The Influence of Internal Parameters on the Electrochemical and Thermal Behaviors of Lithium-Ion Batteries

by

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Abstract

Lithium ion (Li-ion) batteries, consisting of multiple electrochemical cells, are complex system whose high electrochemical and thermal stability is often critical to the well-being and functional capabilities of the electric device. Considering any change in the specifications may significantly affect the overall performance and life of a battery, an investigation of the impacts of the electrode thickness and initial electrolyte salt concentration on the electrochemical and thermal properties of lithium-ion cells based on experiments and a coupling model composed of a 1D electrochemical model and a 3D thermal model is conducted in this work. Pertinent results have demonstrated that the electrode thickness as well as the electrolyte salt concentration can significantly influence the battery from many key aspects such as the energy density, voltage, temperature, distribution and proportion of different heat sources and ability to prevent lithium plating.

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Nomenclature

a_s	active surface area per electrode unit volume, $\text{cm}^2 \text{cm}^{-3}$
A	surface area of electrode, cm^2
c	volume-averaged concentration of lithium in a phase, mol cm^{-3}
$c_{s,max}$	maximum concentration of lithium in solid phase, mol cm^{-3}
$c_{s,0}$	initial concentration of lithium in solid phase, mol cm^{-3}
c_p	specific heat capacity of component inside cell, $\text{J kg}^{-1} \text{K}^{-1}$
D	diffusion coefficient of lithium species, $\text{cm}^2 \text{s}$
D_s	diffusion coefficient of lithium in the electrode particles, $\text{cm}^2 \text{s}$
e^-	electrons
F	Faraday's constant, 96487 C mol^{-1}
h	convective heat transfer coefficient, $\text{W m}^{-2} \text{K}^{-1}$
i_e	solution phase current density, A cm^{-2}
i_s	solid phase current density, A cm^{-2}
I_{app}	applied current, A
j^{Li}	reaction current density, A cm^{-3}
k	conductivity of different components inside cell, $\text{W m}^{-1} \text{K}^{-1}$
k^{eff}	effective electrolyte conductivity, S m^{-1}
l_c	thickness of copper foil, cm
l_n	thickness of negative electrode, cm
l_s	thickness of separator, cm

l_p	thickness of positive electrode, cm
l_a	thickness of aluminum foil, cm
l_{Doyle}	thickness of components in Doyle's battery model, cm
l	thickness of entire electrochemical cell, cm
L_1	thickness of experimental battery, cm
L_2	width of experimental battery, cm
L_3	length of experimental battery, cm
q	heat generation rate, W m^{-3}
q_r	irreversible (reaction) heat generation rate, W m^{-3}
q_{rev}	reversible heat generation rate, W m^{-3}
q_j	ohmic heat generation rate, W m^{-3}
r	radial coordinate along active material particle, cm
R	universal gas constant, $8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$
R_s	radius of solid particles, cm
t	time, s
t_+^0	transference number of lithium ion with respect to the velocity of solvent
T	temperature, K
U	open circuit potential, V
dU/dT	entropy change term, mV K^{-1}
U_{ref}	reference open-circuit potential of an electrode reaction, V
x	x coordinate
x	negative electrode solid phase stoichiometry

y	y coordinate
y	positive electrode solid phase stoichiometry
z	z coordinate

Greek symbols

ε	volume fraction or porosity of a phase
η	surface over-potential of an electrode reaction, V
κ	reaction rate constant
σ	conductivity of solid active materials in an electrode, S cm ⁻¹
ρ	density of the battery, kg m ⁻³
Φ	electrical potential in a phase, V

Subscripts

amb	ambient
e	electrolyte phase
f	conductive filler additive
i	i^{th} component
n	negative electrode
p	positive electrode or polymer phase
ref	with respect to a reference state
s	solid phase

Superscripts

eff

effective value

1 Chapter: Introduction

1.1 Overview and Related Issues

Lithium ion (Li-ion) batteries have replaced the nickel-based systems in small-electronics, automobile, satellite, and several other applications over the past decades due to their superior performances. And in recent years, more and more research efforts have been made on developing advanced Li-ion batteries, among which the determination of the electrochemical and thermal behaviors of Li-ion battery under different operating conditions has been an important field of study due to its importance and fundamental property. For example, a review of the high temperature operation tests on Li-ion batteries was conducted by Bandhauer et al. [1], through which they concluded that the battery performs differently in various aspects, such as the capacity supply and degradation rate, when operating at different temperatures. Other investigators employed different discharging modes, e.g., constant current discharge [2], pulsed discharge [3] and high rate discharge [4], in order to evaluate the performance of Li-ion batteries used for different applications that operate in respective modes. Also, the impact from the configuration of the battery system was studied by Fan et al. [5], and it was demonstrated that an improper cell layout can lead to an uneven heat distribution across the battery pack, which is widely believed to damage the system silently and irretrievably and promote safety issues.

Despite that significant efforts in the past have been focusing on the evaluation of the battery performance under various external conditions like temperature and discharging profile, the understanding of many internal processes undergoing in the battery during discharge has not been clear. Therefore, many recent studies have attempted to identify the contributions made by individual intrinsic specifications to the change of the properties and

behaviors of Li-ion battery. For example, considerable research efforts have been made to promote the advancements of the Li-ion battery by developing new electrode and/or electrolyte chemistries and designing varying battery geometries [6-10].

Generally, high specific energy and energy density are highly required for a Li-ion battery to be used in many applications such as aerospace, plug-in hybrid electric vehicle and electric vehicle. To achieve this, the electrodes, as the main power storage component in a battery cell, designed with different material loadings, particle sizes, porosities and thicknesses, have been tested in various experiments [11-15, 60]. For instance, Zheng reported an optimized LiNiCoAlO cathode consisting of polyvinylidene difluoride and acetylene black, wherein the volumetric energy density of the electrode was improved by using less inactive material without loss of the power density [16]. Also, an increase of the specific capacity from 102 mAh/g to 138 mAh/g was observed in LiMn₂O₄ powder when the average diameter of active particles is reduced from 1000 nm to 60 nm [17]. In addition, some studies on the influence of electrode thickness were reported: two types of electrodes (LiNiCoMnO and LiFePO₄) with different thicknesses were used for investigating the impact of electrode thickness on the overall performance of the batteries [18], and the results revealed that thicker electrodes can provide a higher energy density but a faster capacity fading rate and a lower power density; batteries with various thicknesses of LiMn₂O₄ cathodes were also assembled to test the optimum cathode loading that can help to construct a high performance battery [11]. However, the analyses relevant to the batteries with different electrode thicknesses in most literatures are only based on the experimental obtained results, from which the explanation of the capacity fading difference between cells is not evident and satisfying. Meanwhile, only the external behaviors and overall cell

performance of batteries are able to be observed and analyzed in the literatures. Comparatively, much less efforts were made to elaborately depict the internal electrochemical and thermal processes of the cells considering different electrode thicknesses, which allows a fundamental understanding of the phenomena accompanied with the batteries using different electrode thicknesses.

Beside the impacts from electrode thickness, the electrolyte, which is directly related to the transportation of lithium ions across the electrochemical cell, the diffusion environment for cations and anions, and many other important electrochemical processes, is seldom studied in the past articles, especially the impact from the concentration of electrolyte on the performance of Li-ion battery. And in different articles, different initial electrolyte salt concentrations are used. A 1D electrochemical battery model was firstly built by Doyle et al. [65] based on the LiMn_2O_4 cathode, which laid the foundation for this area. Later, Gu and Wang [66] coupled an electrochemical model with a thermal model and tracked the coupling temperature variations during charge and discharge, which were used to calibrate the electrochemical model for the temperature dependent parameters. In both of the models, the electrolyte salt used was LiPF_6 in a non-aqueous liquid mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), and the concentration of the binary solution was 2000 mol m^{-3} (M). However, in some other works [4, 67], the electrolyte concentration used in the model was 1.2 M. To date, no much research interest has been focused on the investigation of how the electrolyte salt concentration impacts the electrochemical behaviors of lithium ion batteries during charging and discharging.

1.2 Objectives and Thesis Organization

To this end, an investigation on the electrochemical behavior and the associated thermal response of the Li-ion batteries with different electrode thicknesses and initial electrolyte salt concentrations on both the battery level and the detailed components level is carried out in this work, and the in-depth analyses on several key battery properties (e.g., voltage, heat generation of different sources, and temperature etc.) for one cell with different depths of discharge as well as for a battery with different parameters are conducted based on experimental results and extensive simulation results. The model adopted for this simulation is developed with a 1D electrochemical model coupled with a 3D thermal model, and validated by examining the temperature profiles collected from a set of experimental discharge tests.

In the thesis, Chapter 2 gives a state of the art review of the Li-ion battery, the thermal issues and the development of modeling technology of Li-ion battery. All the details related to the experiments and simulations are given in Chapter 3. Chapter 4 illustrates the impact of electrode thickness on the performance of Li-ion battery through comparing both the electrochemical and thermal results during the discharge process from experimental and simulated results. In Chapter 5, the importance of selecting an appropriate initial electrolyte salt concentration for Li-ion battery is discussed through the simulation results for both charge and discharge courses. The final conclusion and future work are made in Chapter 6, which give an overall evaluation of the internal parameters' effect on the performance and stability of Li-ion battery and the relevant extension of the current work.

1.3 List of Contributions

In this thesis, a series of contributions have been done. First, the coupling model designed with half current collect thickness has a great improvement on the thermal results, which has not been proposed by any other published studies before. And the entropy heat involved model shows more accurate temperature results during simulations. Secondly, although some experiments in the past have shown the influences of electrode thickness on the performances of Li-ion batteries, their explanations on the results are superficial and without enough supports. While this thesis has a comprehensive explanation on the performances of Li-ion battery with various electrode thicknesses through analyses of results from the numerical simulations and experiments, especially the results of 1D electrochemical model which detailedly explain the thermal behaviors accompanied with Li-ion batteries with different electrode thicknesses. Thirdly, the influence of initial salt concentration on the performance of Li-ion battery is seldom discussed in previous publications and is stated in this thesis in detail. All of the contributions from this thesis can help the industries to develop Li-ion batteries with improved performances by simply vary internal parameters and can let the researchers have a deep understanding on the operation of Li-ion battery.

Meanwhile, my published and submitted papers related to this thesis are also given below:

1. R. Zhao, J. Gu, J. Liu. "An investigation on the significance of reversible heat to the thermal behavior of lithium ion battery through simulations," *Journal of Power Sources*, 266, pp. 422-432, 2014.
2. R. Zhao, S. Zhang, J. Liu, J. Gu. "Effects of salt concentration on the electrochemical

and thermal behaviors of lithium ion cells,” In Proceedings of 9th International Green Energy Conference, Tianjin, May 25-28, 2014.

3. R. Zhao, S. Zhang, J. Liu, J. Gu. “The Effects of Electrode Thickness on the Electrochemical and Thermal Characteristics of Lithium Ion Battery,” Submitted to Applied Energy.

2 Chapter: Background and Literature Review

2.1 Lithium-ion Battery

Batteries are often classified as primary (non-rechargeable) or secondary (rechargeable) depending on their capability of being electrically recharged, and this is determined mainly by the reversibility of the anodic and cathodic electrode reactions [19]. In 1990, with solving various problems and improving the performance of the lithium-ion battery, Sony first commercialized the Li-ion battery. Nowadays, Li-ion batteries have emerged as the most promising energy storage technology in recent years due to their higher energy density, lighter weight, no memory effect, and lower self-discharge rate, when compared to other rechargeable battery technologies [20].

Fig. 2.1 shows the Ragone plot of Li-ion battery and other rechargeable batteries. The parallel axial is the specific power, which represents the discharge rate and is also known as the acceleration capability of vehicle equipped with a type of battery. While the vertical axial indicates the specific energy, which means the capacity of the battery and how long the vehicle can drive. From the comparison, it can be seen that Li-ion battery has higher specific energy and power compared to other rechargeable batteries, and it can satisfy the applications in both plug-in hybrid electric vehicles (PHEV) and hybrid electric vehicles (HEV). Owing to the excellent performances, the market share of Li-ion battery is increasing year by year. Fig. 2.2 reveals the market production of different types of rechargeable batteries (Li-ion, Ni-MH, Ni-Cd) from 1991 to 2009. It can be seen that the market share of Li-ion battery is increased from no more than 10% in 1991 to more than 10 times that of Ni-MH battery and Ni-Cd battery in 2009.

Figure 2.1. Ragone plot of various electrochemical energy storage and conversion devices [21].

Figure 2.2 Market share of secondary cells [22].

2.1.1 Internal Structure of Li-ion battery

To better understand the working mechanism and simulate the discharging and charging processes of Li-ion battery, the internal structure and each components inside the Li-ion battery should be studied firstly. Fig. 2.3 shows the internal structure of one unfolded Li-ion battery, in which the white plastics are the separators, and the black ones are either current collectors with positive electrodes (cathode) or negative electrodes (anode). It can be seen that the Li-ion battery is composed of many layers of electrochemical cells (one piece of separator and one piece of positive electrode and negative electrode). The schematic illustration of the model is also given below (Fig. 2.4). As shown, the left figure represents one electrochemical cell inside the Li-ion battery, which consists of copper current collector, negative electrode, separator, positive electrode and aluminum current collector from left to right, where the electrolyte permeates the positive and negative electrodes and separator and act as a medium to transfer the ions during electrochemical reactions. While the right figure (Fig. 2.4 b) is the 3D thermal model of the coupling model used to simulate the temperature variation of the Li-ion battery. The developments of each components and the Li-ion battery model will be detailed given below.

Figure 2.3. Internal structure picture of a commercial Li-ion battery.

Figure 2.4. Schematic illustrations of a) 1 D electrochemical model and b) 3 D thermal model.

2.1.1.1 Negative Electrode (Anode)

The most common negative electrode used in the Li-ion batteries are carbon materials, which consist of coke and graphite. In general, the potential of carbon electrodes vs. Li/Li^+ is from the range of 0 to 0.8 V when different amount of Li-ions are intercalated. However, the limited specific capacity ($< 400 \text{ mAh g}^{-1}$) and problem of stability (such as Li-plating) induce intensive researches in the field for alternative negative electrode materials. Overall, the materials used as the negative electrodes can be classified into three parts: 1) silicon and silicon based composites, 2) metal oxides and 3) metals and alloys.

It is known that silicon features the high specific capacity of reversible lithium insertion. During the intercalation, the intermetallide has the highest lithium content with the composition of $\text{Li}_{4.4}\text{Si}$, which corresponds to a specific capacity of 4200 mAh g^{-1} [23-27]. However, the increase in the specific volume under insertion of a great amount of lithium was the obstacle for the application of this kind of material as the active negative electrode materials [27-31]. Thus, many research efforts have been focused on the nano-sized materials and electrodes to overcome the mechanical fracture under repeated electrochemical reactions. For example, in ref [32], films with thickness of 50 nm obtained capacities above 3000 mAh g^{-1} for more than 1000 cycles, while the cycle number decreased to 200 cycles when the film thickness increased to 150 nm.

Meanwhile, it is also found that due to the film disintegration (lithium insertion-extraction results in agglomeration of silicon particles [27, 33]), the thin-film electrodes will transform from film to powder during the cycling, and the surface treatment and binder for silicon electrodes are very important for the adhesive support [34-39]. Due to the elongation problem, the commonly used binder, poly-vinylidene fluoride (PVdF), is unable

to be used because it cannot sustain the large volume change of the silicon during the lithium intercalation. Therefore, other types of binder have been introduced: mixture of styrene–butadiene rubber with the sodium salt of carboxymethyl cellulose [40] and carboxymethyl cellulose in the form of sodium salt [41-42].

Another method to develop a more stable negative electrode is synthesis of silicon composite with other materials, and the most commonly used material is carbon. However, the increase in the content of carbon in the silicon composite will dramatically decrease the reversible capacity of the electrode.

Metal based (metal, alloy, and metal oxide) negative electrode also attracted a lot of research interest in the recent studies. The relevant researches can be found in articles focus on negative electrodes based on oxide-tin [43-45], NiO nanotubes [46], ZnO nano-rods [47], Ni₃Sn₄ [48], SnSb [49], etc. And attention should be paid that it is the smallness of metal particles that prevents them from degradation, as the specific volume increases. Meanwhile, the metal based negative electrode has the relatively lower specific capacity (lower than 1000 mAh g⁻¹) when comparing with the silicon based electrode.

2.1.1.2 Positive Electrode (Cathode)

All the conventional materials (lithiated cobalt and nickel oxides and also lithium–manganese spinels) for lithium-ion battery positive electrode are designed with relatively high operating potentials (generally between 3.7 V and 4.2 V). For example, the operating potential of LiMn₂O₄ positive electrode is given in Fig. 2.5 [50], in which the working platform is between 3.5 V and 4.3 V, and the corresponding highest specific capacity is 125 mAh g⁻¹.

The conventional materials for positive electrode pose certain problems regarding operational safety of lithium-ion batteries due to the material instability. Thus, attention has paid to materials with relatively lower positive potentials, and the most probable variant of replacement of conventional materials is considered to be lithiated iron phosphate that has already reached the commercialization stage [51]. In the meantime, to obtain higher power density, some researches also focus on the high-voltage positive electrode material (i.e. materials, with lithium insertion/extraction occurring at the potentials close to 5 V), for example, $\text{Li}[\text{Ni}_{0.5-x}\text{Mn}_{1.5+x}]\text{O}_4$. Although this kind of material offers a high-voltage cathode (Figure 2.6), the specific capacity remains below 130 mAh g^{-1} , especially if it loses Li to an anode SEI layer on the initial charge [50].

Figure 2.5. Voltage curves for Li^+ insertion and extraction of LiMn_2O_4 [50].

Figure 2.6. Comparison of charge/discharge voltage curves of $\text{Li}[\text{Ni}_{0.5-x}\text{Mn}_{1.5+x}]\text{O}_4$ with those of LiCoO_2 and LiFePO_4 [50].

2.1.1.3 Separator

The ideal separator should have infinite electronic resistance and zero ionic resistance, but in practice, the resistivity of separator is in the order from 10^{12} - $10^{14} \Omega \text{ cm}$, still in the range of insulator, and the ionic resistivity is non-zero due to the finite porosity and tortuosity. And in general, a thin membrane with a high porosity and a large mean pore size can increase the ionic conductivity, enabling the specific power of Li-ion battery, but such a membrane has the disadvantages like: low mechanical strength and easiness of suffering electrical shorting. The membranes in recent usage have thicknesses around 20-30 μm with the porosity around 40 % to 70 %.

The thermal behavior and mechanical behavior of the separator are crucial for the application in the Li-ion battery due to one important role separator played in the Li-ion battery, to prevent the contact between two electrodes. Generally, the separator is capable of fusing (thermal shutdown) under high temperatures, and the thermal shutdown graph referred from [52] is shown in Fig. 2.7. As can be seen, polypropylene (PP) membrane exhibited shutdown at around 165 °C and the resistance increased approximately by two orders of magnitude, while a polyethylene (PE) separator showed shutdown at around 135 °C and the electrical resistance increased by about three orders of magnitude after cooling down. So the most commonly used separators are PE or PP/PE/PP due to their high resistances after thermal shutdown.

Figure 2.7. Separator thermal shutdown [52].

However, the conventional separators are easily to experience the shrinkage under high temperatures, which should be avoided due to the safety concern. Thus, many research

groups have investigated many other types of separator based on polyimide (PI) [53] and glass fiber separators [54] to increase its thermal stability and mechanical strength. For example, Jiang *et al.* have manufactured nanofibrous PI based separators through the method of electrospinning technology with imidization as well as the mechanical pressing processes, and the experimental tests have validated that the separators have excellent thermal stability and mechanical strength. From Fig. 2.8, it can be seen that at 150°C, the PI separator is capable of keeping its original size, while the PP separator is shrunk due to the thermal instability.

Figure 2.8. The photographs of the PP membrane and PI nonwoven before (a) and after (b) thermal treatment at 150 °C for 1 h [53].

2.2 Thermal Issues of Li-ion Battery

Heat is generally accompanied with the operation of lithium-ion battery, which can be classified into three sources based on different mechanisms, i.e. ohmic heat source caused by the internal resistance during the transfer of ions; reaction heat source caused by

the electrochemical reaction during intercalation and de-intercalation; as well as the reversible heat from the entropy change of active materials. Thermal instability is one of the most noteworthy disadvantages of Li-ion battery, and more and more researches have been focusing on reducing the heat generation of Li-ion battery as well as transferring the heat out to the surroundings. The first method is aimed at changing the internal specifications, structure or parameters of Li-ion battery to decrease the heat generation and to fundamentally solve the thermal issue, while the second method is known as the thermal management system, which is trying to solve the thermal problem by equipping systems to absorb the heat from Li-ion battery and finally reduce the temperature of battery. Many researchers have investigated the thermal management systems based on either passive cooling system or active cooling systems or the combination of them, while only a few researches have been done on the first method. In this thesis, the author will give a detailed explanation on the first method by changing the internal parameters: the electrode thickness and the initial electrolyte salt concentration.

The performance, life time, and safety of Li-ion batteries are all affected by the operating temperatures, and the major thermal issues, capacity fading and thermal runaway, will be given here in details.

As a branch of performance degradation, the capacity fading of Li-ion battery is mainly caused by the transform of active materials into inactive ones, which is accompanied with Li-ion battery at any discharge rates under any temperatures but with different fading rates. Vetter et al. [55] discussed that elevated temperatures can enhance the kinetics of the lithium insertion/removal processes into/from the host lattice, but it is widely believed that the morphology and composition of the SEI changes at elevated

temperatures [2, 57-59]. Bandhauer et al. [1] summarized the capacity fading tests done by other research groups, and the researches related to the impact from temperature are listed in Table 1. It can be seen that the electrode material, electrolyte and operating depth of discharge (DOD) ranges all can influence the capacity fading of Li-ion batteries, and for all of them, batteries cycled at higher temperature are always corresponded to faster capacity fades.

Besides fast capacity fading, high operating temperature also can trigger the thermal runaway, which is mainly caused by the heat-generating exothermic reactions, e.g. chain electrochemical/chemical reactions and combustion, and it must be avoid for Li-ion battery application due to the serious consequences it may result in. In general, when the temperature inside the battery is not well dissipated or controlled, the temperature may increase to the threshold for self-heating of active materials or solid electrolyte interface (SEI), which may lead to higher temperatures and further trigger severer reactions. For example, Accelerating rate calorimeter (ARC) studies from MacNeil *et al.* [61] revealed that exothermic side reactions of lithiated carbon can cause self-heating, which starts typically at temperatures of approximately 80°C in various electrolytes, and the onset temperature also depends on the electrolyte salt and can be as low as 60°C for electrolytes containing LiBF₄. Yang *et al.* [62] also proposed a general path to thermal runaway in Li-ion battery: the SEI and graphite electrodes begin to exothermically decompose at temperature about 85°C, and when temperature is approximate to 110°C, a secondary film will form and decompose. The heat generated at this stage is absorbed by either the electrolyte for evaporation (at about 140°C) or the separator for melting (between 130°C and 190°C). Once the separator is shrunk or melted, the positive and negative electrodes

inside the battery will be contacted with each other and leads to the internal short circuit, which will increase the heat generation and leads to the combustion of materials when the temperature is reached to the critical point.

2.3 Review of Li-ion Battery Modeling

To determine the temperature variations of Li-ion batteries, two types of model have been proposed. One is sole thermal model and the other one is the electrochemical-thermal coupling model. The first modeling method is based on the thermal dynamic equation given as:

$$\rho C_p \frac{dT}{dt} = \nabla \cdot (k \nabla T) + Q \quad (1)$$

The right hand side of the equation indicates the energy that can be absorbed by the battery itself, and the ρ and c_p mean the density and specific heat capacity of the battery. The first term on the right hand side is the heat transferred to the surroundings, and can be expressed with equation:

$$-k \frac{\partial T}{\partial x} = h(T - T_{amb}) \quad (2)$$

if only the convective heat transfer way is considered.

The last term of the dynamic equation is the heat generated during the operation of Li-ion battery, which is generally classified into two parts: the joule heat (q_{joule}) and entropy heat ($q_{entropy}$) in previous articles:

$$q_{\text{joule}} = I \times (E - V) \quad (3)$$

$$q_{\text{entropy}} = I \times T \times \frac{dE}{dT} \quad (4)$$

where E is the open circuit voltage of the battery and the V is the close voltage of battery, T and I indicates the temperature and current of battery, respectively. To obtain the temperature curve of battery during discharge process, the researchers need to find the open-circuit voltage (E) and the entropy term dE/dT . Two methods of acquiring the values can be reviewed from previous studies: one is to remove the voltage drop from the internal resistance [63], while the other way is to obtain the data from the manufacturers [64].

As for the electrochemical-thermal coupling model, it involves the equations to describe the flow of current and ions during the electrochemical reactions. Doyle et al. [65] first developed the electrochemical model and validated the model by comparing the voltage curves with the experimental ones. Then, Gu and Wang [66] coupled the electrochemical model from Doyle et al. with the thermal model considering the reversible heat and joule heat and applied the model on a Ni-MH battery, from which the prediction of the coupling model showed improvements comparing to sole electrochemical model on both the electrochemical and thermal results. In last decade, the coupling model is more and more used on Li-ion battery systems [67-70]. Although the calculation time for the coupling model may be longer than the independent thermal model, it can reveal the electrochemical and thermal performances of battery very clearly from the fundamental perspectives. In this thesis, the coupling model is developed with considering three heat sources in the thermal parts, and the relevant equations and explanations of the model are given in the third part, experimental setup and mathematical modeling.

Table 1. Summary of reviewed capacity fade high temperature cycling studies [1].

Author	Materials	DOD range	Cycle rate	Number of cycles	Test temperature	Capacity fade	Key conclusions
Ramadass et al.[2, 57]	C/LiCoO ₂	4.2–2.0 V	C/1.8	500	25°C 50°C	22.5% 70.6%	Degradation of negative electrode dominated capacity loss
Ehrlich [71]	C/LiCoO ₂	4.2–2.5 V	C/1	500	21°C 45°C	9.0% 13.0%	
	C/LiMn ₂ O ₄	4.2–2.5 V	C/1	500	21°C 45°C	28.0% 51.0%	
Amine et al. [72]	MCMB/LiFePO ₄ (LiPF ₆ electrolyte)	3.8–2.7 V	C/3	100	37°C 55°C	40.0% 70.0%	Dissolution of Fe ²⁺ ions high for both coated and uncoated positive electrodes; high temperature capacity fade can be reduced by selecting appropriate electrolyte
	MCMB/LiFePO ₄ (LiBOB electrolyte)			100	37°C	20.0%	
Liu et al. [73]	C/LiFePO ₄	90% DOD	C/2	2628	15°C	7.5%	Capacity fade was primarily due to loss of lithium from repair of SEI on negative electrode; saw no evidence of Fe dissolution in the electrolyte
		50% DOD	6C	757 1376	60°C 45°C	20.1% 22.1%	

3 Chapter: Experimental Setup and Mathematical Modeling

3.1 Experimental Setup

In the present study, all experimental tests are performed on commercially available LiMn_2O_4 batteries purchased from the Electric Car Parts Company. To validate the impact of electrode thickness on the performance of Li-ion battery, totally two types of batteries are used in the experiments: 1) thick electrodes battery with a capacity of 10 Ah (Cell 1, Fig. 3.1) and 2) thin electrodes battery with a capacity of 9 Ah (Cell 2, Fig. 3.2). The specifications of the two batteries are listed in Table 2 and the parameters (includes electrode thicknesses) of the components inside the battery are given in Table 3 [75-77], in which the thicknesses of each components in experimental batteries (Cell 1 and Cell 2) are measured using the thickness gauge as shown in Fig. 3.3. Before experimental tests, all the batteries are conditioned by discharging to cutoff voltage of 3 V 5 times using the ESI battery analyzer (PCBA 5010-4, Fig. 3.4) at room temperature (298 K), which allow the formation of solid electrolyte interface (SEI) and the irreversible capacity fade for new batteries [74].

Figure 3.1. Photograph of 10 Ah battery (Cell 1, ECPC-SP1037) with thick electrodes used.

Figure 3.2. Photograph of 9 Ah battery (Cell 2, ECPC-SP8532) with thin electrodes used.

Figure 3.3. Thickness gauge used in the experiments with an accuracy of ± 0.001 mm.

Figure 3.4. ESI battery analyzer (PCBA 5010-4) used in the experiments.

To validate the effectiveness of the coupling model in simulating the thermal responses of the Li-ion battery, the temperature curves of two batteries in experiment and

in simulation are compared. At room temperature, two conditioned batteries undergo the galvanostatic discharge course at 1 C rate in a thermal insulated box, during which the surface temperatures of batteries are collected through K-type thermocouples (Fig. 3.5, accuracy $\pm 0.1^{\circ}\text{C}$) attaching at the surface centers of the batteries.

Figure 3.5. Multimeter and K-type thermocouple used in the experiments.

In the capacity fading tests of two batteries, both Cell 1 and Cell 2 are charged at 0.5 C rate with potentiostatically conditioned until the current decreased to $C/50$, which is closely followed by a discharge process at a constant current rate of 0.5 C. After 100 cycles at 0.5 C, a same test scheme is applied on both batteries with changing the current rate to 1 C for another 100 cycles. During the testing process, the discharge curves and internal

resistances of two batteries at 0.5 C (1st cycle, 50th cycle and 100th cycle) and 1 C (101st cycle, 150th cycle and 200th cycle) are collected for comparison.

Table 2. Specification of the LiMn₂O₄ batteries.

	Cell 1	Cell 2
Thickness of battery [mm]	10	8.6
Width [mm]	100	115
Height [mm]	140	140
Weight [g]	250	316
Nominal voltage [V]	3.7	3.7
Nominal capacity [Ah]	10	9
Specific energy [Wh kg ⁻¹]	150	100
Energy density [Wh L ⁻¹]	265	230
Maximum cut-off charge voltage [V]	4.2	4.2
Minimum cut-off discharge voltage [V]	3.0	2.0
Charge working temperature [°C]	0-40	0-40
Discharge working temperature [°C]	-20-55	-20-55
Maximum charge rate [C]	1	5
Maximum discharge rate [C]	2	20

Table 3. Parameters (electrode thickness, conductivity, density and specific heat capacity) used in the 3D thermal model [75-77].

Parameter	Cu foil	Negative electrode	Separator	Positive electrode	Al foil
<i>thickness, $l_{cell\ 1}^*$ (μm)</i>	15	65	35	75	20
<i>$l_{cell\ 2}^*$ (μm)</i>	15	37.5	35	24	20
<i>l_{Doyle} (μm)</i>	15	100	35	174	20
<i>$l_{cell\ 2_2}$ (μm)</i>	15	75	35	48	20
<i>$l_{cell\ 2_3}$ (μm)</i>	15	112.5	35	72	20
<i>$l_{cell\ 2_4}$ (μm)</i>	15	150	35	96	20
<i>k ($\text{W m}^{-1} \text{K}^{-1}$)</i>	398	5	0.334	5	238
<i>ρ (kg m^{-3})</i>	8930	2500	1009	1500	2702
<i>C_p ($\text{J kg}^{-1} \text{K}^{-1}$)</i>	385	700	1978	700	903

* Measured values

3.2 Mathematical Modeling

To study the electrochemical variable variation and heat generation at the electrode level and to view the total power dissipation density and temperature change at the battery level, a 1D electrochemical model and a 3D thermal model are developed and coupled, in which the heat generated from the 1D electrochemical model is applied to the 3D thermal model as the heat source, and meanwhile the average temperature of the 3D thermal model is, in turn, used as an input for the 1D electrochemical model during simulation.

Fig. 2.4a gives a typical schematic illustration for the 1D electrochemical model of a Li-ion cell, which involves five main regions: two current collectors (aluminum and copper

foil), positive composite electrode, negative composite electrode and separator. Typically, the electrode region is composed of a mixture of active insertion material particles, electrolyte, binder and conductive filler, while the separator consists of polymer and electrolyte. $\text{Li}_x\text{Mn}_2\text{O}_4$ and Li_yC_6 are used as the positive and negative material in this study, respectively. LiPF_6 salt in a non-aqueous liquid mixture of 1:2 v/v ethylene and dimethyl carbonate is employed as the binary electrolyte, which permeates in both separator and electrodes. Since the total number of current collectors in battery is half of the number of electrodes and separators, and electrochemical reactions take place on both sides of a current collector, the cell used in the 1D heat generation analysis is designed with the current collector of half the thickness of the actual current collector, thus greatly improving the rigorousness and conciseness of the model. And this modification has never been proposed before.

During the course of discharge, the Li-ions inside the solid Li_yC_6 particles move to the surface to react. Once being charged, these ions diffuse through the electrolyte and the separator to the positive electrode where they react and intercalate into the $\text{Li}_x\text{Mn}_2\text{O}_4$ particles. Simultaneously, the electrons produced in the above reactions leave the oxidized negative electrode and flow through the external circuit in the opposite direction of the current. The reactions occur during this process are given by:

where x and y are the number of moles of lithium ion involved in the electrode reaction.

The following gives a detailed explanation for the 1D electrochemical model, which combines and refines several relevant models developed in the literatures [4, 65, 69], as well as the 3D thermal model.

3.2.1 Electrochemical Model

First, in the binary electrolyte phase, the material balance is given by Fick's second law coupled with a source term:

$$\varepsilon_e \frac{\partial c_e}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c_e}{\partial x} \right) + \frac{(1 - t_+^0)}{F} j^{Li} \quad (5)$$

Since no mass flux of lithium ions exists at the boundary of electrode/current collector, the boundary condition for these sites yields:

$$-D \frac{\partial c_e}{\partial x} \Big|_{x=0} = -D \frac{\partial c_e}{\partial x} \Big|_{x=l_n+l_s+l_p} = 0 \quad (6)$$

On the interfaces of both anode/separator and separator/cathode, the concentration of electrolyte is continuous, that is:

$$c_e \Big|_{x=l_n^-} = c_e \Big|_{x=l_n^+} \quad (7)$$

$$c_e \Big|_{x=(l_n+l_s)^-} = c_e \Big|_{x=(l_n+l_s)^+} \quad (8)$$

Then the charge balance in the electrolyte phase based on Ohm's law is given by:

$$-\left(k^{\text{eff}} \frac{\partial \Phi_e}{\partial x}\right) + \frac{2RT(1 - t_+^0)}{F} \left(k^{\text{eff}} \frac{\partial (\ln c_e)}{\partial x}\right) = \mathbf{i}_e \quad (9)$$

where the effective ionic conductivity k^{eff} , calculated by $k^{\text{eff}} = k\varepsilon_e^{1.5}$, is the Bruggeman correction for the tortuosity effect. The value of k is dependent on the electrolyte material used. For the electrolyte consisting of LiPF_6 in a 1:2 volume ratio mixture of EC and DMC, it was found that [65]:

$$k = 1.0793 \times 10^{-4} + 6.7461 \times 10^{-3} c_e - 5.2245 \times 10^{-3} c_e^2 + 1.3605 \times 10^{-3} c_e^3 - 1.1724 \times 10^{-4} c_e^4 \quad (10)$$

A zero gradient boundary condition restricts the solution of Eq. (9) at the two electrode/current collector interfaces:

$$k^{\text{eff}} \frac{\partial \Phi_e}{\partial x} \Big|_{x=0} = k^{\text{eff}} \frac{\partial \Phi_e}{\partial x} \Big|_{x=l_n+l_s+l_p} = 0 \quad (11)$$

Next, in the solid phase of electrodes, the material and charge balance are respectively given by:

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right) \quad (12)$$

and

$$-\sigma^{\text{eff}} \frac{\partial \Phi_s}{\partial x} = \mathbf{i}_s \quad (13)$$

where the effective conductivity is determined by $\sigma^{\text{eff}} = \varepsilon_s \sigma$, where s refers to the positive

and negative electrodes. The boundary conditions for the solid electrode particle are:

$$\frac{\partial c_s}{\partial r} \Big|_{r=0} = 0 \quad (14)$$

$$-D_s \frac{\partial c_s}{\partial r} \Big|_{r=R_s} = \frac{j^{Li}}{a_s F} \quad (15)$$

where a_s denotes the solid electrode surface area per unit volume, which is calculated by:

$$a_s = \left(\frac{3}{R_s} \right) (1 - \varepsilon_e - \varepsilon_p - \varepsilon_f) \quad (16)$$

At the interface of current collector/electrode, the charge flux is the same as the current density applied on the electrode:

$$-\sigma^{\text{eff},n} \frac{\partial \Phi_{s,n}}{\partial x} \Big|_{x=0} = \sigma^{\text{eff},p} \frac{\partial \Phi_{s,p}}{\partial x} \Big|_{x=l_n+l_s+l_p} = \frac{I_{app}}{A} \quad (17)$$

While for the interfaces between the separator and electrodes, no charge flux exists:

$$\sigma^{\text{eff},n} \frac{\partial \Phi_{s,n}}{\partial x} \Big|_{x=l_n} = \sigma^{\text{eff},p} \frac{\partial \Phi_{s,p}}{\partial x} \Big|_{x=l_n+l_s} = 0 \quad (18)$$

The reaction current density j^{Li} in the above equations is determined by the Butler-Volmer equation:

$$j^{Li} = a_s k c_e^{0.5} (c_{s,max} - c_s)^{0.5} c_s^{0.5} \left[\exp\left(\frac{0.5F}{RT} \eta\right) - \exp\left(-\frac{0.5F}{RT} \eta\right) \right] \quad (19)$$

where k represents the product of the forward and backward rate constant, and the over-

potential of the intercalation reaction, η , is defined as:

$$\eta = \Phi_s - \Phi_e - U \quad (20)$$

where U is the open circuit potential, which is given by Taylor's first order expansion at a reference temperature (25°C):

$$U = U_{\text{ref}} + (T - T_{\text{ref}}) \left(\frac{dU}{dT} \right) \quad (21)$$

and the expressions for the open-circuit potentials of the cathode and the anode at 25°C are respectively given by:

$$\begin{aligned} U_{\text{ref},+} = & 4.19829 + 0.0565661 \tanh[-14.5546x + 8.60942] \\ & - 0.0275479 \left[\frac{1}{(0.998432 - x)^{0.492465}} - 0.190111 \right] \\ & - 0.157123 \exp(-0.04738x^8) \\ & + 0.810239 \exp(-40(x - 0.133875)) \end{aligned} \quad (22)$$

$$U_{\text{ref},-} = -0.16 + 1.32 \exp(-3.0y) + 10.0 \exp(-2000.0y) \quad (23)$$

while the temperature coefficients of the open-circuit voltage of the anode and the cathode are [78, 79]:

$$\begin{aligned} \frac{dU}{dT} = & 344.1347148 \times \frac{\exp(-32.9633287y + 8.316711484)}{1 + 749.0756003 \exp(-34.79099646y + 8.887143624)} \\ & + 0.2698001697 - 0.8520278805y + 0.362299229y^2 \end{aligned} \quad (24)$$

and

$$\begin{aligned}
\frac{dU}{dT} = & 4.31274309 \exp(0.571536523x) + 1.281681122 \sin(-4.9916739x) \\
& - 0.090453431 \sin(-20.9669665x + 12.578825) \\
& - 0.0313472974 \sin(31.7663338x - 22.4295664) - 4.14532933 \\
& + 8.14711343x - 26.064581x^2 + 12.7660158x^3 \\
& - 0.184274863 \exp\left(-\frac{x + 0.5169435168}{0.04628266783}\right)^2
\end{aligned} \tag{25}$$

All the parameters used in the electrochemical model are given in Table 4.

Table 4. Parameters used in 1D electrochemical model [65, 69].

Parameter	Negative electrode	Separator	Positive electrode
Particle radius, R_s (μm)	12.5	-	8.5
Solid phase Li-diffusivity, D_s (m^2/s)	3.9×10^{-14}	-	1×10^{-13}
Electrolyte volume fraction, ε_e	0.357	0.724	0.444
Polymer phase volume fraction, ε_p	0.146	0.276	0.186
Conductive filler volume fraction, ε_f	0.026	0	0.073
Maximum solid phase concentration, $c_{s,max}$ (mol/m^3)	26390	-	22860
Initial solid phase concentration, $c_{s,0}$ (mol/m^3)	14870	-	3900
Initial electrolyte concentration, c_e (mol/m^3)	2000	2000	2000
Particle film resistance, R_f (Ωm^2)	0	-	0
Solid phase conductivity, σ (Sm^{-1})	100	-	3.8
Li-ion transference number, t_+^0	0.363	0.363	0.363

3.2.2 Thermal Model

Conservation of energy for a Li-ion battery considering convection term and heat generation term can be expressed as:

$$\rho C_p \frac{dT}{dt} = \nabla \cdot (k \nabla T) + q_r + q_{rev} + q_j \quad (26)$$

where the three “ q ” s are the volumetric heat generation rate of different heat sources from the electrochemical model, i.e., reaction heat (q_r), reversible heat (q_{rev}) and ohmic heat (q_j):

$$q_r = \frac{\int_0^{l_n+l_s+l_p} j^{Li} (\Phi_s - \Phi_e - U) dx}{l} \quad (27)$$

$$q_{rev} = \frac{\int_0^{l_n+l_s+l_p} j^{Li} T \frac{\partial U}{\partial T} dx}{l} \quad (28)$$

$$q_j = \frac{\int_0^{l_n+l_s+l_p} \left[\sigma^{\text{eff}} \left(\frac{\partial \Phi_s}{\partial x} \right)^2 + k^{\text{eff}} \left(\frac{\partial \Phi_e}{\partial x} \right)^2 + \frac{2k^{\text{eff}} RT}{F} (1 - t_+^0) \frac{\partial (\ln c_e)}{\partial x} \frac{\partial \Phi_e}{\partial x} \right] dx}{l} \quad (29)$$

where l is the total thickness of the five components (anode, separator, cathode and two half current collectors) in the cell. In Li-ion battery, each current collector is generally shared by two adjacent reaction cells, therefore the thickness of the current collector used in simulation is half of its actual thickness.

At the surface boundary of the battery, convective cooling is considered:

$$-k \frac{\partial T}{\partial x} = h(T - T_{\text{amb}}) \quad (30)$$

where h refers to the convective coefficient and its value is set as low as $0.1 \text{ W m}^{-2} \text{ K}^{-1}$.

This simulates a condition with a very poor heat transfer rate (e.g., aerospace applications) and can lead to a dramatic temperature rise in batteries, which also facilitates a clearer inspection on the differences in temperature elevation between batteries.

The density, heat capacity and thickness of each component are used to determine the average values of the density and heat capacity of the entire battery:

$$\rho C_p = \sum_i \frac{\rho_i C_{p,i} l_i}{L_1} \quad (31)$$

where l_i is the thickness of the component i , and L_1 denotes the thickness of the entire battery. The thermal conductivity of the battery should be considered separately in different directions. As suggested by Fig. 1b, there exist series thermal resistors in x direction and parallel thermal resistors in y and z directions, therefore we define:

$$k_x = \frac{\sum_i l_i}{\sum_i \frac{l_i}{k_i}} \text{ and}$$

$$k_y = k_z = \sum_i \frac{l_i}{L_1} k_i \quad (32)$$

The associated specifications of the experimental and simulated cells are listed in Table 3.

4 Chapter: The Evaluation of the Impact of Electrode Thickness on the Electrochemical and Thermal Behaviors of Li-Ion Battery

4.1 Overview

Previous researches have experimentally revealed the disadvantages of battery assembled with thick electrodes [11, 18], but the results obtained were mainly from external perspectives, such as the energy density, capacity fading, and basically no efforts have focused on the variations of internal parameters, which are essential for the fundamental understanding of the limitations of battery with different thicknesses electrodes used. Meanwhile, many studies have verified the adverse effects that may accompanied with the battery operated in high temperatures [1, 2, 5]. Therefore, this chapter will investigate the impact of electrode thickness on the performances, both in electrochemical and thermal aspects, of Li-ion battery based on the experiment and simulation results.

4.2 Model Validation and Experimental Results

Fig. 4.1 compares the temperature curves of two experimental batteries under adiabatic condition in both the experiment and simulation of the 1 C discharges, and all the results from experiments are averaged from 3 repetitive tests. It can be seen that the results obtained from the developed models are well consistent with the data acquired from the experiment, which demonstrates the effectiveness of the coupling model in simulating the thermal response associated with the operation of Li-ion battery with different internal

parameters. Furthermore, the coupling model is also validated by comparing voltage and temperature results with published papers, which shows a great consistency.

Also, as shown, the temperature responses of the two batteries with different electrode thicknesses exhibit dramatic difference in both experimental and simulated results. At the end of discharge, the temperature of the battery with thick electrodes reaches 318 K, much higher than the battery with thin electrodes (306 K), and the temperature change during the discharge of Cell 1 is 2.5 times (20 K : 8 K) that of Cell 2, suggesting a worse thermal performance.

Figure 4.1. Temperature curves of Cell 1 and Cell 2 acquired from experiments and simulations under 1 C discharge rate.

Generally, batteries experience high temperature during discharge may suffer many adverse effects, such as reduction in life span and capacity utilization, increase in thermal instability and a series of other possible safety issues. Pesaran found that the best operating

temperature range for Li-ion battery is between 298 K and 313 K, and the desirable temperature distribution should be within 5 K [80]. Motloch et al. also reported the influence of high temperature on Li-ion batteries: the life span of Li-ion battery can be reduced by about two months for every degree of temperature rise in an operating range of 303 – 313 K [81].

To investigate the capacity fading of two batteries, both batteries are employed in life cycle tests at room temperature. The results given here are the ratios of obtained capacity to the initial capacity (normalized capacity) of the batteries discharged under two rates (0.5 C and 1 C) for 200 cycles. As shown in Fig. 4.2, Cell 1 fades much faster than Cell 2, with the fading rate for the first 100 cycles of $6.32 \text{ mAh cycle}^{-1}$, which is 7 times that of Cell 2 ($0.89 \text{ mAh cycle}^{-1}$). Then in the next immediate 100-cycle test at 1 C rate, the capacity fading rate of Cell 1 is almost 9 times higher than Cell 2, with the values of 7 mAh cycle^{-1} and $0.72 \text{ mAh cycle}^{-1}$, respectively. Other than the difference in capacity fading rate, the capacity loss in Cell 1 is much larger than Cell 2 when the current rate switches from 0.5 C to 1 C, which is due to the higher internal resistance of Cell 1. As shown in Fig. 4.3, the resistances of the batteries during the processes of discharge are compared. Because of the shorter diffusion distance for electrochemical reactions, Cell 2, with thin electrodes used, has a lower average resistance of 3 mOhm during discharge, compared to the average value of 10 mOhm for Cell 1 with thick electrodes.

Figure 4.2. Capacity fading curves of Cell 1 and Cell 2 under two operating rates, 0.5 C and 1 C.

Figure 4.3. Internal resistances of Cell 1 and Cell 2 at the 5th cycle of the 1 C discharges collected from battery analyzer.

Then, the mechanism of fading and the difference in fading rate of the two batteries

with different electrode thicknesses are studied, with the discharge curves at 1st cycle, 50th cycle, 100th cycle; 101st cycle, 150th cycle and 200th cycle collected for comparison. As shown in Fig. 4.4, for battery with thin electrodes (Cell 2), the 0.5 C discharge curves (1st, 50th, 100th cycles) basically overlap, so do the 1 C discharge curves (101st, 150th, 200th cycles). The negligible difference between these discharge curves at the same rate in different cycles indicates the stability of the electrochemical reactions with the proceeding of discharge and the barely aged active materials inside the electrodes. The gap between 0.5 C discharge curves and 1 C discharge curves is mainly due to the difference in IR drop caused by the difference of the discharge rate. However, for thick electrode battery (Cell 1), the discharge curves are different at the assigned cycles, and with the increase of cycle number, the discharge process stops earlier. The overlapping of the discharge curves at the initial stage of discharges is attributed to the invariant internal resistance, which is validated from the internal resistances collected from the analyzer during the cycle test. Therefore the capacity fading of Cell 1 started from the middle of discharges is probably not caused by the increase of the battery internal resistance, but is mainly attributed to the aging of active materials. And detailed analyses on the difference in capacity fading rate of two batteries will be provided later based on simulation results.

Figure 4.4. Comparison of discharge curves of a) Cell 1 and 2) Cell 2 at assigned cycles from experiments.

4.3 Simulated Thermal Behaviors of Two Experimental Batteries

Simulations are then performed on two experimental batteries based on previously

validated coupling model, from which the ohmic heat and the total heat generation of two batteries are collected and compared.

Ohmic heat source is aroused from the resistance of transportation of Li-ions during electrochemical reactions, which is closely related to the thicknesses of electrodes, as much more ohmic heat will be generated in battery assembled with thicker electrodes. It can be seen and validated from Fig. 4.5, where the ohmic heat generation rate of Cell 1 (Fig. 4.5a) is almost 10 times that of Cell 2 (Fig. 4.5b). Due to that fact that more Li-ions are flowed through the interfaces between electrodes and separator than other areas, more ohmic heat is generated at the separator/electrode interface, which has the adverse contribution to the even heat distribution inside the battery cell. Thus, the increase in ohmic heat will increase the overall thermal instability across the electrochemical cell, especially at the region close to the separator, as is evident in Fig. 4.6a (the total heat generation of Cell 1), which will finally result in the uneven fading rate across the electrodes and affect the performance and safety of the battery.

Figure 4.5. Simulated ohmic heat generation rates along the thicknesses of the battery cells with a) thick electrodes and b) thin electrodes during 1 C discharge.

The total heat, a combination of three heat sources, of these two simulated batteries are given in Figure 4.6. As can be seen, Cell 1, with thick electrodes used, generates more heat on the anode compared to Cell 2 using thin electrodes. This is mainly attributed to the difference in their electrode thicknesses as well as the ratios of the thicknesses of positive and negative electrode, which are directly related to the internal resistance and the reaction

current density of Li-ion battery, respectively. And both of these two factors can influence the generation rate of three heat sources. In addition, the distribution of heat generation rate in Cell 1 is more uneven than that in Cell 2, causing the fading of active materials along the electrodes exhibit different rates: the materials close to the separator fade faster than the materials at the interfaces between current collectors and electrodes.

By comparing the ohmic and total heat generations in two cells, the thermal (temperature) and electrochemical (capacity fading and discharge curves) differences between the cells can be explained. The difference in the temperature response of two cells (Fig. 4.1) is due to their different heat generation rates. The faster aging rate and split of discharge curves in cycle test for Cell 1 (Fig. 4.2 & Fig. 4.4a) is mainly attributed to its more intensive temperature response as well as the uneven heat distribution across its electrodes, which can lead to fast aging of active materials. Whereas the invariant internal resistance, slight temperature change and even heat distribution in Cell 2 bring about its overlapping discharges curves and slight capacity fade at different rates in the cycle test.

Figure 4.6. Simulated total heat generation rates for the battery cells with a) thick electrodes and b) thin electrodes during 1 C discharge.

4.4 Simulated Electrochemical and Thermal Behaviors of Batteries at High Rate

As known, Li-ion battery typically perform worse at higher discharge rate, both in electrochemical and thermal perspectives. To investigate the impact from the electrode thickness solely, excluding the influence caused by the ratio of positive and negative electrode thicknesses, simulated 8 C discharge process is carried out on Cell 2, Cell 2_2

(twice the electrode thickness of Cell 2), Cell 2_3 and Cell 2_4.

Fig. 4.7 compares the simulated discharge curves of the four batteries, and it can be seen that with the increase of electrode thickness, cells experience early stops of discharge. For Cell 2_4, the discharge only lasts 330 s, much shorter than the 420 s of Cell 2, and the capacity Cell 2_4 obtained during the discharge process is only 73.3 % of its nominal capacity, which is much lower than the 93.3 % for Cell 2. On top of that, during the whole period of the discharge, the voltage of Cell 2 is higher than that of other cells, which ensures a sufficient power supply and stability in real applications.

Figure 4.7. Simulated discharge curves of Cell 2, Cell 2_2, Cell 2_3 and Cell 2_4 at 8 C rate.

As an important indicator to the degree and smoothness of the electrochemical reactions taking place inside Li-ion battery, the Li-ion concentration at the surface of solid particles are depicted along the electrochemical cell in Fig. 4.8. As the electrodes become thicker (in Cell 2_4), the distribution of Li-ion concentration along both electrodes

becomes uneven, demonstrating that the insertion reactions take place in different depths and the active particles are utilized to different degrees across the cell. This can trigger uneven heat distribution along the cell, which is detrimental to the health of the battery [82, 83]. While on the contrary, Li-ion concentration is evenly distributed with a value of 4000 mol m^{-3} on the negative electrode of Cell 2 even at the end of discharge.

In addition, the ratios of Li-ion concentration to the maximum concentration on the positive electrodes of two batteries are presented in Fig. 4.9. It can be seen that since the discharge process stops early, the average ratios of Cell 2_4 at the assigned time points are lower than that of Cell 2, which indicates the underutilization of the active materials in the positive electrode of Cell 1. Moreover, due to the concentration polarization as well as the diffusion limitation, the distribution of the ratio along the positive electrode is uneven. However, in Cell 2, because the electrodes employed are thinner, the utilization of active materials in positive electrode at the end of discharge reaches 0.97, much higher than the utilization of Cell 1, and the distribution of the ratio for Cell 2 is uniform at all the selected time points, which suggests fluent electrochemical reactions and also ensures a high power and capacity output.

Figure 4.8. Simulated Li-ion concentrations at the particle surfaces of a) Cell 2_4 and b) Cell 2 during 8 C discharge at assigned time points.

Figure 4.9. Utilization of active materials in the positive electrode of a) Cell 2_4 and b) Cell 2 from simulation.

Furthermore, the influences of electrode thickness on the overpotential and electrolyte potential of Li-ion batteries (Cell 2 and Cell 2_4) are investigated through simulation, as they are inherent to the irreversible heat and the ohmic heat as indicated in Eqs. (1) and (3), respectively. The difference of electrolyte potential profiles at the beginning and at the end of the discharge stage is also of interest due to its intrinsic relevance to the concentration

polarization, which can result in underutilization of the electrodes' charge-storage capability and therefore often be regarded as a significant contributing factor in the performance degradation of Li-ion battery.

Considering that only the slopes of the curves and the difference between two curves are concerned, the electrolyte potential curves have been arbitrarily taken to equal to zero at the center of the separator (Figure 4.10). It can be observed that the electrolyte potential in Cell 2 remains almost unchanged during the discharging period, which suggests a small concentration polarization. As the electrodes become thicker, the gradient of concentration grows larger and the ohmic drop goes higher, thereby the polarization effect imposed by the concentration difference across the cell becomes larger. For Cell 2_4, the electrolyte potential drop across the cell is initially around 0.3 V and increases to 0.75 V at the end of discharge, which is induced by the development of concentration gradient and the penetration of the reaction front into the cathode, and will further cause the growth of ohmic heat generation during discharge.

Figure 4.10. Comparison of the overpotential (10 s) with the electrolyte potentials at the beginning, 10 s, and the end, 330 s and 420 s for a) Cell 2_4 and b) Cell 2, respectively, of discharging.

Fig. 4.11 shows the ohmic heat generation rates of the cells at 8 C discharging rate. As a result of the concentration polarization and the long diffusion distance, the contribution of ohmic heat to the total heat as well as the value of ohmic heat dramatically increases in Cell 2_4. As shown, the maximum ohmic heat generation of Cell 1 reaches more than $5 \times 10^5 \text{ W m}^{-3}$, about three quarters of the maximum total heat (shown in Figure 4.12).

Moreover, due to the high proportion of ohmic heat, Cell 2_4 also experiences uneven heat distributions during the discharging period. Whereas in Cell 2, although the ohmic heat generation at 8 C is more than 60 times that of the cell discharged at 1 C rate, due to its low internal resistance, the share of ohmic heat to the total heat is still insignificant (approximately 10 %) as compared to the other two heat sources. Thus, the overall heat distribution is much flatter in Cell 2 than that in Cell 2_4, which will benefit the cycle life and wellbeing of the battery.

Figure 4.11. Simulated ohmic heat generation rates of a) Cell 2_4 and b) Cell 2 at assigned time

points during 8 C discharges.

Figure 4.12. Simulated total heat generation rates of a) Cell 2_4 and b) Cell 2 at assigned time points during 8 C discharges.

As a result of the higher heat generation rate, the temperature of Cell 2_4 at the end of the 8 C discharge is as high as 347 K, as shown in Fig. 4.13, much higher than that of the Cell 2, 315 K. Such a high temperature in Cell 2_4 has the potential to trigger safety issues,

e.g. thermal runaway, and must be avoided during real applications. Therefore, a thermal management system should be equipped with the battery, either in an active way [84] or a passive way [85-87].

Figure 4.13. Simulated temperature curves of Cell 2, Cell 2_2, Cell 2_3 and Cell 2_4 from the 8 C discharge simulations

4.5 Summary

The experimental results, and simulation results from the coupling model together illustrate the influence of electrode thickness on the performance of Li-ion battery in both the electrochemical and thermal perspectives in this chapter. And the coupling model implemented in this chapter is validated through the comparison of the temperature curves obtained from experiments with that from the simulation results.

Through the work represents in this chapter, it is known that although battery

assembled with thick electrodes can increase the proportion of active materials and thus increase the energy density, the adverse effects imposed by the thick electrodes on both the thermal (temperature, heat generation and distribution) and electrochemical performance (voltage curve, polarization and capacity fading) of Li-ion battery should arouse special attention.

5 Chapter: The Evaluation of the Impact of Initial Electrolyte Salt Concentration on the Performance of Li-ion Battery

5.1 Overview

As an important parameter, initial electrolyte salt concentration also plays a crucial role on the operation of Li-ion batteries, from both the thermal and electrochemical perspectives. Since previous research works seldom investigate the impact from the initial electrolyte salt concentration on the performance of Li-ion battery, and different initial salt concentrations have been used in different Li-ion battery models without giving a reasonable explanation [4, 65-67], this chapter will elaborate the differences in the performances of batteries with different initial electrolyte salt concentrations, 1000 mol m^{-3} , 1500 mol m^{-3} and 2000 mol m^{-3} for Cell #1, Cell #2, (different from the Cell 1 and Cell 2 in Chapter 4) and Cell #3, respectively, from both the charging and discharging perspectives based on my previous published work [56]. The thermal and electrochemical parameters of the three cells used in simulations are listed in Table 3 and 4 except the initial salt concentration values, and the thicknesses of electrodes are from Doyle's model as indicated by l_{Doyle} in Table 3.

5.2 Charging Process

During the charging course, Li-ions migrate from the cathode (positive electrode) to the anode (negative electrode) and the electrons move through the external circuit to the anode to complete the electrochemical reaction. In simulation, all the three cells are

involved in 2C (3.5 A m^{-2}) and 4C (7 A m^{-2}) galvanostatic charge processes and the differences in selected electrochemical properties caused by the different electrolyte salt concentrations are discussed in the following section.

5.2.1 Simulated Results and Discussion

First, the charge curves of Cell #1-3 under 4 C charge rate are compared in Fig. 5.1. It can be seen that the cells with different initial electrolyte salt concentrations have very different charging responses during the entire charge course, although their voltage increases in the first few seconds are similar, which is due to the comparable ohmic overpotential. Among these three cells, Cell #1, as indicated by the blue line in Fig. 5.1, takes the shortest charging time (150 s) and yields the steepest charging curve, suggesting an unstable electrochemical reaction taking place and an incomplete utilization of the active material, i.e., a low capacity obtained from charging. In contrast, the charge process for Cell #3 lasts as long as 750 s until the voltage reaches 4.5 V and the overall voltage curve is more stable compared to the other cells. Cell #2 with the moderate salt concentration performs medially, with a stop voltage of 4.4 V and a charging time of 500 s.

Figure 5.1. Simulated voltage curves of Cells #1-3 with different initial salt concentrations during a 4 C galvanostatic charge course.

The electrolyte salt concentrations along the cells at the end of the 4 C charge course are shown in Fig. 5.2. As can be seen, in Cell #1 (with the lowest initial concentration, 1000 mol m^{-3}), a great portion of the anode has a zero salt concentration at 150 s, which indicates not only a low conductivity of the electrolyte but also an early stop of the charge, and this can be explained through the reaction mechanism of the charging battery. During the charge process, the right region of the anode is filled with the Li-ions coming from the cathode prior than the left part. Once the right region is fully intercalated, the Li-ions need to move further to the left to complete the electrochemical reaction. However, as the charge proceeds, the electrolyte salt concentration at the left region of the anode tapers to 0 due to the concentration polarization, the diffusion of Li-ion from right to left is then constrained, which finally leads to the early stop of the charge process. With a 500 mol m^{-3} greater initial salt concentration, Cell #2 can be charged for 500 s before the salt concentration on

the left part of the anode drops to zero, thereby increasing the charge capacity. As for Cell #3, the electrolyte salt concentration at the left of the anode still remains 200 mol m^{-3} at the end of charge, which ensures a longer charge time and higher capacity.

Figure 5.2. Simulated electrolyte salt concentrations along the cells with different initial salt concentrations at the end of charge.

The ratio between the average and maximum Li-ion concentration in the active material solid particles is another important electrochemical parameter that implies the depth and stability of the electrochemical reaction across an electrode. A higher value of this ratio indicates a smoother insertion of Li-ions into the active material particles. Since the anode is the receiver of lithium ions during the charge process, the Li-ion concentration ratio for the anode particles should be of particular concern. Fig. 5.3 gives the ratios along the anodes of the three cells with different initial electrolyte salt concentrations. As shown, Cell #3 has the highest ratio curve among all the cells and the value varies slightly from

0.42 to 0.55, which demonstrates an evenly distributed reaction depth and therefore a uniform lithiation reaction across the anode. For the other two cells, however, the ratio profiles are much lower and the ratio values along the anodes of Cell #1 and Cell #2 increase from 0.096 to 0.15 and from 0.18 to 0.45, respectively. The low ratio for Cell #1 indicates a poor utilization of the active materials in the anode particles, while the great variation of the ratio along Cell #2 reflects an insufficient supply of Li-ions at the end of charge.

Figure 5.3. Simulated ratio of the average to maximum Li-ion concentration in negative electrode particles at the end of charge.

Finally, the capability of the cells to prevent the anode from lithium plating (Li-plating) is studied. Li-plating has been widely reported for generating numerous adverse effects on the health of Li-ion battery [88, 89]. The so-called dendrite growth on the interface between the anode and the separator can lead to internal short-circuit and pre-mature failure of the

battery. Meanwhile, Smart and Ratnakumar [90] claimed that the presence of metallic Li on the anode generally induces further degradation in the anode/electrolyte interface, and the Li metal is known to be very reactive towards electrolytes. In view of numerous existing literatures based on both experimental trials and theoretical studies, it is reasonable to conclude that Li-plating can pose a serious threat to the safety and reliability of the Li-ion battery.

Generally, the potential difference between the solid particles of anode and the electrolyte can reflect the likelihood of the occurrence of the lithium plating, and a sub-zero value indicates the ability to react. Since the front of the anode (right end in the figure) is filled with lithium ions earlier than the back (left end in the figure), if plating of lithium were to occur, it would be expected to occur at the anode/separator interface first. In Fig. 5.4, the potential differences are plotted along the anodes of the cells at 150 s when Cell #1 stops charge due to the zero concentration. Although the potential differences (also called anode potential) in all the cells are higher than zero, the curve for Cell #1 greatly drops by 0.95 V across the anode, while Cell #2 and Cell #3 only experience slight decreases of 0.17 V and 0.1 V, respectively. The potential difference at the right end of the anode of Cell #1 does not reduce to 0 due to the early stop of the simulation, but in real case, the charge process could be continued through the control system of a charger or tester, therefore the lithium plating would probably occur. To verify this possibility, a simulated 2 C galvanostatic charge, instead of 4 C, is carried out with all the cells. As shown in Fig. 5.5, at 1650 s, negative potential differences can be observed at the right part of the anode for Cell #1 and Cell #2, while for Cell #3 with the highest initial salt concentration, the potential difference still remain positive at the anode/separator interface.

Figure 5.4. Simulated potential differences between active solid particles and electrolyte across the anodes of Cell #1-3 under 4 C galvanostatic charge at 150 s.

Figure 5.5. Simulated potential differences between active solid particles and electrolyte across the anodes of Cell #1-3 under 2 C galvanostatic charge at 1650 s.

To prevent the Li-plating phenomenon and the early stop of the charging process, an increase of the ratio between the anode thickness and the cathode thickness is performed. In simulation, the thickness of the cathode is adjusted from 0.174 mm to 0.1 mm, which is the same with the anode, thus the thickness ratio increases from 0.575 to 1. To clearly depict the effect of this change on the charge process, the voltage curves of three adjusted cells under 7 A m^{-2} charge course are drawn in Fig. 5.6. As can be seen, by increasing the ratio, the charge time for Cell #3, which has the highest initial salt concentration, reduces from 750 s to 520 s, and this can be mainly attributed to the loss of active materials in the cathode, i.e., less Li-ions are available in the cell to react. For the modified Cell #2, interestingly, the charge curve almost overlaps the curve of Cell #3, which indicates a sufficient utilization of the active materials and a weaker impact of the initial electrolyte salt concentration on the performance of the cell. Although the Cell #1 after being modified is still the cell that undergoes the fastest charge process, its improvement compared to the original cell is obvious, provided that the charge time increases dramatically (40%) from 150 s to 210 s and the maximum voltage also rises from 4 V to around 4.2 V.

Figure 5.6. Simulated voltage curves of adjusted Cells #1-3 with different initial salt concentrations during a 7 A m^{-2} galvanostatic charge course.

To clearly illustrate the improvement of the capabilities of the adjusted cells to prevent the Li-plating at the end of the charging process, the anode potentials vs. (Li^+/Li) of the three cells under 3.5 A m^{-2} (2 C) charge course are presented in Fig. 5.7. As shown, all of the three cells are kept out from reaching a negative potential vs. Li^+/Li at the end of charge, which suggests that the Li metal is unable to form on their anodes. Improved performance can also be indicated by the potential variations across the anodes. Cell #1, the most possible cell to suffer the Li-plating, has a potential difference variation of 0.23 V along the entire anode with the original electrode geometry, whereas the value decreases to 0.13 V after changing the thickness ratio of the electrodes.

As evident from the charge curves, Fig. 5.6, and the anode potential curves at the end of charge, Fig. 5.7, the cells with adjusted thickness ratio show better performances on both the charge process and the Li-plating prevention when compared with the original cells.

This is mainly due to the decrease of the amount of Li-ions which will insert into the anode particles. When thinner cathode is used, the anode capacity utilization will be correspondingly lower, resulting in a decrease in the range of the stoichiometric coefficient, x , for the anode material, Li_xC_6 . The anode open-circuit potential is expressed in Eq. (23), and the corresponding curve for the anode potential at different states of charge is depicted in Fig. 5.8. As shown, at the fully charged state, where x is close to 0.7 in this figure, the anode open circuit potential approaches 0, which has the probability to cause the Li-plating. From simulation results, the value of x in the original Cell 1 reaches 0.75 at the anode/separator interface at the end of 2 C charge, much higher than the cell with adjusted cathode thickness, whose final value of x is 0.56, which explains the ability of adjusted cell in preventing the Li-plating.

Figure 5.7. Simulated potential differences between active solid particles and electrolyte across the anodes of adjusted Cell #1-3 under 3.5 A m⁻² galvanostatic charge at 1120 s.

Figure 5.8. The open-circuit potential of Li_xC_6 as a function of state of charge relatively to the potential of solid lithium.

5.3 Discharging Process

After investigating the impact of initial electrolyte salt concentration on the performance of Li-ion battery during the charging courses, this section mainly focusing the impact on the discharging course, specifically, on the thermal and electrochemical behaviors of Li-ion battery during discharging courses with different initial salt concentrations.

The relationship between the electrolyte conductivity and the salt concentration is given by Eq. (10), and the correlation of these two variables is plotted in Fig. 5.9. It can be observed that in the range from 0 to 4000 mol m^{-3} , the value of electrolyte conductivity peaks at around 1000 mol m^{-3} while tends to 0 at both ends which is believed to be due to the zero concentration effect and the solubility problem at high concentrations. This

correlation will be used in the following analyses on the electrochemical and thermal behaviors of Li-ion cells with different electrolyte salt concentrations.

Figure 5.9. Correlation between electrolyte salt concentration and electrolyte conductivity

5.3.1 Simulated Results and Discussion

As an overview, Fig. 5.10 shows the end-of-discharge electrolyte salt concentration curves across the cells with various initial concentrations, namely 1000 mol m⁻³, 1500 mol m⁻³ and 2000 mol m⁻³. The horizontal axis does not include the current collectors, and so do the following diagrams. As can be seen, the lower the initial salt concentration is, the higher tendency the concentration tapers down to 0 at the interface between the cathode and the current collector at the end of discharge. While at the anode/current collector interface, the highest concentration (4600 mol m⁻³) is obtained in the cell with the highest initial salt concentration. Both of these phenomena are attributed to the Li-ion diffusion

limitation in the electrolyte, and can impact the performance of Li-ion battery from the electrochemical and thermal aspects. Meanwhile, it is seen that the variation of the electrolyte concentration on the separator is smaller than that in both anode and cathode. This is due to the Li-ions in both electrodes are involved in the electrochemical reaction, where the ions are produced or consumed, which increase the variation of concentration across the electrodes. While no reaction occurs in the separator region, therefore a relatively smaller gradient can be seen.

Figure 5.10. Simulated electrolyte salt concentration curves at the end of discharge for cells with 1000, 1500 and 2000 mol m⁻³ initial electrolyte salt concentrations.

As a significant representation of the performance of a Li-ion battery system, the voltage curves of different cells are given in Fig. 5.11. It should be noted that all the cells stop discharging at about 220 s, far less than the ideal discharging time for the 8C process (450 s). This is due to the fact that the ideal discharging time is determined only based on

the C rates, with the discharging time under 1C rate of 3600 s, however, in real cases, the increase in the discharge rate will exacerbate the ohmic drop ($I \times R$) and the polarizations, which can lead to the early stop of the discharge. As shown in Fig. 5.11, the initial potential drop of Cell 1 is as high as 0.6 V (from 4.2V to 3.6 V), and the cell with the highest initial salt concentration has a relatively higher potential drop than the other two cells due to the higher internal resistance.

Among the three cells, the cell with 1500 mol m^{-3} initial salt concentration has the most stable voltage curve during the discharge period compared to the others, indicating a higher power output and a better stability of the internal electrochemical reactions. Cell with the lowest initial salt concentration has a relatively higher output voltage before 150 s, which is due to the smaller ohmic drop during that period, but suffers a dramatic drop in the voltage at the end of discharge as a result of the premature stop of the electrochemical reaction. While for the cell with the highest initial salt concentration, the voltage curve is relatively lower than the others during the major course of discharge due to the lower salt conductivity, but in the end the cell outperforms the cell with lowest electrolyte concentration thanks to the non-zero concentration.

Figure 5.11. Simulated voltage curves of the cells with different initial electrolyte salt concentrations during 8C galvanostatic discharge.

In the thermal perspective, Fig. 5.12 presents the average heat generation rates of the cells. As shown, the cell with 1000 mol m^{-3} initial electrolyte concentration exhibits the lowest heat generation rate at first due to its high electrolyte salt conductivity. However, a rapid increase of the curve can be observed from 170 s owing to the zero salt concentration at the positive electrode, which corresponds to a low solution conductivity. Compared with Cell 1, the heat generation rates of the other two cells increases more steadily during the whole discharge period on account of the non-zero salt concentration across them. However, the cell with 1500 mol m^{-3} initial salt concentration generates less heat than the 2000 mol m^{-3} one due to the higher overall salt conductivity.

Figure 5.12. Simulated average heat generation rates of the cells with different initial salt concentrations.

To further elaborate the thermal issues accompanied with the cells during the galvanostatic discharge course, the total heat generation rates of the cells are depicted in Fig. 5.13 at different depths of discharge. As can be seen, the cell with the lowest initial electrolyte salt concentration shows a weaker exothermic behavior on the anode and a stronger and more unstable behavior on the cathode as compared to the other ones, especially at the end of discharge. It is also noticeable that the total heat generation rate varies dramatically at the left region of the cathode at 200 s. The instability and non-uniformity can be accounted for by the zero concentration of the electrolyte at the right part of the cathode, which results in all the currents as well as the electrochemical reactions being undertaken by the rest part of the cathode where the supply of lithium ions is sufficient, thus leading to a large amount of heat being generated at the left region. As the initial electrolyte salt concentration goes higher (Fig. 5.13b &c), more heat is generated by

the anode than by the cathode due to the higher salt concentration at the anode, which results in a lower conductivity.

Figure 5.13. Simulated heat generation rates at different depths of discharge across the components in cells using different initial electrolyte salt concentrations: a) 1000 mol m^{-3} , b) 1500 mol m^{-3} and c) 2000 mol m^{-3} .

In order to determine the contribution of three heat sources on the total heat generation, Fig. 5.14a, b and c separately depict the heat generation rate of irreversible heat source, reversible heat source and ohmic heat source in Li-ion batteries using different initial electrolyte salt concentrations at 100 s and 200 s.

In the irreversible heat diagram, the heat generated from the anode is almost unchanged when different concentrations are used or as the discharge proceeds. Knowing that during discharge the Li-ions diffuse from the center of the electrode solid particles to the surface to react and then transfer from the solid phase to the electrolyte phase, the conductivity of electrolyte, and hence the electrolyte concentration, has no significant influence on the electrochemical reaction on the negative electrode, therefore the irreversible heat generation remains fairly constant at the anodes of the three cells. As for the cathode, however, great variations are observed at the end of discharge (200 s) for all the cells, especially the one with 1000 mol/m^3 initial electrolyte salt concentration. According to Fig. 5.10, the salt concentration of this cell finally drops to zero at the right part of its cathode, which undoubtedly restricts the transport of Li-ions and hence shuts down the reactions at that region, as revealed by the zero reaction heat generation rate at the right of the cathode. Whereas at the left part, more and more Li-ions are gathered. With continuous electrons produced by the anode reaction and transported from the external circuit to the reaction region (left part of the cathode), all the electrochemical reactions in cathode take place at this region, thus the reaction heat and reaction current density here markedly increase. Comparably, cells with higher initial salt concentrations have flatter irreversible heat generation curves across the cathodes.

Similar pattern can be observed in the reversible heat source profile. As is the case of the irreversible heat, the reversible heat is also linked with the reaction current density, and the battery with the lowest initial salt concentration can produce a high current density during the electrochemical reaction at the left region of its cathode, leading to a relatively high reversible heat generation rate in this region. Moreover, the fluctuating heat generation across the cathode and the difference of the reversible heat generated on the anodes at two assigned time points are mainly attributed to the changes in the value of $\partial U/\partial T$ at different depths of discharge.

Rather than showing a good stability in the anode heat generation as the irreversible heat and reversible heat do, the ohmic heat source exhibits a very different generation profile on the anode when different electrolyte concentrations are employed or when measured at different time points, i.e., 100 s and 200 s. As shown in Fig. 5.14c, more heat is generated in the cell with higher initial salt concentration or being discharged for a longer time (at 200 s). The explanation could be based on the fact that the low electrolyte conductivity in cell with high initial salt concentration limits the motion of Li-ions on the anode, and thus leading to an increase in ohmic heat generation during the course of discharge, especially at the last period. While on the cathode, the difference in heat generation of different batteries is small, and this can be attributed to the specific process of the electrochemical reactions. During intercalation, the left part of the cathode receives the Li-ions first and hence is the prioritized region for them to react and insert, thus less Li-ions move forward, resulting in that the ohmic effect on the cathode decrease gradually as towards the right side. Meanwhile, considering the thickness of cathode is greater than anode in the simulation, although the salt concentration at the right side of cathode drops

down to zero, the concentration at its left side is high enough for ions transportation (see Fig. 5.10). Even for the battery using the lowest initial electrolyte concentration, the final concentration reaches 1000 mol/m^3 at the left end of cathode, which is corresponding to the highest conductivity shown in Fig. 5.9. As a result, the heat generation arise from the transportation of ions on the cathode varies slightly.

The combination of the three heat sources can give a clear explanation on the previously discussed average heat generation rates and total heat sources. Because both the irreversible and reversible heat change much slighter than the ohmic heat on the anodes, the difference in the total heat generation on the anode among the cells can be mainly attributed to the ohmic heat source, which also explains the higher average heat generation rate in cell with higher initial salt concentration except at the end of discharge. By contrast, the ohmic heat on the cathodes remains more stable than the other two sources due to the different mechanisms of heat generation. The great increase in heat generation rate of the cell with lowest initial salt concentration at the end of discharge is mainly owing to the irreversible and reversible heat which are associated with the reaction current density.

Figure 5.14. Comparison of a) irreversible heat, b) reversible heat and c) ohmic heat in three simulated cells with different initial salt concentration at two selected time points (100 s and 200

s).

As a consequence of the difference in the heat generation rates, the temperature elevation in each cell also yields different patterns. From the temperature response curves shown in Fig. 5.15, it can be seen that the cells with the lowest and medium initial salt concentrations have nearly identical temperature response attributed to the similar heat generation rate, except the fact that the temperature curve of the cell with the lower initial salt concentration stops at around 210 s due to the early stop of the discharge, and the high heat generation rate at the end of discharge cannot be immediately reflected by the temperature curve because of the long response time. As for the cell with the highest initial salt concentration, a similar trend with its heat generation curve is followed, and its temperature is higher than the other two cells during the entire course of the discharge.

Figure 5.15. Temperature curves of the cells with different initial salt concentrations during discharge.

Finally, the diagram of the interrelationship between the initial electrolyte salt concentration and the thermal (three heat sources) and electrochemical behaviors (voltage curve and the reaction current density) of Li-ion battery are summarized in Fig. 5.16. With improper concentrations of electrolyte used in Li-ion battery, due to the diffusion limitation, battery may suffer from the zero concentration or high concentration problem under high rate discharges. Both of too high or too low salt concentration in electrochemical cell can lead to a low electrolyte conductivity, which will increase the resistance of electrolyte and eventually result in the rise of ohmic heat. While the zero concentration may occur in battery with low initial electrolyte salt concentration, and it can make the supply of Li-ions unable to catch up with the electrochemical reactions taken place inside the battery and lead to the early stop of discharges and the variation of reaction current density. Moreover, the distribution and generation rate of reaction heat and the reversible heat, which are close related to the reaction current density, may have a dramatic change when a zero electrolyte salt concentration emerged in the electrochemical cell.

Figure 5.16. Interrelationship between the electrolyte salt concentration and the electrochemical and thermal properties of Li-ion battery.

5.4 Summary

This chapter elaborates the influences of initial electrolyte salt concentration on the electrochemical and thermal behaviors of Li-ion battery during both the charging and discharging processes. A low initial electrolyte salt concentration is not recommended for both the charge and discharge because it may lead to an early stop of electrochemical reactions, high probability of lithium plating and the uneven heat distribution, etc. While the high initial electrolyte salt concentration is not suitable for high rate discharges due to the fact that battery may experience a relatively high temperature during the operation, which has the adverse effects on the wellbeing and performance of battery during the life cycle.

6 Chapter: Conclusion and Future Work

6.1 Conclusion

In this thesis, both the experimental work and numerical simulations are provided to show the impact of internal parameters on the performance of Li-ion battery. The coupling model used in this thesis is also generalized to other Li-ion battery or battery packs with different specifications and parameters used, and accurate results can be obtained by simply varying the input parameters and initial values of the coupling model.

Based on experimental results, and simulation results obtained from validated coupling models, the impacts from the electrode thickness and initial salt concentration on the thermal (temperature, total heat generation, different heat sources, etc.) and electrochemical (voltage, Li-ion concentration, overpotential, etc.) behaviors of Li-ion battery are investigated in this study and are summarized as below:

1. Although battery assembled with thick electrodes can increase the proportion of active materials and thus increase the energy density, the adverse effects imposed by the thick electrodes on the thermal and electrochemical performances of Li-ion battery should arouse special attention.
2. Under same discharge rates, battery with thicker electrodes has more intensive and uneven temperature response across the electrochemical cell, wherein the ohmic heat takes the main responsibility for the uneven heat distribution due to its heat generation mechanism. Both of the two factors can lead to the depletion of active materials and fast capacity fading of the entire battery.
3. Due to the longer diffusion distance, and more serious concentration polarization,

thicker electrode battery has relatively higher internal resistance, which can result in a lower power output and an earlier stop of discharge compared to battery assembled with thinner electrodes, especially at high rates.

4. With the increase of discharge rate, the contribution ohmic heat made to the total heat becomes bigger, especially in thick electrode battery, and this will finally deteriorate the health of Li-ion battery.

5. Due to the diffusion limitation, the electrochemical reactions are unevenly taking place inside the cell with thick electrodes, particularly under high rates, which will not only lead to the underutilization of active materials, but will also increase the thermal instability of Li-ion battery and result in early stop of discharging processes.

6. The cell with the lowest initial salt concentration ends the charge and discharge prematurely as a result of the zero concentration on the anode and cathode, respectively, while the cells with higher initial salt concentrations can last longer in the charge and discharge processes.

7. As far as the electrochemical reactions during charging process are concerned, the Li-ion intercalation in the cell with lower electrolyte salt concentration takes place more non-uniformly and incompletely than the other cells.

8. The low initial salt concentration cell has a higher risk for lithium plating at the end of charge, especially at the interface between the anode and the separator, which can destroy the health and threaten the safety of the battery.

9. By varying the ratio of anode and cathode thicknesses, the Li-plating inside Cell 1 can be theoretically well controlled, and the performance of the charging process can be significantly improved.

10. The cell with the lowest electrolyte salt concentration has the lowest heat generation rate except at the end of discharge, while the highest concentration cell generates more heat than the others throughout the discharge period.

11. The irreversible and reversible heat contribute most to the high heat generation rate at the end of discharge for the cell with the lowest initial salt concentration, while the ohmic heat mainly determines the high heat generation rate of the cells with 1500 and 2000 mol/m³ initial salt concentrations in major period of the discharge.

12. In terms of the individual electrodes, as the electrolyte concentration increases, more heat is generated at the anode, while less heat is generated at the cathode.

6.2 Future Work

The future works should be conducted in the following subjects:

- 1) More experimental works will be involved in by assembling batteries with different internal parameters and compared with the simulation in both the short term and long term performances.
- 2) The model used in simulation will be improved with faster calculation time and more accurate results.
- 3) Influences from other internal parameters on the performances of Li-ion battery will be investigated.
- 4) Real time control of Li-ion batteries/packs during applications relying on the coupling model will be studied.

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