Applied Energy 228 (2018) 633–644

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Model-based thermal runaway prediction of lithium-ion batteries from kinetics analysis of cell components

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HIGHLIGHTS

- The battery TR mechanism is characterized by DSC tests on cell components.
- Six exothermic reactions are determined as the dominant heat sources.
- The kinetics parameters of each exothermic reactions are identified.
- A battery TR model is established by coupling all the exothermic reactions.
- The model predictions fit well with the variant TR tests results.

ARTICLE INFO

Keywords:
Lithium-ion battery
Battery safety
Thermal runaway
Kinetics analysis
Differential scanning calorimetry

ABSTRACT

Thermal runaway (TR) is a major safety concern in lithium-ion batteries. Model-based TR prediction is critically needed to optimize safety designs of cells. This paper presents a novel scheme for developing reliable battery TR model from kinetics analysis of cell components. First, differential scanning calorimetry (DSC) tests on the individual cell components and their mixtures are conducted to reveal the TR mechanism and characterize the exothermic reactions, of which the major six (such as the decomposition of solid electrolyte interface (SEI) film) are determined as the dominant heat sources. The kinetics parameters of each exothermic reactions are identified from the DSC tests results at variant heating rates using Kissinger's method and nonlinear fitting method. A predictive battery TR model is established by superimposing the chemical kinetics equations of the six exothermic reactions. The model fits well with the adiabatic TR test results and the oven tests results of a 24 Ah lithium-ion battery, indicating that the model can well reflect the battery TR mechanism and be trusted to predict battery safety performance without assembling a real battery.

1. Introduction

Lithium-ion batteries, with high energy density and extended cycle life, are the most widely used power sources for electric vehicles (EVs) [1–5]. Recent years, battery manufacturers are developing new materials to improve the energy density of lithium-ion batteries. For example, to develop the lithium-ion battery with a high energy density of 300 Wh kg^{-1}, the cathode materials may change from $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ to Ni-rich $Li(Ni_xCo_yMn_z)O_2$ cathode like $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$ or Li-rich manganese oxide etc., whereas the anode materials are changing from graphite to Si-C composite anode [3,4]. However, electrode materials with higher energy density have lower thermal stability, leading to potential safety problems, such as thermal runaway (TR) [6–10]. As a result, more attention should be paid to the thermal stability of the high energy density electrode materials, when applied in mass-produced large format lithium-ion batteries.

To evaluate the safety of the lithium-ion battery, manufacturers may need to produce a certain number of batteries and perform a series of safety tests [11]. Several "build and break" cycles are essential for developing a battery with a new chemistry design. However, "trial-and-error" tests are laboring work with low efficiency and provide limit information for battery safety improvement. Therefore, mathematical modeling should be developed to predict battery safety behaviors, which can help to reduce the number of "trial-and-error" tests and optimize battery designs.

Several investigations on the TR mechanism of lithium-ion batteries

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https://doi.org/10.1016/j.apenergy.2018.06.126
Received 28 January 2018; Received in revised form 20 June 2018; Accepted 25 June 2018

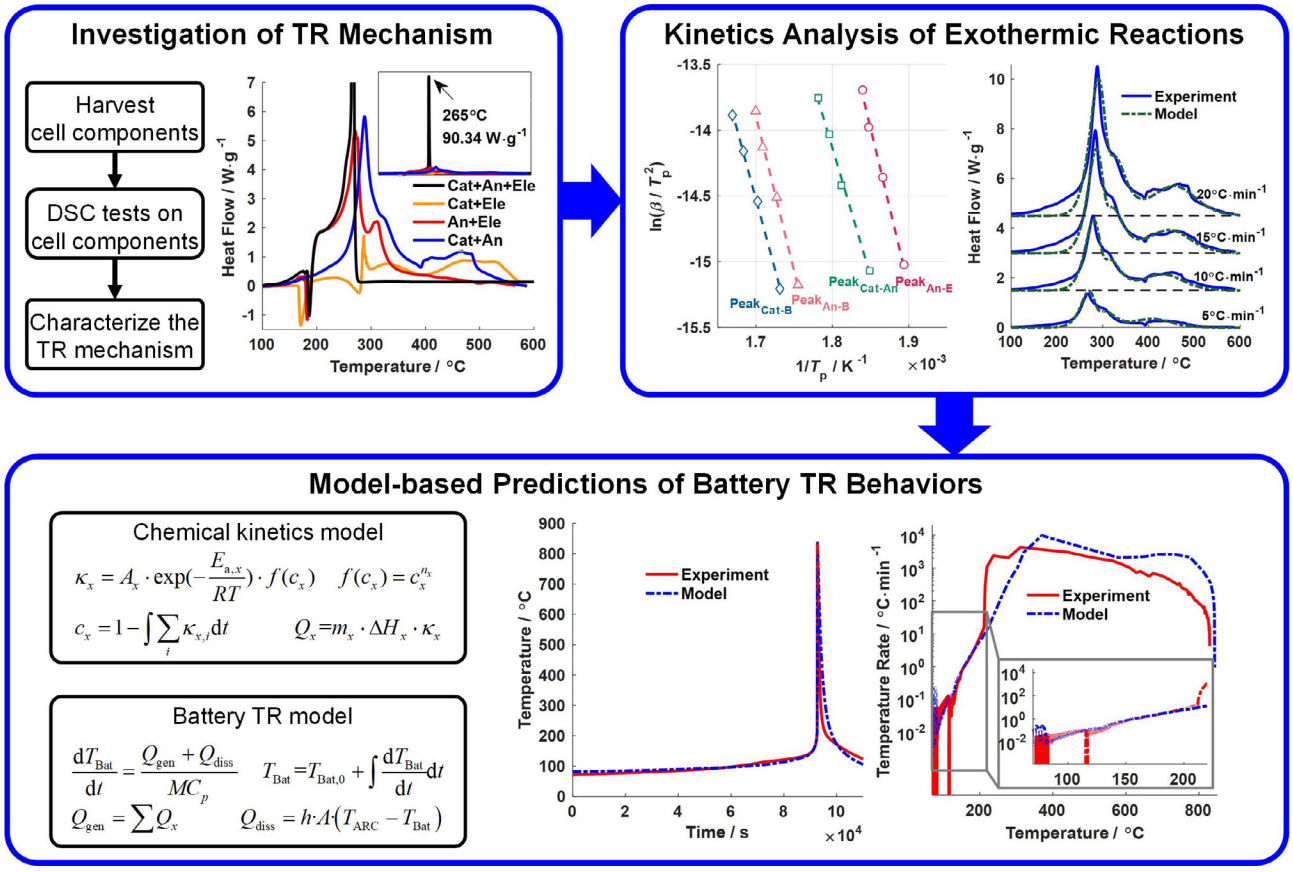

Fig. 1. Model-based TR prediction of lithium-ion batteries from kinetics analysis of cell components—an overview of this paper.

were conducted from both the component level and cell level, using differential scanning calorimetry (DSC) and accelerating rate calorimeter (ARC) [6,7,12–15]. Several exothermic reactions have contributions to the battery TR features. When the temperature rises up to 70–90 °C, the battery starts self-heating due to the decomposition of solid electrolyte interface (SEI) film [14–17], followed by the reaction between anode active material and electrolyte [18,19], and the reaction between anode active material and binder [20,21] at elevated temperature. The cathode active material also decomposes and generates oxygen as the battery temperature goes higher [22–25]. The released oxygen can oxidize the electrolyte [22,26,27] or even react with the anode active material [28,29], bringing the battery temperature to a higher value. Combustion of the flammable gases, such as the gasified solvents and the gases (such as H_2, CO, CH_4, C_2H_6, C_2H_4) released from the chemical reactions, would happen at high temperature if ignition source exists, resulting in fire and explosion [30–32]. The combustion always occurs outside the battery and may cause significant damage on the accessories in the battery module [31,33,34].

Chemical kinetics models based on Arrhenius equations, with the kinetics parameters (pre-frequency factor, activation energy, mechanism function and reaction enthalpy) determined from ARC or DSC tests, have been developed to reveal the reaction mechanisms and predict the thermal stability of cell components. Dahn et al. has calculated the kinetics parameters of several exothermic reactions from the Arrhenius plots in the ARC tests, and established models for the SEI film decomposition reaction [16], the reaction between lithiated graphite and electrolyte [17], and the Li_xCO_2 decomposition reaction [35–37]. The kinetics parameters of the decomposition reactions of several cathode materials, such as Li_xCO_2 and $Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, have been investigated based on DSC tests results using Kissinger's method and Ozawa's method [24,38–41]. For anode materials, Chen et al. [19,42] has calculated the activation energy of the SEI film decomposition reaction in four types of graphite anodes from DSC tests results. Ping et al. [26,43] has proposed a deconvolution method to separate the overlapped exothermic peaks in the C80 tests results and then analyzed the kinetics parameters of each deconvoluted reaction. Furthermore, Spotnitz et al. [6] has summarized the reaction kinetics of variant cathode and anode materials. However, those existing thermal kinetics studies of cell components mainly focused on one or two specific exothermic reactions, while battery TR predictions need to establish chemical kinetics models for all the exothermic reactions. Thus, further investigations are required to characterize all the exothermic reactions during the TR process and identify their kinetics parameters.

TR models have been established based on the kinetics studies of cell components to predict the battery safety behaviors. Dahn et al. [44] has developed a battery TR model based on the kinetics models of three exothermic reactions. Dahn's model could predict the onset of battery TR well when comparing to the oven tests, but failed in the prediction of the maximum temperature, since not all the exothermic reactions were included in the model. Kim et al. [45] has established a three-dimensional thermal abuse model to study the effects of size and local hot spot on battery TR behaviors. Based on Dahn's model and Kim's model, some researchers have investigated the influences of heat release conditions [46–48], cell physical configurations [48,49], and the venting behaviors [50,51] on battery TR behaviors. Moreover, researchers have extended the battery TR model to investigate the