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Experimental and theoretical analysis of a method to predict thermal runaway in Li-ion cells

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HIGHLIGHTS

- Derives a non-dimensional thermal parameter to predict thermal runaway.
- Experimental measurements are in good agreement with the model predictions.
- Predicts safe and unsafe regions of the thermal design space.
- Results may facilitate thermal management design for enhanced safety.

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ABSTRACT

Thermal runaway is a well-known safety concern in Li-ion cells. Methods to predict and prevent thermal runaway are critically needed for enhanced safety and performance. While much work has been done on understanding the kinetics of various heat generation processes during thermal runaway, relatively lesser work exists on understanding how heat removal from the cell influences thermal runaway. Through a unified analysis of heat generation and heat removal, this paper derives and experimentally validates a non-dimensional parameter whose value governs whether or not thermal runaway will occur in a Li-ion cell. This parameter is named the Thermal Runaway Number (*TRN*), and comprises contributions from thermal transport within and outside the cell, as well as the temperature dependence of heat generation rate. Experimental data using a 26650 thermal test cell are in good agreement with the model, and demonstrate the dependence of thermal runaway on various thermal transport and heat generation parameters. This parameter is used to predict the thermal design space in which the cell will or will not experience thermal runaway. By combining all thermal processes contributing to thermal runaway in a single parameter, this work contributes towards a unified understanding of thermal runaway, and provides the fundamental basis for design tools for safe, high-performance Li-ion batteries.

1. Introduction

Thermal runaway in Li-ion cells is a widely researched phenomenon that presents severe safety challenges [1–3] and often requires conservative design and run-time control of energy conversion and storage devices, resulting in reduced performance [4,5]. Fundamentally, thermal runaway in a Li-ion cell is a cascade of successive processes and reactions that feed into one another through heat generation that increases with temperature, eventually leading to explosion and fire [1,3]. Pertinent processes in thermal runaway include decomposition of the solid-electrolyte interface [6], various chemical reactions involving the electrolyte and electrode binder [7–9], and eventually, decomposition of electrolyte [10] and positive electrode active material [11]. A large amount of literature is available on understanding each of these processes [1,3,6,7,12,13]. In particular, the reaction kinetics and heat generation profiles of these processes have been widely studied, both theoretically [12] and through experimental measurements using tools such as Differential Scanning Calorimetry (DSC) and Accelerated Rate Calorimetry (ARC) [6,7,13]. These processes are usually modeled using Arrhenius reaction kinetics, with a reaction rate, and hence heat generation rate, that increases exponentially with temperature [1,3]. Numerical values of these reaction rates and heat generation rates, as well as their temperature dependence have been determined [3]. Some work also exists on overall heat generation rate measurement from a Li-ion cell at large discharge

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rates where thermal runaway may be a concern [14,15].

Some research has also been carried out on thermal modeling and measurements for Li-ion cells in thermal runaway situations [12,16–21]. Analytical methods and simulation tools [12,16–18] have been used for modeling thermal behavior of a cell at elevated temperatures. Experiments have been carried out to measure temperature of a cell or an appropriate thermal surrogate [19–21] during runaway. However, not much work has been carried out on connecting heat removal and heat generation processes that occur during thermal runaway. While heat generation is a function of the chemical reactions occurring within the cell, heat removal from the cell comprises of two processes that occur in series [22,23] – thermal conduction within the cell to its outside surface, and heat removal, usually through convection from the outside surface to the ambient. The nature of interaction between these heat generation and heat transfer processes eventually determines the thermal state of the cell, and whether thermal runaway occurs or not. It is critical to model both in a holistic fashion to better understand, and design means to prevent thermal runaway. Specifically, it is of interest to determine how the thermal transport properties of the cell and its ambient influence and govern the occurrence of thermal runaway. Such experimentally-verified theoretical limits on the occurrence or avoidance of thermal runaway may result in valuable design tools for safety of Li-ion cells.

The interaction between heat generation and heat removal has been represented in past papers in the form of a Semenov plot [24,25] that compares the rates of heat generation and heat removal as functions of the temperature of the cell. A Semenov plot uses the imbalance between the two processes – which increase exponentially and linearly respectively as functions of temperature – as the basis for predicting thermal runaway [24,25]. However, this approach assumes the cell to be a lumped thermal mass with uniform temperature throughout the cell volume. As shown by recent models [22,23] and measurements [26,27], this may not be an accurate assumption. As a consequence, the Semenov analysis predicts the thermal runaway process to be independent of the thermal conductivity of the cell, which is not accurate in several cases. For example, the Biot number [28] for a typical 26650 cell in natural convection conditions can be estimated to be 2–6.5 based on recent thermal conductivity measurements of the cell [29,30]. A value of $Bi > 1$ indicates strong temperature gradients within the cell, making the lumped mass based Semenov analysis inaccurate. Because the Semenov approach neglects heat transfer within the cell, it has not been possible so far to predict what internal and external thermal conditions are needed to prevent thermal runaway for a specific cell chemistry with well-known chemical kinetics and heat generation rates as functions of temperature. Accounting for this phenomenon will help optimize materials design from a thermal perspective, and help maintain a balance between internal and external heat transfer towards avoidance of thermal runaway.

This paper carries out theoretical and experimental analysis of thermal runaway in Li-ion cells by extending the Semenov analysis to account for heat transfer within the cell. The governing energy conservation equation that accounts for both heat generation and heat removal processes is solved to determine a non-dimensional parameter – which is named the Thermal Runaway Number (TRN) – whose value is shown to govern whether thermal runaway will occur or not. This parameter includes contributions from heat transfer processes within and outside the cell, as well as the rate of increase in heat generation with temperature. Results indicate that thermal conductivity within the cell is a critical thermal property governing runaway. Experiments that implement a temperature-dependent heat generation with a controllable temperature slope are carried out to validate the theoretical model. These experimental data are in good agreement with theoretical results, and demonstrate successful avoidance of thermal runaway through changes in the convective heat transfer coefficient external to the cell. Design guidelines that predict the parameter space in which thermal runaway can be prevented are developed using the model. The experimentally-verified fundamental insights in this paper may lead to design guidelines for thermal properties of the cell and its ambient for prevention of thermal runaway.

2. Mathematical modeling

Consider a cylindrical Li-ion cell of radius R, radial thermal conductivity k_r, heat capacity C_p and mass density ρ. The cell experiences a temperature-dependent internal heat generation rate $Q(T)$ throughout its volume, and is being cooled at the outside surface with a convective heat transfer h due to a mechanism such as coolant flow. The interest is in determining the parameter space within which the cell will not undergo thermal runaway, i.e. the cell temperature does not become unbounded. In this case, the governing energy equation for the temperature rise $T(r,t)$ in the cell is given by

$$k_r\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)+Q(T)=\rho\cdot C_p\frac{\partial T}{\partial t} \tag{1}$$

subject to

$$\frac{\partial T}{\partial r}=0 \quad \text{at } r=0 \tag{2}$$

and

$$-k_r\left(\frac{\partial T}{\partial r}\right)=h\cdot T \quad \text{at } r=R \tag{3}$$

Equations (1)–(3) can be solved to determine if there is a set of conditions that will prevent thermal runaway by ensuring a bounded solution for T at all times. To do so, a Taylor series expansion of $Q(T)$ is first carried out about a temperature $T=T_0$, and second order and higher terms are neglected. This results in

$$k_r\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)+Q(T_0)+\beta(T-T_0)=\rho C_p\frac{\partial T}{\partial t} \tag{4}$$

where $\beta=\frac{dQ}{dT}$ is the slope of $Q(T)$.

In order to solve equation (4), it is noted that the heat generation term can be split linearly into two components, $(Q(T_0)\text{-}\beta T_0)$ and βT. The first component is a constant quantity, which from thermal conduction theory [31] is known to result in a steady state with a bounded temperature field. However, the second heat generation component βT increases with temperature, and may lead to an unbounded temperature. Solving only for $T_2(r,t)$, which represents the temperature rise due to the second component of heat generation, it can be shown using the technique of separation of variables [31] that

$$T_2(r,t)=\sum_{n=1}^{\infty}C_n J_0\left(\frac{\mu_n r}{R}\right)\cdot\exp\left(\frac{k_r}{\rho\cdot C_p}\left(\frac{\beta}{k_r}-\frac{\mu_n^2}{R^2}\right)\cdot t\right) \tag{5}$$

where J_0 is the Bessel function of the first kind of order 0, C_n are constant coefficients, and μ_n are non-dimensional eigenvalues given by the roots of the equation