



# Adiabatic calorimetry test of the reaction kinetics and self-heating model for 18650 Li-ion cells in various states of charge



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## HIGHLIGHTS

- Adiabatic calorimetry is applied to the study of thermal runaway in Li-ion cells.
- A self-heating model was developed based on pseudo-zero-order Arrhenius kinetics.
- Thermal explosion energy increases exponentially with SoC.

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## ABSTRACT

Use of adiabatic calorimetry to characterise thermal runaway of Li-ion cells is a crucial technique in battery safety testing. Various states of charge (SoC) of Li-ion cells were investigated to ascertain their thermal runaway features using a Vent Sizing Package 2 (VSP2) adiabatic calorimeter. To evaluate the thermal runaway characteristics, the temperature-pressure-time trajectories of commercial cylindrical cells were tested, and it was found that cells at a SoC of greater than 50% were subject to thermal explosion at elevated temperatures. Calorimetry data from various 18650 Li-ion cells with different SoC were used to calculate the thermal explosion energies and chemical kinetics; furthermore, a novel self-heating model based on a pseudo-zero-order reaction that follows the Arrhenius equation was found to be applicable for studying the exothermic reaction of a charged cell.

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## 1. Introduction

The Li-ion cell is one of the most common types of batteries and is used in more than 90% of the battery packs or modules found in consumer electronics, such as cellular phones, laptop computers, camcorders, power tools, and electric vehicles. Li-ion cells have a high maximum power density and a wide range of working temperatures, are widely available, and offer effective performance—among other characteristics, they exhibit no memory effect, which allows more flexibility in charging operation because there is no need to fully discharge the cells before recharging and the self-discharge effects are slow when the battery is not in use [1]. The production of large-scale rechargeable batteries is essential

because of demands for increased battery capacity. Li-ion cells, unlike other rechargeable batteries, are classified as potentially explosive materials and require a stricter, safer design for both charging and use. Battery packs that incorporate large-scale cells must feature improved heat dissipation and power management systems. Furthermore, as the high power density of large-scale cells increases, issues related to thermal stability and work uniformity substantially affect the electrochemical or chemical reactions, thermal effects, and safety performance of Li-ion cells.

The conditions of Li-ion cell thermal abuse have raised safety concerns for numerous consumers of electronic products, particularly electric vehicles. In recent years, battery packs installed in electric products have caused numerous fires or explosions following short-circuiting, crushing, or thermal abuse. These accidents were caused by the failure or breakage of the battery packs, which triggered runaway reactions [2]. Three components affect the chemical reactions of a Li-ion cell: The cathode, the anode, and

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Nomenclature			
A	pre-exponential factor ( $\text{min}^{-1}$ )	$p_2$	gauge pressure in the outer containment vessel (psig)
$C_p$	specific heat capacity ( $\text{J g}^{-1} \text{K}^{-1}$ )	$p_{\text{max}}$	maximum absolute pressure (psia)
$dH/dt$	heat generation rate ( $\text{J min}^{-1}$ )	$R^2$	coefficient of determination
$dp/dt$	pressure elevation rate ( $\text{psig min}^{-1}$ )	$R_s$	resistance of the electrolyte ( $\Omega$ )
$(dp/dt)_{\text{max}}$	maximum pressure elevation rate ( $\text{psig min}^{-1}$ )	SoC	states of charge (%)
$dT/dt$	adiabatic self-heating rate ( $^{\circ}\text{C min}^{-1}$ )	$T_0$	initial exothermic temperature ( $^{\circ}\text{C}$ )
$(dT/dt)_{\text{sim}}$	simulated self-heating rate ( $^{\circ}\text{C min}^{-1}$ )	$t_D$	discharging time at a constant C rate (min)
$dx/dt$	conversion rate	$T_{\text{max}}$	maximum temperature ( $^{\circ}\text{C}$ )
$E_a$	apparent activation energy (eV)	$Q_{\text{chem}}$	chemical heat generation rate (W)
$E_{\text{ava}}$	explosion energy (kJ)	$Q_{\text{work}}$	heat produced by electric power (W)
$I$	electric current (A)	$Q_{\text{TNT}}$	explosion energy of TNT ( $\text{kJ g}^{-1}$ )
$k_B$	Boltzmann's constant ( $8.62\text{e}-5 \text{ eV K}^{-1}$ )	$x$	degree of conversion for the n-th order reaction
$m_c$	mass of an 18650 cell's components (g)	$\alpha$	degree of conversion for the pseudo-zero-order reaction
$m_{\text{casing}}$	mass of an 18650 cell's stainless-steel casing (g)	$\Delta H$	heat of reaction (kJ)
$m_{\text{cell}}$	mass of an 18650 cell (g)	$\Delta t$	change in time (min)
$m_{\text{TNT}}$	TNT mass (g)	$\Delta T_{\text{ad}}$	adiabatic temperature rise ( $^{\circ}\text{C}$ )
$n$	reaction order	$\eta$	empirical mass of TNT (%)
$p_1$	gauge pressure in the 316 SS test vessel (psig)	$\phi$	thermal inertia

the electrolyte. The high rate capability and high volume specific capacity of the cathode material,  $\text{LiCoO}_2$ , have been improved in recent years by increasing the voltage that this material can safely sustain. However, cathode materials exhibit oxidative power in the charged state, as expected from their electrode potential. Graphite is used as the anode material, and the electrolyte acts as an ionic conductor that provides the medium for the transfer of charge between the electrodes inside the cell. The electrolyte can vaporize, ignite, or explode when exposed to higher temperatures or short-circuiting conditions. Battery fires are thought to be related to oxidation of the electrolyte, in which case heat release in a charged cell is caused by the reactions or interactions between the cell components [3,4]. The decomposition of the solvent with the evolution of  $\text{O}_2$ ,  $\text{CO}_2$ , HF,  $\text{PF}_5$ ,  $\text{PF}_3\text{O}$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_3\text{H}_6$  gases occurred at elevated temperatures. In addition, accompanying the reaction was typically fires and/or explosion as severe oxidation occurred among  $\text{O}_2$ , the electrolytes and the cathode materials (e.g.,  $\text{LiCoO}_2$  and  $\text{Li}[\text{Co}_x\text{Ni}_y\text{Mn}_z]\text{O}_2$ ) [5–8]. Thermal runaway is associated with short-circuiting or the thermal response of a cell depending on the self-sustaining exothermic reactivity of its components and it is related to improve safety designs of the battery packs.

Recently, we developed a method of adiabatic calorimetry testing to directly measure a cell's global temperature and internal pressure in the event of thermal runaway. Various cathode-active materials and charge levels of the rechargeable Li-ion cell were tested for understanding of their thermal instability [2,5,6,9]. Surface temperature measurements of Li-ion cells provide only a limited view of the internal physical processes that occur during charging, and reliable knowledge of the internal temperature is needed to enable an adaptive charging scheme that can safely reduce the charging time [10]. Although the exothermic reaction of a Li-ion cell initially proceeds slowly, it accelerates exponentially as the temperature increases and the pressure becomes elevated. For experiments conducted the self-heating profiles due to chemical reactions in the interior of a Li-ion cell under adiabatic environment, adiabatic calorimetry studies were ideal for battery safety testing in order to determine the effects of thermal runaway and thermophysical parameters.

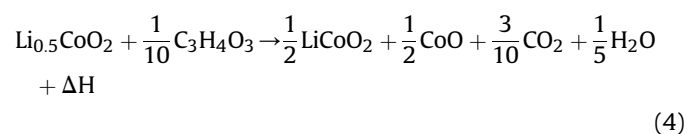
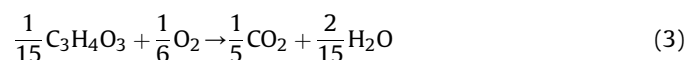
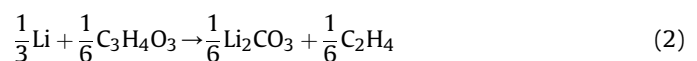
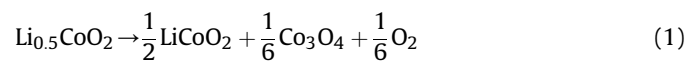
In this study, various states of charge (SoC) of 18650 Li-ion cells were investigated to ascertain their temperature–pressure–time features using a Vent Sizing Package 2 (VSP2) adiabatic

calorimeter. A cell can be regarded as a reaction system in which heat is generated by the reactions among the cell components, and the measured adiabatic calorimetry data were used in thermal explosion energy calculations to map the battery potential. Furthermore, chemical kinetics was applied to develop a self-heating model that obeys the Arrhenius kinetic equations.

## 2. Measurement of thermal explosion energy using calorimetry methods

### 2.1. Instability of active materials in Li-ion cells

A Li-ion cell consists of a cathode and an anode immersed in a dissociated salt electrolyte solution in which  $\text{Li}^+$  is transferred between the two electrodes, causing an electrochemical reaction. For example, layered  $\text{Li}_{0.5}\text{CoO}_2$  is used as the cathode in most Li-ion cells because of its facile synthesis, excellent reversible lithium extraction and storage properties, good capacity, and high voltage. The general chemical reactions of the  $\text{Li}_{0.5}\text{CoO}_2$  cathode,  $\text{LiC}_6$  anode and EC (ethylene carbonate,  $\text{C}_3\text{H}_4\text{O}_3$ ) in such a cell, in which  $\text{Li}^+$  becomes de-intercalated from the cathode and intercalated into the anode, are expressed as follows [2,11]:



The thermal behaviors of coexisting charged components in a cell is exothermic and releases oxygen at elevated temperatures, causing a combustion with the electrolyte till to exhaust one of reactants [12]. An organic electrolyte, which contains cationic

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