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A lumped model of venting during thermal runaway in a cylindrical Lithium Cobalt Oxide lithium-ion cell

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HIGHLIGHTS

- A lumped model for analyzing thermal runaway during venting is presented.
- The importance of including isentropic flow equations is investigated.
- Using the flow equations provides a better understanding of thermal runaway.
- The energy leaving the battery with the ejecta is quantified.
- The model shows good agreement with experiments.

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ABSTRACT

This paper presents a mathematical model built for analyzing the intricate thermal behavior of a 18650 LCO (Lithium Cobalt Oxide) battery cell during thermal runaway when venting of the electrolyte and contents of the jelly roll (ejecta) is considered. The model consists of different ODEs (Ordinary Differential Equations) describing reaction rates and electrochemical reactions, as well as the isentropic flow equations for describing electrolyte venting. The results are validated against experimental findings from Golubkov et al. [1] [Andrey W. Golubkov, David Fuchs, Julian Wagner, Helmar Wiltsche, Christoph Stangl, Gisela Fauler, Gernot Voitice Alexander Thaler and Viktor Hacker, RSC Advances, 4:3633–3642, 2014] for two cases - with flow and without flow. The results show that if the isentropic flow equations are not included in the model, the thermal runaway is triggered prematurely at the point where venting should occur. This shows that the heat dissipation due to ejection of electrolyte and jelly roll contents has a significant contribution. When the flow equations are included, the model shows good agreement with the experiment and therefore proving the importance of including venting.

1. Introduction

Li-ion batteries are found in nearly every application where electrical energy storage is required. The applications vary from small mobile devices to large devices such as vehicles, electricity generators, etc. This trend is due to their prime properties such as high energy density, no memory effect, high thermal stability and environmental friendliness when compared with other types of batteries [2,3].

Despite the fact that Li-ion batteries have a high thermal stability, thermal runaway can be triggered at elevated temperatures or by abusive conditions. High internal temperatures can increase the risk of fires or explosions and propagation within the modules if a cooling system or the battery module are not properly designed [4,5]. Thermal runaway can be triggered by overcharge/overdischarge, internal short circuit, high ambient temperature, presence of foreign objects, etc [6,7].

Once thermal runaway is triggered, Li-ion cells can rupture, ejecting electrolyte, parts of the electrodes and flammable gases which, if not properly controlled, can spread to the adjacent cells in the battery pack [8,9].

Recently, major battery failures were reported during transportation of batteries in airplanes, leading to decisions from some airline companies to cease transportation of Li-ion batteries in both passengers and freight [10,11].

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Nomenclature

A	Can total surface, m^2
A_a	Anode decomposition freq. factor, s^{-1}
A_c	Cathode decomposition freq. factor, s^{-1}
A_{ec}	Electrochemical reaction freq. factor, s^{-1}
A_e	Electrolyte decomposition freq. factor, s^{-1}
A_s	SEI decomposition frequency factor, s^{-1}
A_{vent}	Area of the vent, m^2
E_a	Anode activation energy, J
E_c	Cathode activation energy, J
E_{ec}	Electrochemical reaction activation energy, J
E_e	Electrolyte decomp. activation energy, J
E_s	SEI activation energy, J
M	Mach number
M_e	Molar mass of the electrolyte, $kg\ mol^{-1}$
P	Static pressure, Pa
P_{amb}	Atmospheric pressure, Pa
P_{vent}	Venting pressure, Pa
R	Universal gas constant, $J\ mol^{-1}\ K^{-1}$
SoC	State of Charge
T	Jelly roll lump temperature, K
T_{vent}	Venting temperature, K
V_h	Headspace volume of the cell, m^3
V_{cell}	Can volume, m^3
V_{vent}	Velocity of the electrolyte, $m\ s^{-1}$
$\dot{Q}_a$	Heat rate due to decomp. of anode, W
$\dot{Q}_{boil}$	Heat rate due to boiling of electrolyte, W
$\dot{Q}_c$	Heat rate due to decomp. of cathode, W
$\dot{Q}_{ec}$	Heat rate due to electrochemical reactions, W
$\dot{Q}_{ej}$	Heat rate due to venting of ejecta, W
$\dot{Q}_s$	Heat rate due to decomposition of SEI, W
$\dot{Q}_{vent}$	Heat rate due to venting of electrolyte, W
ε	Surface emissivity
γ	Electrolyte heat capacity ratio
σ	Stefan–Boltzmann constant, $W\ m^{-2}\ K^{-4}$
θ_e	Fraction of electrolyte in liquid phase
$c_{p,e}$	Specific heat of the electrolyte, $J\ kg^{-1}\ K^{-1}$
$c_{p,jr}$	Specific heat of the jelly roll, $J\ kg^{-1}\ K^{-1}$
h_a	Anode enthalpy of reaction, $J\ kg^{-1}$
h_c	Cathode enthalpy of reaction, $J\ kg^{-1}$
h_s	SEI enthalpy of reaction, $J\ kg^{-1}$
h_{conv}	Heat transfer coefficient, $W\ m^{-2}\ K^{-1}$
h_{ec}	Electrochemical reaction enthalpy, $J\ kg^{-1}$
h_{vap}	Enthalpy of vaporization, $J\ kg^{-1}$
k_b	Boltzmann constant, $J\ K^{-1}$
m_a	Anode mass, kg
m_c	Cathode mass, kg
m_e	Electrolyte mass, kg
m_e	Mass of the electrolyte, kg
m_{ej}	Mass of the ejecta, kg
t	Time, s
x_a	Fraction of Li in the Li_{x_a} C_6 anode
x_c	Fraction of Li in the Li_{x_c} CoO_2 cathode
x_s	Fraction of Li in the SEI
y	Fraction of vented electrolyte
z	Thickness of the SEI Layer, m

It is therefore very important to investigate thermal runaway and understand the processes behind it. In an experimental study, Golubkov et al. [1] demonstrate thermal runaway characteristics of three types of commercially available 18650 Li-ion batteries. The authors quantified the amount of gas vented from the cell and measured the mass of each battery component, providing important parameters for analyzing thermal runaway numerically.

A very recent paper in Nature gave insight in understanding the thermal runaway in a 18650 Lithium Nickel Manganese Cobalt Oxide battery cell using high-speed tomography [12]. By heating the battery with a heat gun, the authors found that thermal runaway can lead to the collapse of the electrodes and structure, and also melting of the current-collecting materials. They also report that the ejection of material dissipated a large amount of the heat due to the Joule-Thomson effect and tempered the propagation of thermal runaway for a single cell.

Both Golubkov et al. [1] and Finegan et al. [12] found that venting of gas and ejecta is a major part of thermal runaway process and therefore should be included in numerical studies.

Based on an experiment performed by Richard and Dahn [13], the authors formulated a mathematical model based on the decomposition rates of the anode and the SEI (Solid-Electrolyte Interphase) layer using observations during self-heating [14], while later on Hatchard et al. [15] included the decomposition of the cathode. Their models were formulated by observing the self-heating behavior, and have been used by many authors over the years. Kim et al. [16] formulate a model in which they add the decomposition of the electrolyte for the same experimental finding as in Ref. [15].

The drawbacks of these models are that they fail to predict the exact thermal runaway behavior due to lack of venting and electrolyte vaporization, which constitutes the aim of this project. This study was performed on a 18650 Lithium Cobalt Oxide battery cell, and a lumped model was built with a series of ODEs representing the decomposition rates, the energy balance and the ideal gas flow equations.

By setting up a burst condition for the trigger pressure of the battery relief mechanism, the venting of the electrolyte was modeled (using COMSOL MultiPhysics) as an ideal gas flowing isotropically through an orifice. Moreover, the model includes the partial ejection of the jelly roll, where the amount of ejecta is measured experimentally at NASA GRC Cleveland [17]. The contributions of the different processes modeled in this paper are sketched in Fig. 1.

2. Model Description

2.1. Decomposition rates and reactions

The heat generated inside the battery cell was determined by the thermal decomposition of the anode, cathode, SEI layer and electrolyte, and also due to the electrochemical reactions [18]. Moreover, the processes involved in the electrolyte are complex phenomena which involve evaporation, boiling and venting, which is finally accompanied by explosions of ejecta, as stated previously.

The rates for the decomposition of the cathode, anode, SEI and electrolyte are described by Arrhenius equations [15] [16]:

$$\frac{dx_c}{dt} = A_c x_c (1 - x_c) exp\left(\frac{-E_c}{k_b T}\right) \tag{1}$$