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Thermal safety of lithium-ion batteries with various cathode materials: A numerical study

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ABSTRACT

Lithium-ion batteries for electrical vehicle and large-scale energy storage applications have developed significantly in recent years. However, the safety issue is still a major technical challenge and has become a key factor retarding further deployment of lithium-ion batteries. Numerous experimental studies on the thermal stability of cathode materials have been performed to seek safer battery materials. In this work, a three-dimensional thermal model describing oven abuse processes of lithium-ion batteries was established to study the thermal stability and thermal safety of cathode materials. Five various cathode materials (i.e. $LiCoO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$, $LiMn_2O_4$, and $LiFePO_4$) were taken; their response to oven thermal abuse was simulated and discussed in detail. Simulation results show that the $LiMn_2O_4$ cell has the best thermal stability and the $LiFePO_4$ cell has the best thermal safety of all the five various lithium-ion batteries. Effects of oven temperature on battery thermal behaviors during oven thermal abuses were particularly analyzed and the critical oven temperatures to trigger thermal runaway were obtained for these batteries as well.

1. Introduction

Safety worry has become a key issue concerning lithium-ion batteries, especially for electric vehicle and large-scale energy storage applications compared with portable electronics application due to the demands on higher energy and power densities [1,2]. The mutual conversion of chemical energy and electrical energy occurs inside lithium-ion batteries with the release of minimal heat and negligible gas during normal charge and discharge processes. However, with abusive conditions or operations such as elevated ambient temperature, short circuit, mechanical crush and overcharge, the battery converts more chemical energy into heat and a series of intensive exothermic reactions of the electrolyte and electrode materials may be aroused, leading to fast heat accumulation inside the battery, which eventually causes a significant deterioration at the battery performance and even worse can cause combustion, fire, and explosion risks, i.e. safety accidents.

To study and improve the safety of the lithium-ion battery, numerous studies have been performed. Air cooling [3–6], liquid cooling [7–9], heat pipe [10–13] and phase change material [14–17] were used to improve the safety of lithium-ion battery packs; positive temperature coefficient (PTC) device [18–20], reaction temperature sensing (RTS)-based control [21], safety vent [22] and current interrupt device (CID) [23] were utilized to decrease the probability of safety accidents for lithium-ion batteries; improving the thermal stability of electrode materials and electrolyte can increase the safety of lithium-ion battery [24–29].

Numerous experimental studies on the thermal stability of cathode materials have been conducted to explore the mechanisms of thermal runaway and/or seek more secure cathode materials. MacNeil et al. [30] used differential scanning calorimetry (DSC) to investigate the thermal stability of seven different cathode materials in 1 M $LiPF_6$ EC/DEC electrolyte. It was found that the cathode materials could be ranked from least safe to most safe in the following order: $LiNiO_2$, $LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{0.7}Co_{0.2}Ti_{0.05}Mg_{0.05}O_2$, $LiCoO_2$, $Li_{1+x}Mn_{2-x}O_4$, $Li[Ni_{3/8}Co_{1/4}Mn_{3/8}]O_2$, $LiFePO_4$. Jiang et al. [31] compared the thermal stability of three different cathode materials, $LiCoO_2$, $Li[Ni_{0.1}Co_{0.8}Mn_{0.1}]O_2$ and $LiFePO_4$ in different solvents and electrolytes using accelerating rate calorimetry (ARC). $LiFePO_4$ showed the highest stability among the three materials in EC/DEC solvent, in LiBoB EC/DEC electrolyte or in $LiPF_6$ EC/DEC electrolyte. Thermal runaway hazards related to adiabatic runaway reactions in 18650 $LiCoO_2$ and $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ batteries were studied in an adiabatic calorimeter with vent sizing package 2 (VSP2) by Jhu et al. [32]. The $LiCoO_2$ battery was proved to be more hazardous than the $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ battery. Golubkov et al. [33] tested

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the thermal runaway characteristics of three types of commercially-available 18650 lithium-ion batteries, the cathode materials of which were $LiFePO_4$ (LFP), $Li[Ni_{0.45}Mn_{0.45}Co_{0.10}]O_2$ (NMC) and a blend of $LiCoO_2$ and $Li[Ni_{0.50}Mn_{0.25}Co_{0.25}]O_2$ (NMC/LCO), respectively. The experimental results showed that the LFP cell had the highest thermal runaway onset temperature (~195 °C) and the smallest temperature increase during thermal runaway (~210 °C). The onset temperature shifted down to ~170 °C and ~150 °C and the temperature increase during thermal runaway rose to ~500 °C and ~700 °C were found for the NMC and NMC/LCO cells, respectively. Mendoza-Hernandez et al. [34] compared the thermal runaway behavior of 18650 $LiCoO_2$ and $LiMn_2O_4$ cells at differing state of charges (SOCs) by ARC measurements. The cell using $LiCoO_2$ cathode material was found to be less thermally stable than the $LiMn_2O_4$ cell and the thermal runaway onset temperature for $LiCoO_2$ cell was lower than that of $LiMn_2O_4$ cell during overcharge processes.

As an important and effective tool, numerical simulation has been widely used to study the safety property of lithium-ion battery. A lumped thermal model for oven abuse tests of prismatic batteries was developed by Hatchard et al. [35]. Simulation results were found to accord reasonably well with ARC data. Spotnitz et al. [36] extended the model for more abuse operations besides oven test, like overcharge, nail penetration, short-circuit, and crush for $Li_xNi_{0.8}Co_{0.2}O_2$ and $LiMnO_4$ batteries. Kim et al. [37] then extended the one-dimensional thermal abuse model to three-dimensional for simulating oven tests of cylindrical $LiCoO_2$ batteries. It was found that smaller cells dissipated heat faster than larger cells and less vulnerable to thermal runaway. Oven tests of prismatic graphite/$LiPF_6$/$LiCoO_2$ batteries with stacked electrode design were numerically studied by Peng et al. [38]. Simulation results showed that heat release condition, oven temperature, and tab arrangement interacted with each other to determine the thermal behaviors of batteries. Lopez et al. [39] modeled the thermal behaviors of 18650 cylindrical spiral-wound and prismatic spiral wound $LiCoO_2$ cells subjected to elevated temperatures owing to constant power heating. The influence of convective heat release condition, cell physical configuration, and electrolyte combustible property on the cell thermal behavior was also investigated. Chiu et al. [40] implemented the porous electrode theory to model the nail penetration process of 5.25Ah $LiMn_2O_4$ soft package prismatic cells. The onset temperature of thermal runaway and the cell temperature profile were obtained, both of which agreed well with experimental data. Zhao et al. [41] developed a three-dimensional electrochemical-thermal coupled model to simulate the internal short circuits of a 5Ah $Li_yCo_{1/3}$ $Ni_{1/3}$ $Mn_{1/3}O_2$ cell with a stacked-electrode design. The results showed that the short-circuit resistance and the number of shorted electrode layers had the most significant influence on the cell electrochemical and thermal behaviors.

For the numerical simulations focused on the study of thermal behaviors of lithium-ion batteries during abuse processes, the influence of battery shape, structure, capacity and different abuse operations on battery thermal behaviors were widely studied; however, there is generally a lack of detailed and systematic numerical study on thermal stability and thermal safety of battery materials, particularly for the miscellaneous cathode materials. The present work deals with a detailed numerical study on thermal stability and thermal safety of cathode materials. A three-dimensional thermal abuse model describing oven test processes of Li-ion cells is established and a series of simulations are performed for lithium-ion batteries with five various cathode materials (i.e. $LiCoO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$, $LiMn_2O_4$, and $LiFePO_4$) to investigate their thermal stability and thermal safety. The effects of oven temperature on battery thermal behaviors during oven thermal abuses are also analyzed.

2. Physical and mathematical model

2.1. Physical model

A typical lithium-ion cell consists of several layers: a copper current collector, negative electrode, separator, positive electrode and aluminum current collector. Fig. 1 schematically shows the interior structure of a battery unit cell, which has dimensions 196 μm (thicknesses of sub-regions along x direction are 9 μm, 59 μm, 20 μm, 92 μm, and 16 μm, respectively) × 0.065 m × 0.1 m. The cell properties considered in the present work are taken in terms of a graphite negative electrode, $LiPF_6$/EC:ECM:DMC electrolyte, and one of the five various positive electrodes (i.e. $LiCoO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $Li_{1.1}(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$, $LiMn_2O_4$, and $LiFePO_4$).

2.2. Thermal abuse model

A three-dimensional thermal abuse model is established and various heat generation source terms due to internal exothermic reactions are added to the energy conservation equation, as

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot k \nabla T + Q \tag{1}$$

Tables 1 [42] and 2 [36,37,42–44] summarize the thermophysical properties (density ρ, heat capacity c_p, and thermal conductivity k) of materials. The thermophysical properties are weighted sum of all the composing components' thermophysical properties with the component volume fraction as the weight factor for the composite electrodes and the separator. For example, the heat capacity of the composite negative electrode ($c_{p,ne}$) is calculated as

$$c_{p,ne} = \sum_j \varepsilon_j c_{p,j} \tag{2}$$

The subscript j indicates the composing components of the negative electrode, which includes electrolyte, graphite and additives (see Table 3). The last row of Table 3 [42] lists the component volume fraction (ε) in electrodes and separator.

Heat release capacity of a battery normally relies on heat convection and radiation. The heat release rate q is calculated by the following general expression.

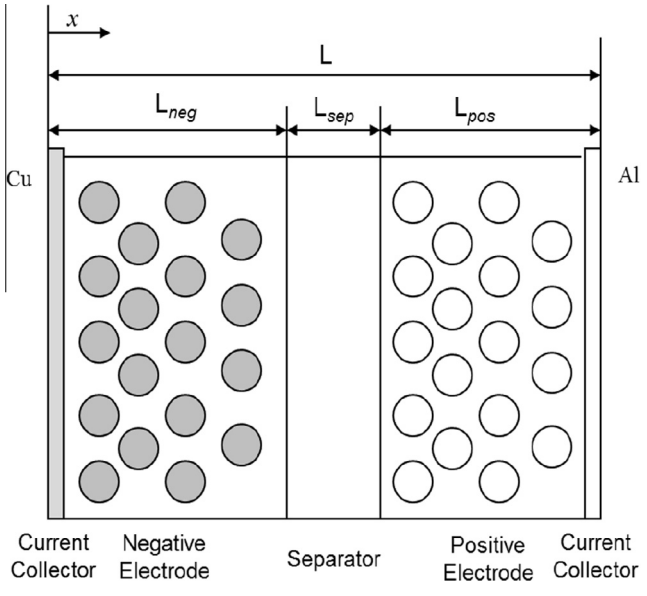

Fig. 1. Physical model of a lithium-ion cell.