling plate and then is dissipated away by the cooling medium through the channels.

We studied the thermal behavior of single cells and battery modules with and without a cooling system at different current rates, ambient temperatures, and flow rates. We started with the extreme case, 5C discharge, during which a substantial amount of heat is generated. Figure 6.16 shows the temperature profile for a single cell and 4S1P battery module with and without air-cooling system when the inlet mass flow rate is set to 1g/s at 30 °C. Under the mentioned conditions, using cooling plates, $T_{\max}$ falls from 338.15 to 319.53 K for a single cell, and it falls from 376.8 to 337.7 K for a 4S1P module. Many researchers have found that the optimum operating temperature range for lithium-ion batteries is between 15 °C and 40 °C¹⁸¹. For this reason, the cooling performance of the air-cooling system with the inlet mass flow rate of $\dot{m} = 1$ g/s is not enough at 5C discharge. According to Table 6.1, at 5C discharge, air must be fed with the mass flow rate of 120 g/s to keep the whole battery pack temperature under 40 °C. However, supplying the mentioned flow rate leads to huge power consumption and is not feasible economically. Therefore, WCS is preferred at 5C discharge. As shown in Figure 6.17 and Table 6.1, WCS with $\dot{m} = 36$ g/s, presents excellent cooling performance as it keeps the cells surface temperature (Figure 6.17-a) and cell inner temperature (Figure 6.17-b) under the maximum operating temperature limit with relatively low power loss (1.49 W). Furthermore, temperature difference between the battery cells is 1.34 °C which is 28.4 without using the thermal management system at 5C.

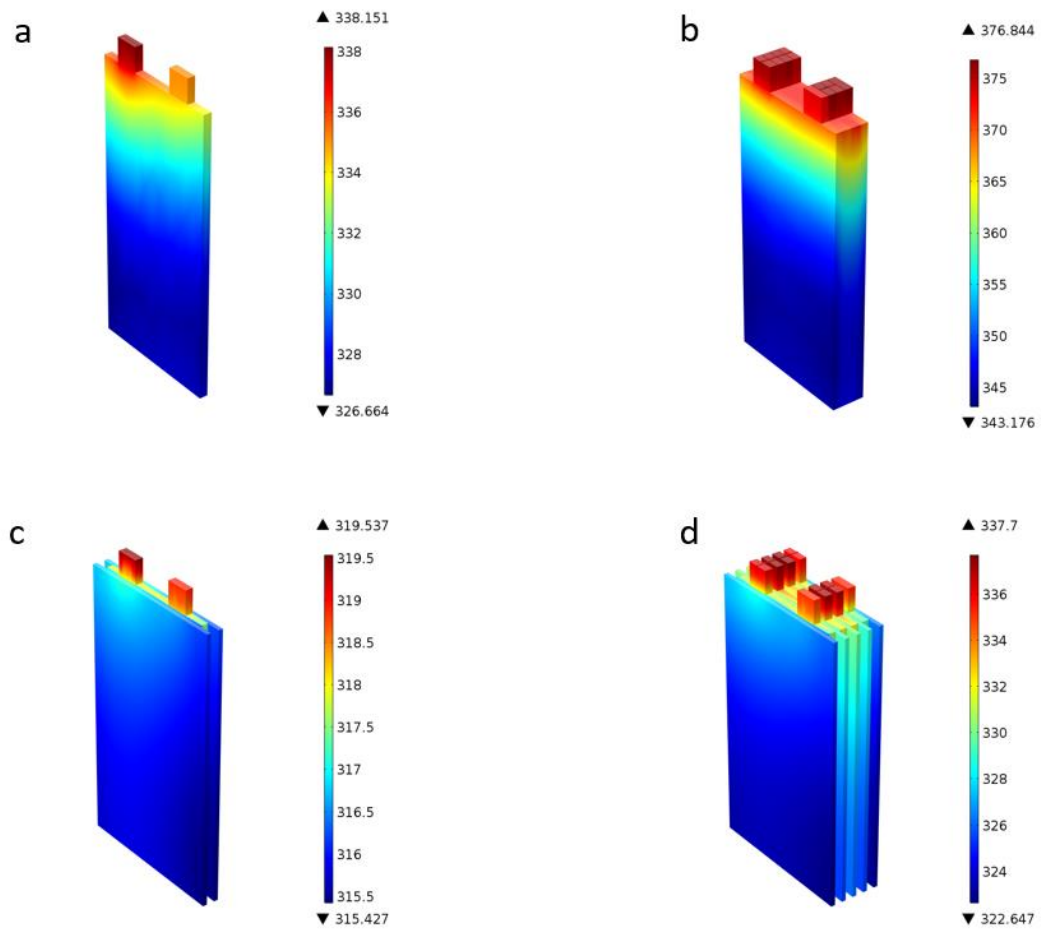
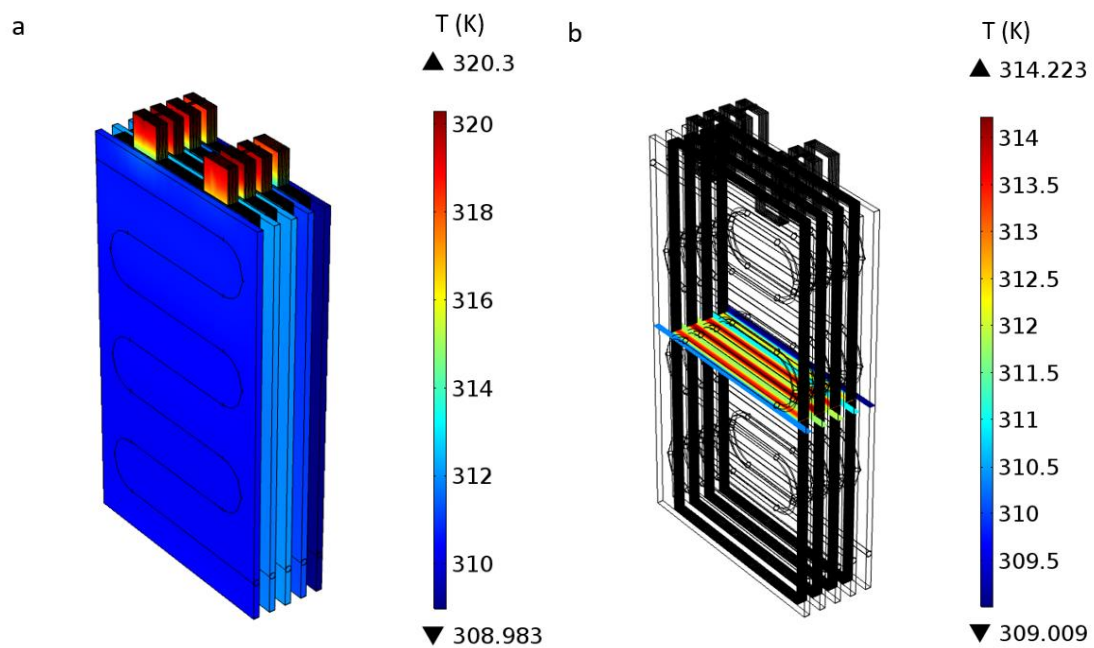


Figure 6.16. Temperature profiles of a (a) single cell, (b) 4S1P module, (c) single cell with cooling system, and (d) 4S1P module with cooling system at 5C discharge rate, 30 °C and $\dot{m} = 1$ g/s.



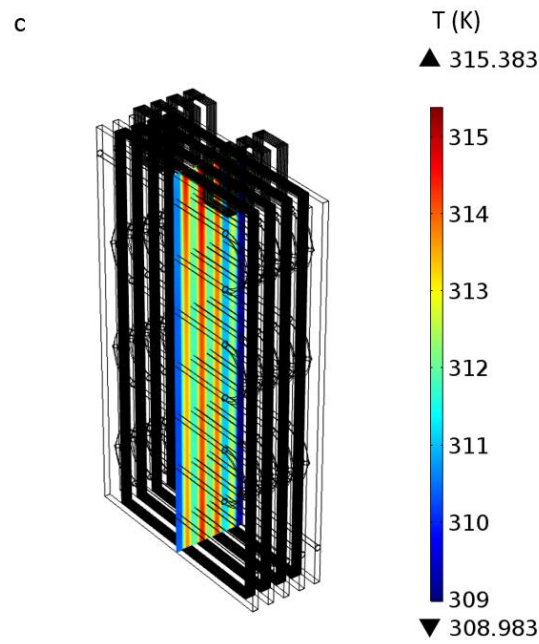


Figure 6.17. Temperature Profile of the 4S1P module with the water-cooling system at 5C discharge rate, 30 °C, and $\dot{m} = 36$ g/s. (a) 3D volume, (b) x-y cut plane, (c) x-z cut plane.

Temperature rise at 3C is significantly lower than 5C discharge. As shown in Figure 6.18, $T_{\max}$ falls from 324 to 314 K in a single cell and falls from 342.2 to 325.83 K in a 4S1P module using a cooling plate. At the same time, the cooling plates reduce the ΔT value from 3.61 to 1.4 K and from 12.38 to 6 K for a single cell and 4S1P module, respectively. Considering the optimum operation temperature range for LiFePO₄ battery, despite this cooling performance satisfies the single cell, it is not sufficient for 4S1P battery module and higher mass flow rates should be used. The calculated values for WSC and ACS are listed in Table 6.1.

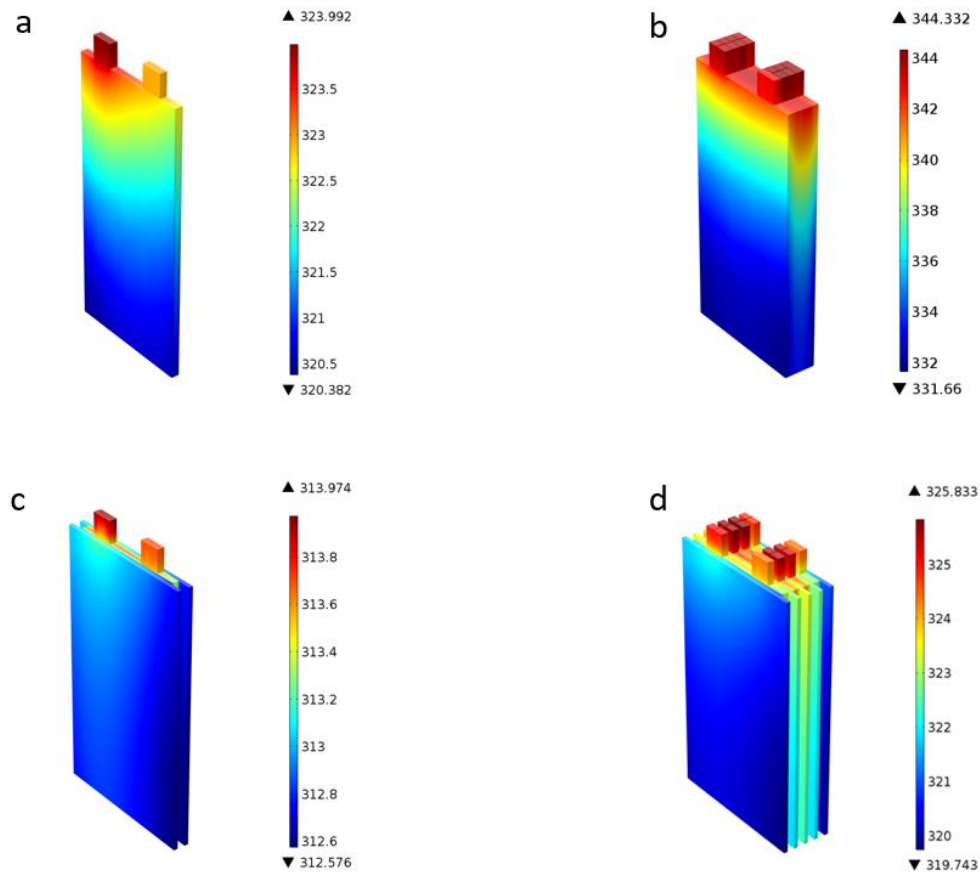


Figure 6.18. Temperature profiles of a (a) single cell, (b) 4S1P module, (c) single cell with cooling system, and (d) 4S1P module with cooling system at 3C discharge rate, 30 °C and $\dot{m} = 1$ g/s.

At 1C discharge (Figure 6.19), the temperature rises from 303.15 to 310 K in one cell and increases to 323.8K in a 4S1P module. Although 1C discharge appears to be a safe current rate, the use of a cooling plates makes a difference in temperature rise and uniformity on the battery module. For example, $T_{\max}$ falls from 311 to 307.8 K in a single cell and falls from 323.8 to 314.3 K in 4S1P. According to the obtained results, ACS with the $\dot{m} = 1$ g/s at 30 °C is enough in keeping the battery temperature in a safe range and there is no need to WCS at 1C discharge.

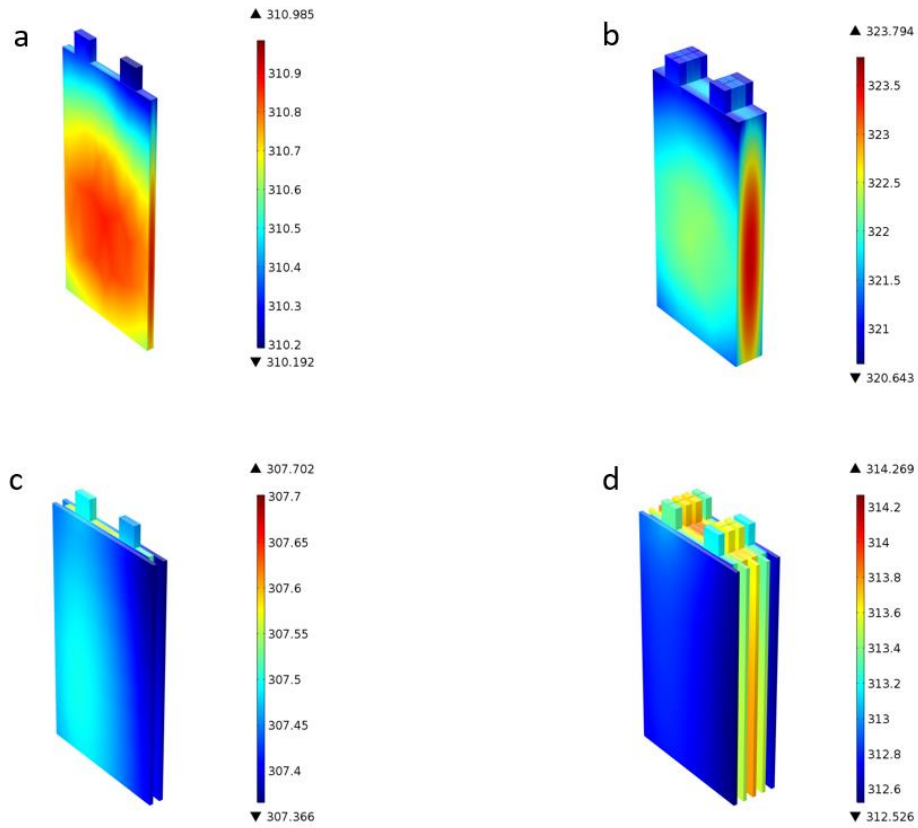


Figure 6.19. Temperature profiles of a (a) single cell, (b) 4S1P module, (c) single cell with cooling system, and (d) 4S1P module with cooling system at 1C discharge rate, 30 °C and $\dot{m} = 1$ g/s.

Table 6.1 Cooling performance of WCS and ACS.

Discharge	Air			Water		
	$\dot{m}(\frac{g}{s})$	$\Delta T(^{\circ}C)$	P(W)	$\dot{m}(\frac{g}{s})$	$\Delta T(^{\circ}C)$	P(W)
5C	120	5.9	4e7	36	1.34	1.49
3C	35	2.91	3e5	8	0.94	0.048
1C	1	1.33	68.35	0.3	0.4	8e-6

Finally, we studied the effects of a cooling system on voltage-time graphics. Generally, the higher nominal voltage means higher power output and longer discharge time means higher capacity or energy output. Figure 6.20. **Effect of cooling on discharge voltage at (a) 5C and (b) 3C.** illustrates the effects of a cooling system on voltage-time graphics at 5C (Figure 6.20-a) and 3C (Figure 6.20-b). At higher temperatures, power and energy outputs of the batteries are higher due to the increased Li ion diffusion rate. Therefore, Power and energy outputs at batteries without the cooling system and with

higher temperature rise are slightly more than the batteries with a cooling system. As shown in Figure 6.20-a and Figure 6.20-b, the nominal voltage and discharge time in the battery with WCS is lower than the batteries with ACS and no cooling system. This difference is more noticeable at 5C discharge due to the higher temperature difference of the battery modules operated with and without a cooling system.

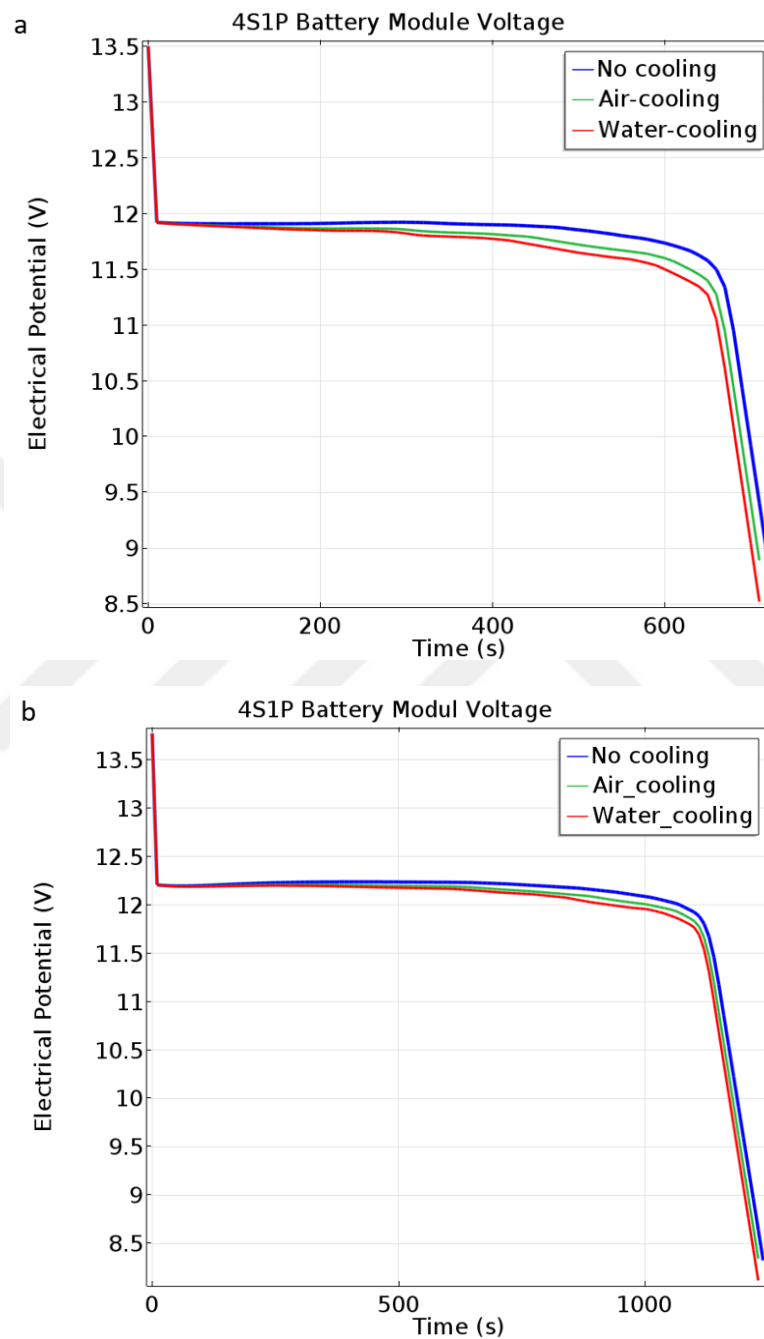


Figure 6.20. Effect of cooling on discharge voltage at (a) 5C and (b) 3C.

7 Chapter 7: Summery and Future work

7.1 Summery

In most recent couple of decades, developing popularity of Electrical Vehicles (EVs) and Hybrid Electrical Vehicles (HEVs) related with ecological worries over oil-based transportation foundation, has pulled in many research considerations over rechargeable Li-ion batteries (LIBs). High capacity and electrochemical potential, high energy density, and stability makes LIBs as a promising alternative energy source for vehicles. However, because of the security issues, high cost, and thermal performance, these batteries have not been broadly conveyed industrially, which are difficulties identified with the proper thermal management. LiFePO₄ as an active material (AM) for cathode, is a very promising material compared to the other materials such as LiCoO₂, LiMn₂O₄ due to the low cost, better safety profile, low toxicity, and a long cycle life.

As of late, building up another procedure to infer a superior thermal management on a Li-ion battery has pulled in consideration of numerous researches. Furthermore, significant attention is being paid to how temperature elevation and thermal management affect capacity and power fade, thermal runaway, and poor cold temperature and high temperature performance of Lithium ion cells. In this work, electrochemical and thermal behavior of LiFePO₄ battery is modeled in 3D by finite element simulation software named COMSOL MULTYPHISICS 5.2. Each cell having a copper negative current collector, graphite negative electrode, LiPF₆ w/EC: DEC (1:1) electrolyte, LiFePO₄ positive electrode and aluminum current collector is modeled the same with the purchased commercial 20Ah batteries. The model results for capacities and surface temperature change on cells are validated at high ambient temperatures (20°C, 30°C, 40°C, 50°C) and low ambient temperatures (-20°C, -10°C, 0°C, and 10°C) for various discharge rates (1C, 2C, 3C, 4C, and 5C). Developed model is used to investigate the effects of a number of layers (single layer, 4 layers, 8 layers, 16 layers, and 20 layers) inside the cell on temporal and spatial temperature profile and heat generation rates. Generally, the more the layer numbers are inside the battery, the higher the cell inner resistance will be. Therefore, number of hot spots will be more for multilayer cells. In addition, cells with different dimensions and same volume are developed to find the optimum cell dimension with a minimum temperature rise and temperature nonuniformity. According to our results, thinner cell with a wider surface area showed the optimum thermal behavior.

The second part of the thesis was about designing a thermal management system for high capacity Li-ion battery. We designed an air-based and water-based cooling system for the battery packs and then optimized the cooling performance of them. Using the optimized parameters, we compared the cooling performance of the passive air-based and water-based thermal management systems and specified the preferred BTMS at different battery performing conditions such as different ambient temperatures and different current rates. The experimental cooling system is developed

and fabricated based on the simulation results. The obtained temperature results from experiments were in good agreement with the simulation results.

7.2 Future Work

We studied the cooling performance of the developed passive cooling system with water-based and air-based cooling systems using the model. However, in the experimental part, the developed cooling channels for air cooling system (Figure 6.5) was not appropriate for liquid-based cooling because of the leakage problem. Therefore, we designed and fabricated a new cooling channels for liquid-based cooling. Figure 7.1 shows the schematic of the new channels with one main inlet and outlet which are then divided to four channels. The developed channels then will be imbedded in thin aluminum plates and the whole system will be used for temperature control of the batteries. A liquid coolers and pump device (Labo Ch-750) shown in Figure 7.2 will be used for temperature control and pumping the liquid through the channels. Using this devise, both active and passive thermal management system is possible. Furthermore, it could be used for heating the battery cells in subzero ambient temperatures and cool down the battery at a higher ambient temperature.

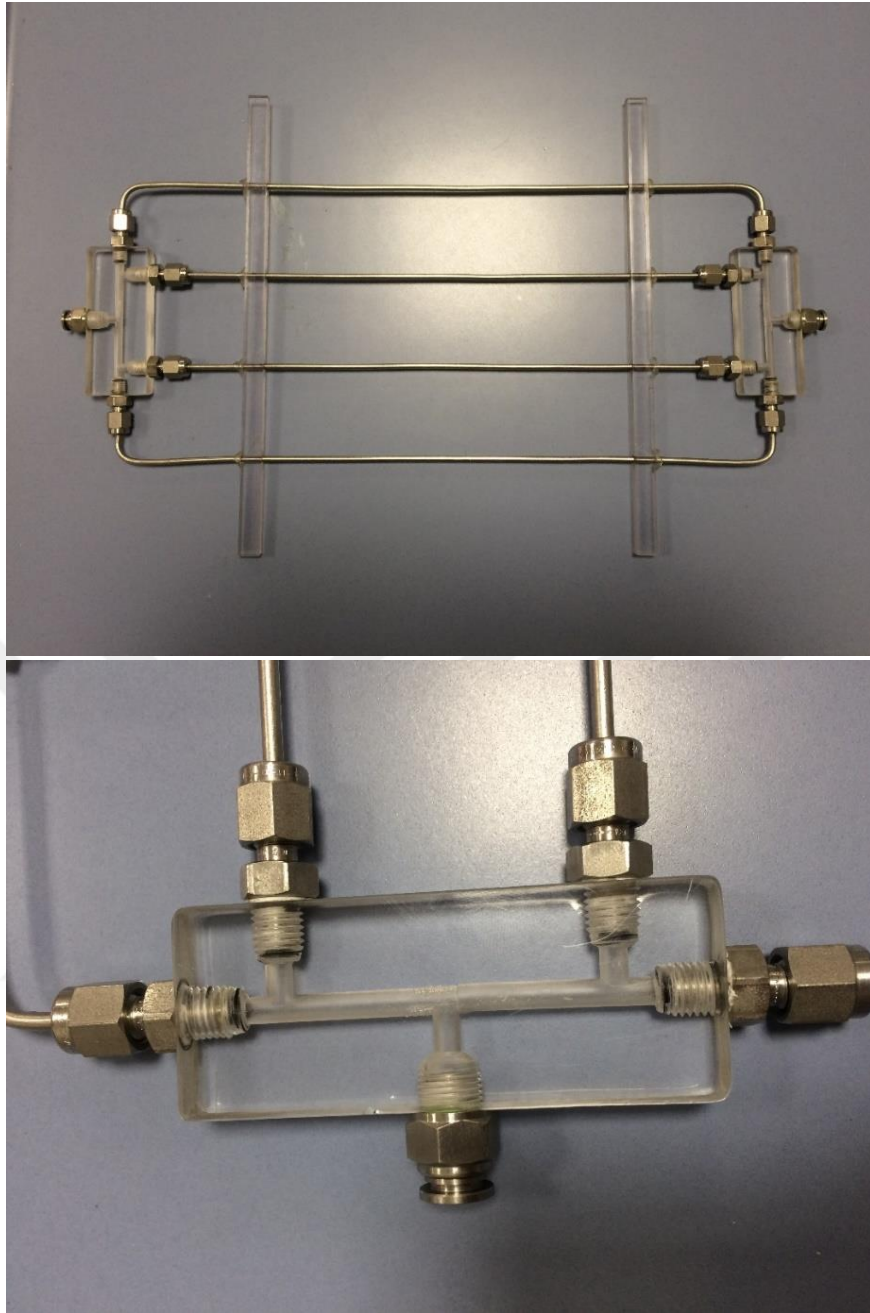
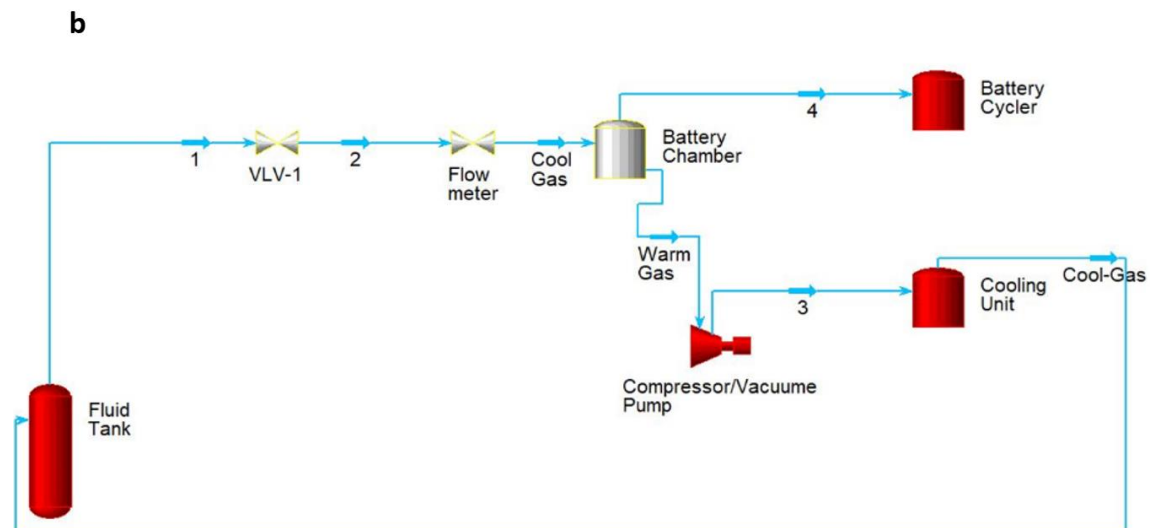
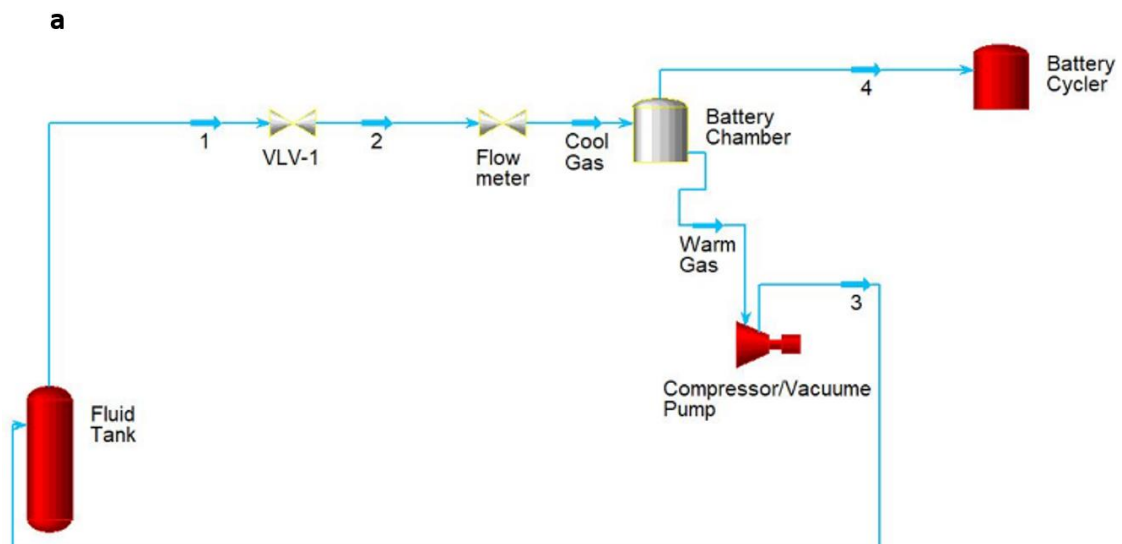


Figure 7.1. Schematic of liquid cooling channels.



Figure 7.2. Schematic of liquid coolers and pump (Labo Ch-750).

We also aim to develop an alternative novel BTMS. In general, there are two types of cooling, active and passive. In active system, the fluid which is cooled or heated externally is sent to the battery pack. In the passive system, the fluid is not subjected to any heating or cooling. In both, the aim is to remove the heat generated during charge/discharge. Nowadays, air is used both in terms of cheapness and availability. However, due the low thermal conductivity and existence of the reactive nitrogen, oxygen and moisture with the active material in the LIB, special design is required for cooling system. Therefore, as future study, we aim to use helium gas which has higher thermal conductivity and heat capacity and low density. The heat transfer from the battery to the fluid will be more effective, and the temperature distribution on the battery surface will be minimized. Previous studies have shown that if a cooling system is not used, 8°C difference on the surface may occur. With the superior physical properties of the helium, we aim to reduce this temperature difference down to 2°C or less. Another gain is the less mass of gas circulating in the cooling system. The total weight will be reduced by using a gas that is 7 times lighter than the air. More importantly, a more secure battery system will be created by the presence of non-reactive helium gas in the cooling system. If any of the cells is damaged, lithium and helium will not react, and dangerous gases will not be released. Helium is a preferred material for cooling in long-term superconducting magnets and fusion reactors, but there is no example of helium use in EVs as a cooling fluid. Therefore, this study will be important in terms of developing a new product. BTMS will be created with the materials supplied from the domestic market. This study may result in a patentable product which is capable of providing an alternative cooling system for electric vehicles. Possible designs for an active and passive helium gas-based BTMS are illustrated in Figure 7.3.



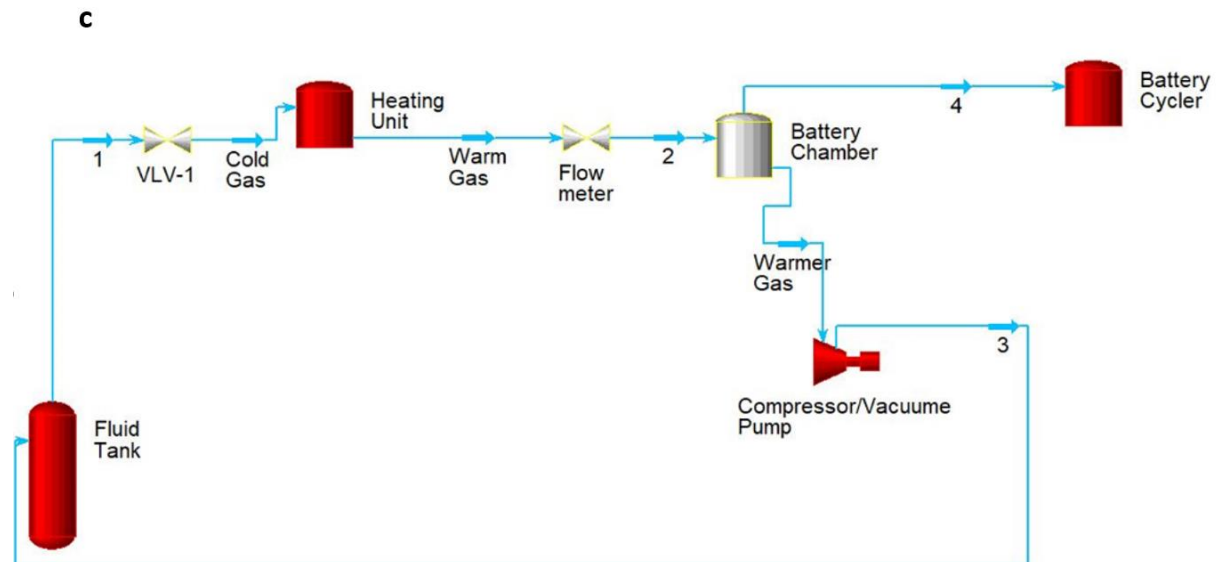


Figure 7.3. Schematic of (a) a passive cooling system, (b) an active cooling system, (c) and an active heating system



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