



Electrolyte conditions in lithium-ion batteries in presence of a thermal gradient

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Abstract

Heat release within a Li-ion battery is a significant safety concern. If the temperature rises above a certain threshold, secondary chemical reactions begin with potential thermal runaway outcomes. This work investigates spatially dependent electrolyte conditions in the presence of a thermal gradient to produce an electrolyte-centric thermal runaway model in the absence of passage of electrical current. Li ions, momentum, and thermal flux are the main components of the analysis, which accounts for free convection within the electrolyte. Numerical simulation techniques are used for this purpose. The model shows that hot spots can be found at the interface between the anode and the liquid electrolyte. The temperature trends are in line with previous thermal models for an entire Li-ion cylindrical battery. A thorough comprehension of the transport processes inside the battery contributes to mitigate damage induced due to thermal abuse conditions.

Introduction

Heat release within a lithium-ion (Li-ion) battery is a significant concern to maintain proper battery operation and avoid safety hazards. Most charging and discharging redox reactions have their optimum performance at relatively mild temperature conditions, while these reactions usually decrease in efficiency at low and elevated temperatures. If the temperature rises above a threshold of about 80 °C, secondary chemical reactions begin [1, 2]. The first undesired reaction to occur is the solid electrolyte interface (SEI) layer decomposition. Then, at higher temperatures, the electrolyte solution can potentially react with the intercalated Li in the anode. Active cathode material decomposition and electrolyte decomposition may also occur at even higher temperatures.

Richard and Dahn analyzed the thermal stability of the SEI layer in contact with different electrolyte solutions [1]. Their experiments obtained some kinetic and thermodynamic parameters of the reaction, such as activation energy, pre-exponential factor, and specific heat released due to the reaction. According to their results, the decomposition occurs from 80 to 120 °C [2], with a maximum reaction rate at temperatures about 100 °C [3]. The reaction is exothermic, and the main product is Li_2CO_3 , a stable compound of the SEI layer. Hatchard et al. [4] formulated the heat released through the SEI decomposition reaction ($Q_{\text{SEI,d}}$ [W/m^3]) using the following equation:

$$Q_{\text{SEI,d}} = H_{\text{SEI,d}} * A_{\text{SEI,d}} * x_{\text{SEI,d}} * e^{-\left[\frac{E_{\text{aSEI,d}}}{R*T}\right]} \quad (1)$$

where $H_{\text{SEI,d}}$ [J/kg] is the heat released due to the SEI decomposition reaction per amount of reactant; $A_{\text{SEI,d}}$ [s^{-1}] and $E_{\text{aSEI,d}}$ [J/mol] are the pre-exponential factor and the activation energy of the reaction; and $x_{\text{SEI,d}}$ is the mass fraction of Li contained in the metastable form in the passivation layer.

The heat released during the SEI decomposition process can potentially trigger other side reactions if not appropriately dissipated. Once the SEI layer starts decomposing, the anode is exposed again to the electrolyte solution, allowing intercalated Li located in the anode to react with the electrolyte solution. The contact between the anode and the electrolyte solution produces new Li_2CO_3 , which is the stable

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component of the SEI layer, a reason why this process is also commonly known as SEI regeneration reaction. In trying to simulate thermal abuse behavior in cylindrical and prismatic Li-ion cells, previous studies [4, 5] have modeled the heat released due to the reaction between intercalated lithium and the electrolyte solution ($Q_{\text{SEI,rg}}$ [W/m^3]) as:

$$Q_{\text{SEI,rg}} = H_{\text{SEI,rg}} * A_{\text{SEI,rg}} * x_{\text{SEI,rg}} * e^{-\left[\frac{z_{\text{SEI}}}{z_{\text{SEI,o}}}\right]} * e^{-\left[\frac{E_{\text{SEI,rg}}}{R*T}\right]} \quad (2)$$

where $x_{\text{SEI,rg}}$ is the mass fraction of lithium intercalated in the anode; and z_{SEI} is the dimensionless thickness of the SEI layer.

According to these works, the SEI regeneration process occurs at temperatures above 120 °C, contributing to a further increment in the system's temperature due to its exothermic behavior [5]. The heat released due to the first two decomposition reactions in the anode interface can potentially increase the cell to temperatures where another cell component may degrade. At about 170 °C, the cathode active material may become thermally unstable and decompose to a reduced form. Among the possible cathode active materials, LiCoO₂ (LCO) starts its decomposition reaction at about 170 °C [5], and the heat released due to the reaction (Q_{Cath} [W/m^3]) can be expressed as:

$$Q_{\text{Cath}} = H_{\text{Cath}} * A_{\text{Cath}} * \gamma^n * (1 - \gamma)^n * e^{-\left[\frac{E_{\text{Cath}}}{R*T}\right]} \quad (3)$$

where γ is the conversion rate of cathode active material, with its respective reaction order n .

The cathode decomposition is an exothermic process where oxygen gas may be released as one of the main products of the reaction. This autocatalytic phenomenon, where different battery components decompose, releasing more and more heat, is commonly known as thermal runaway mechanism.

According to Botte et al., at over 200 °C most of the organic solvents used for Li-ion battery electrolyte solution and the combinations of these solvents start decomposing [6]. The solvents react with the oxygen released in previous side reactions. Kim et al. [7] represented the heat released due to electrolyte decomposition reaction (Q_{ElecSol} [W/m^3]) through the following formula:

$$Q_{\text{ElecSol}} = H_{\text{ElecSol}} * A_{\text{ElecSol}} * C_{\text{ElecSol}}^m * e^{-\left[\frac{E_{\text{ElecSol}}}{R*T}\right]} \quad (4)$$

In light of the discussion above, it is clear that several thermal-abuse models have been developed at the macroscopic level. Among them, a few have accounted for the layered structure of Li-ion batteries [2, 5, 7]. These models have weighted most of the individual components' physico-chemical properties, like specific heat, and density, and have

reflected the non-isotropic behavior of thermal conductivity of the different constituent layers. However, these studies have considered each layer behaving as a solid homogeneous media. As an example, Spotnitz and Franklin [2] accounted for the separator properties for their thermal model, disregarding the free electrolyte solution between the opposite electrodes. Studying the process of electrodeposition in Li-ion batteries, Mistry et al. distinguished among bulk electrolyte and confined electrolyte solution, having the latter strong influence in the ionic transport which controls the electrodeposition process [8]. However, the researchers observed that at high temperature conditions there is an improvement in the transport of ions, which indicates a minor influence of the electrolyte confinement region and major impact from the free electrolyte zone [8]. Electrolyte solution not only transport ions from one electrode to the other, but it may also transfer heat through fluid convection.

During the 1990s, part of the scientific community perceived lead-acid batteries as the power source to be used in future EV applications. Among them, some groups of researchers have studied the electrolyte solution convection in lead-acid batteries [9–13]. Alavyoon et al. performed experimental and simulation studies where they concluded that free convection and acid stratification carries out a relevant role on the electrolyte solution between the electrodes in a lead-acid battery [10].

To the best of our knowledge, prior works have not fully considered the heterogeneity of Li-ion battery components in the thermal models. This does not allow a complete picture of the thermal behavior of the electrolyte solution to emerge under thermal gradient conditions, which is needed for understanding thermal runaway mechanisms. The work presented here focuses on the electrolyte solution by considering it as a dynamic element, where convection may occur due to variations in fluid density responding to external and local internal conditions. The next section of this paper introduces the “**Methodology**”, and the following section shows on the “**Results and discussion**”. Finally, the last section presents the “**Conclusions**”.

Methodology

Li-ion batteries are usually formed by several layers of Al current collector, anode, electrolyte solution/separator, cathode, and Cu current collector. This work focuses on the heat and mass transfer through the electrolyte solution of a Li-ion battery, and considers a 18,650 cell with a standard LiCoO₂ cathode, graphite anode, and LiPF₆ in a EC:EMC:DMC (1:1:1) electrolyte solution. The study aims to expand previous thermal abuse models developed by Hatchard et al. [4] and Kim et al. [7] for a complete 18,650 cell but focusing on the electrolyte solution layer. The model is applied on a

domain of $65 \text{ mm} \times 50 \text{ }\mu\text{m}$, which are the height of a 18,650 cell and the approximate thickness of the electrolyte solution/separator layer, respectively.

Li ions material balance and energy balance are applied to consider heat and mass transfer through the liquid electrolyte solution. Besides, as the fluid inside the battery is not static, free convection may occur due to the density gradient in the solution [10]. Density variation may happen when temperature gradients or concentration variations inside the solution are substantial. Momentum balance is applied to account for potential velocity variations.

The model computes for the temperature distribution inside the electrolyte compartment considering energy conservation law. Constant temperature Dirichlet boundary conditions are applied for the lateral boundaries of the model domain. For the top and bottom boundaries of the domain, heat exchange with the external environment is applied, with an external convective coefficient of $40 \text{ W}/(\text{m}^2 \text{ K})$ and ambient temperature of $155 \text{ }^\circ\text{C}$.

Energy balance

To account for all the effects of secondary chemical reactions, a thermal balance of the device should be performed. From the energy equation [14], assuming constant pressure and neglecting the viscous dissipation term, the energy balance can be written as:

$$\rho \cdot C_p \cdot \frac{DT}{Dt} = \nabla \cdot (k \nabla T) + Q_{\text{Chem}} \quad (5)$$

where ρ [kg/m^3], C_p [$\text{J}/(\text{kg} \cdot \text{K})$], and k [$\text{W}/(\text{m} \cdot \text{K})$] are the density, heat capacity, and thermal conductivity of the electrolyte solution, and Q_{Chem} [W/m^3] is the total heat released due to the undesired secondary reactions. The total heat released due to undesired reactions is the summation of the heat released by the SEI decomposition ($Q_{\text{SEI,d}}$), the intercalated Li/ electrolyte reaction ($Q_{\text{SEI,rg}}$), the cathode decomposition (Q_{Cath}), and the electrolyte decomposition reaction (Q_{ElecSol}).

Material balance

To account for the Li ions flux inside the electrolyte solution, a material balance of Li ion molecules in the electrolyte is performed. The material balance for the Li ions can be stated as:

$$\frac{\partial c}{\partial t} = -\nabla \cdot N + R_{\text{Chem}} \quad (6)$$

where $c[M]$ is the Li ion concentration in the electrolyte solution, N [$\frac{\text{moles Li}^+}{\text{m}^2 \text{ s}}$] is the flux of Li ions, and R_{Chem} [$\frac{\text{moles Li}^+}{\text{m}^3 \text{ s}}$] is the production of Li ions in homogeneous chemical reactions. As the first three secondary chemical reactions occur in the electrode's surface, and the electrolyte decomposition reaction does not result in a net change in Li ions, R_{Chem} is zero. From the Nernst-Planck equation, the ionic flux may be written as:

$$N = -D \cdot \nabla c + t_+ \cdot \frac{I}{F} + v \cdot c \quad (7)$$

which accounts for the transport of Li ions by ionic diffusion, the second term represents the transport of Li ions by migration due to the presence of an electric field, and the last term portrays the convective transport. Assuming electroneutrality in the electrolyte solution, the migration term can be neglected from the material balance as the divergence of the current density equals to zero. Combining the last two equations and the proposed assumptions, the Li ions material balance in the electrolyte solution can be expressed as:

$$\frac{Dc}{Dt} = \nabla \cdot (D \cdot \nabla c) - c(\nabla \cdot v) \quad (8)$$

where D [$\frac{\text{m}^2}{\text{s}}$] is the Li ion diffusion coefficient in the electrolyte solution.

Momentum balance

The Boussinesq approximation is used to describe density variation due to temperature or concentration gradients [14]. Applying the equation of motion to our system and combining it with the Boussinesq density approximation for a two-dimensional model, the momentum balance can be represented as:

$$\frac{\partial v_x}{\partial t} = \frac{\mu}{\rho} \left(2 * \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_y}{\partial x \partial y} \right) + \frac{1}{\rho} \left(2 * \frac{\partial \mu}{\partial x} * \frac{\partial v_x}{\partial x} + \frac{\partial \mu}{\partial y} \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} \right) \right) - \left(v_x * \frac{\partial v_x}{\partial x} + v_y * \frac{\partial v_x}{\partial y} \right) \quad (9)$$

$$\frac{\partial v_y}{\partial t} = \frac{\mu}{\rho} \left(\frac{\partial^2 v_y}{\partial x^2} + 2 * \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_x}{\partial y \partial x} \right) + \frac{1}{\rho} \left(\frac{\partial \mu}{\partial x} \left(\frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} \right) + 2 * \frac{\partial \mu}{\partial y} * \frac{\partial v_y}{\partial y} \right) - \left(v_x * \frac{\partial v_y}{\partial x} + v_y * \frac{\partial v_y}{\partial y} \right) - g \bar{\beta} (T - \bar{T}) - g \bar{\gamma} (c - \bar{c}) \quad (10)$$

where Eqs. (9) and (10) are the x and y components of the equation of motion, and v_x [m/s] and v_y [m/s] are the horizontal and vertical components of the velocity of the solution.

Combining the Li ions material balance, the momentum balance, and the energy balance, a system of four PDEs is formed. The system has four dependent variables (c , v_x , v_y , T) and three independent variables (x, y, t). The equations are solved considering variable coefficients, through the finite difference approximation technique, using MATLAB.

Results and discussion

This work simulates the thermal behavior in a layer of carbonate-based electrolyte solution inside a 18,650 Li-ion battery. Considering previously developed thermal runaway models [4, 5, 7], the initial condition of this study is 25 °C throughout the electrolyte domain, and the external ambient temperature is uniformly at 155 °C. The electrolyte solution is initially static, and the initial concentration of the solution is 2.0 M.

Once the simulation starts, the higher external temperature produces an increment in the internal temperature close to the boundaries. Figure 1 illustrates the calculations of temperature distribution inside the electrolyte solution layer, at different simulation times.

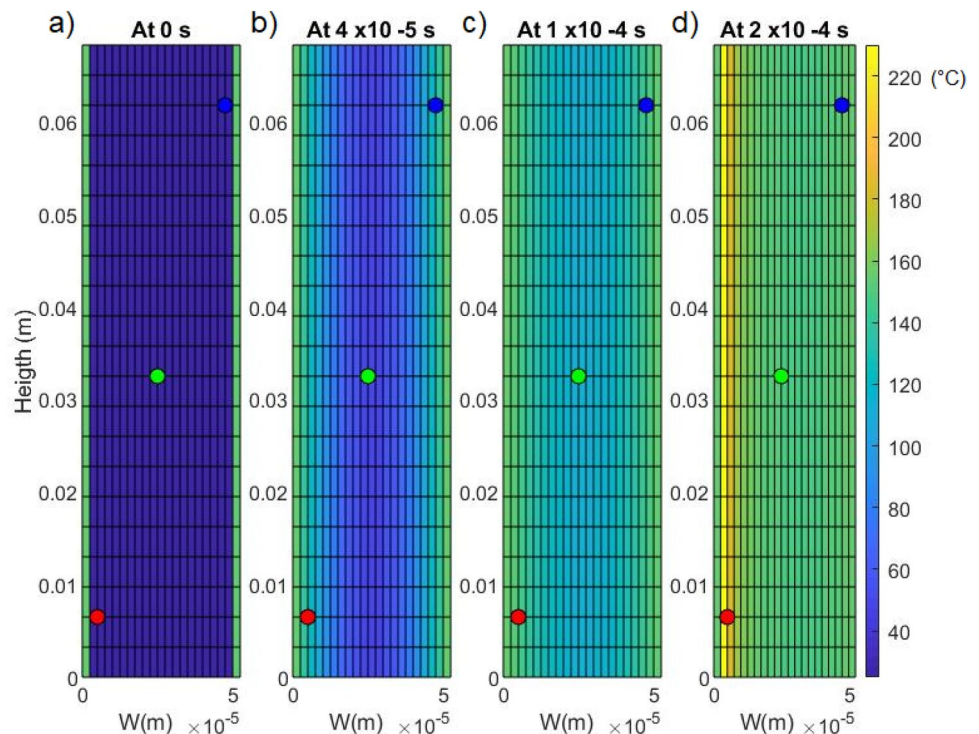
Figure 1 shows the estimation of temperature variation inside the electrolyte solution. Comparing Fig. 1a and b it can be deduced that there is a fast temperature rise at the

beginning of the simulation due to the high-temperature difference between inside and outside temperature. From Fig. 1b it could be stated that at about 4×10^{-5} s, there is still a significant difference in temperature between the middle of the domain, green point, and closer to the boundaries of the domain. Figure 1c indicates that after 1×10^{-4} s, the temperature becomes relatively uniform and close to the boundary value temperature. Figure 1d shows that after 2×10^{-4} s, temperature increment in the left-hand side of the domain is remarkable. Considering that until this time, the temperature distribution in the domain was close to the temperature at the boundaries, it could be inferred that from this time on, the temperature rise is due to an internal heat source located at the left side of the domain. This is an important observation, as it states there is a hot spot in the electrolyte layer. Assuming extrapolation of this finding to a multiple-layer Li-ion battery, like a 18,650 cell, it suggests that multiple localized heat sources may be found on an entire battery.

Figure 2 illustrates the predictions of temperature evolution at different regions of the electrolyte solution layer. As shown in Fig. 1, the red point represents the region at the left-hand side of the electrolyte solution domain, close to the SEI layer. The green point is in the middle of the electrolyte solution. Finally, the blue point represents the region of the electrolyte domain close to the cathode surface.

In Fig. 2, the model shows the center of the electrolyte solution layer requires more time to reach the outside temperature, which is expected. The figure also indicates that at the beginning of the simulation, the red line and the blue

Fig. 1 Estimation of temperature distribution in a layer of electrolyte solution inside a 18,650 Li-ion battery: **a** at initial conditions, with 25 °C throughout the modeling domain; **b** at about 4×10^{-5} s; **c** at about 1×10^{-4} s; **d** when thermal runaway side reactions began to be perceptible, at about 2×10^{-4} s



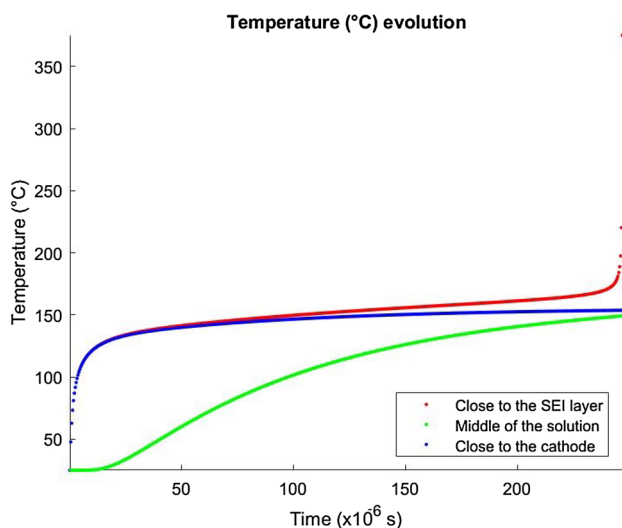


Fig. 2 Estimation of temperature evolution in a layer of electrolyte solution inside a 18,650 Li-ion battery. The red points represent the temperature at the left border of the domain, at the interface between the electrolyte solution and the SEI layer. The green points represent the temperature estimation at the middle of the electrolyte domain. The blue points illustrate the temperature at the right-hand side of the domain, at the interface between the electrolyte solution and the positive electrode surface

line coincide, converging slowly to the boundary value temperature. This even temperature rise is caused by the heat exchanged through the lateral boundaries of the domain. However, at about 125 °C the red line starts increasing faster than the blue line, which means that the temperature at the anode side of the electrolyte domain increases at a higher rate than at the cathode side of the domain. This increment in temperature rise is caused by the heat released by the secondary chemical reactions in the battery at elevated temperatures, which agrees with reported results [4, 5, 7]. According to Hatchard et al., the temperature increase between about 100 °C to 150 °C is caused by the decomposition of the metastable component of the SEI first, and accelerated by the reaction of intercalated lithium in the anode later [4]. In light of this, it may be said that the model fairly represents the temperature trend due to the decomposition reactions close to the anode interface. From Fig. 2, the model shows that once the electrolyte surpasses 150 °C, the temperature begins rising steeply, which is in line with what previous research has stated as the thermal runaway temperature threshold [4].

Conclusions

This work utilizes detailed modeling to investigate the thermal behavior in the electrolyte solution of a Li-ion battery. The model accounts for the thermal flux in the electrolyte

and also considers free convection of the solution caused by density variation due to the variations in temperature and concentration throughout the electrolyte compartment. The temperature trends are in line with previous thermal abuse models developed for an entire Li-ion cylindrical battery, which serves as model validation. The simulation focuses on the temperature distribution at the electrolyte solution layer and shows that hot spots can be found at the interface between the anode and the electrolyte solution. Further investigation may supplement this work by obtaining the temperature profile in the adjacent Al current collector, anode, cathode, and Cu current collector layers. Considering this assembly of layers, a complete temperature profile of a “single-layer” electrochemical cell can be obtained. The model can potentially be extended to a complete Li-ion cylindrical battery, where this assembly of layers is spirally wound and repeated in the radial direction. The proposed extension of this model can contribute to a more accurate thermal representation of Li-ion batteries, accounting for the heterogeneities of its components.

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Data availability The datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest On behalf of all the authors, the corresponding author states there is no conflict of interest.

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