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Mathematical model for thermal behavior of lithium ion battery pack under overcharge

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ABSTRACT

An overcharge model of lithium ion battery pack was built by coupling the electrochemical model with thermal abuse model. The pack consists of three fully-charged batteries, each of which has a capacity of 10 Ah, using $Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ as the positive electrode. The three batteries in the pack were juxtaposed, and only the middle one was overcharged. The influences of current, convection coefficient and gap between batteries on the thermal runaway propagation were studied. The results of temperature and voltage obtained from the models were validated experimentally, and they were agreed well with the experimental data with the relative error within 6%. The results showed that the onset temperature of thermal runaway of the charged battery increased with an increase in the current, while the temperatures for the other two decreased. The temperature rate of the charged battery changed little when the convection coefficient was greater than 40 W/m^2 K. The clamp of lithium ion battery pack had an important effect on the thermal runaway propagation. The occurrence of thermal runaway propagation was depended on whether there was the existence of clamp when the battery gap exceeded 5 mm.

1. Introduction

Due to the depletion of fossil fuel and the deterioration of the environment, it is extremely urgent to develop the green energy technology. Lithium-ion battery (LIB) is considered as one of the most appropriate green energy technologies because of its high energy and power capacity [1]. LIBs have been widely used in the fields of portable electronic devices, electric vehicles (EV), hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV) and energy storage in the past decades [1,2]. Although the probability of fire and explosion accidents caused by LIBs is controlled within one in 1 million, the number of the LIBs used is so large that the accidents occur almost every day in the worldwide, especially the phones and lap-tops LIBs [3,4]. The safety of LIB has been received much attention [5,6].

The safety accidents of LIBs may be arisen under the abnormal conditions, such as crush, nail penetration, overcharge, over-discharge, short circuits and so on, which are unpredictable in practice [7]. The thermal runaway (TR) is considered as an internal factor that causes the safety accidents of LIB. Many TR models were built to study the TR mechanisms of LIB under different abuse conditions in order to find possible solutions to the LIB safety problems. Hatchard et al. [8] built a one-dimensional (1D) model to simulate the electrochemical and thermal responses of battery, which was exposed to the oven. The 1D TR model was extended to 3D by Gi-Heon et al. [9]. The kinetic equations were used to simulate the heat generation from various exothermic reactions in these TR models, and the reaction kinetic parameters were obtained through the accelerating rate calorimetry (ARC) and differential scanning calorimetry (DSC) tests. Panchal et al. [5,10–12] developed an electrochemical-thermal model to study the temperature distribution under different discharge/charge conditions by considering the entropy changes and ohmic heat. Feng et al. [7] built a lumped model to predict the thermal runaway propagation with a large format LIB under nail penetration condition. It was found that the TR propagation could be prevented by increasing the gaps between LIBs.

Overcharge is one of the most common behaviors in a variety of abnormal situations, and it can be caused by the malfunction of the charger or the inappropriate design of battery management system [13]. During the overcharge process, the LIB temperature rises quickly due to a large amount of heat generation, including joule heat and the heat generated by a series of side chemical reactions at both negative and positive electrodes [14]. When the positive voltage exceeds 4.35 V, the dissolution of the positive active material in electrolyte will take place [15,16]. The solid electrolyte

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interphase (SEI) will break down and release heat when the internal temperature is higher than 90 °C [3,9], followed by the oxidation of electrolyte, the reactions between the intercalated lithium in the negative electrode and the electrolyte, the decompositions of the negative and positive electrodes, etc. [3,17–19]. The models about these reaction kinetics have been studied continuously. Arora et al. [20] built a mathematical model to predict lithium deposition on the negative electrode under a variety of operating conditions. The lithium deposition was also discussed by Fang et al. [21]. Zeng et al. [22] simplified the energy balance equations to predict the heat generation and calculate the chemical reactions heat during overcharge. Park et al. [23] built a thermal-electrochemical coupled model to discuss the effects of the active particles dissolution on the TR, especially the Mn dissolution. It can be seen that most of these models focused on part of the electrochemical reactions, and it is hard for them to reveal the full overcharge failure mechanism of LIB. Few models were built to discuss the TR propagation of LIB pack during overcharge.

In this paper, a TR propagation model of LIB pack during overcharge was built based on the single LIB overcharge model by coupling the electrochemical model with thermal abuse model. The accuracy of the LIB overcharge model was validated through experiments. The failure mechanism of the single LIB and the LIB pack during overcharge process were discussed. The effects of modeling parameters, such as overcharge current, convection coefficient and battery gap, on TR propagation were also studied. The effect of the LIB pack clamp on the TR propagation was investigated at various gaps.

2. Method

A prismatic LIB used in this work is shown in Fig. 1, using Li$[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_2$ as positive electrode, graphite as negative electrode, and $LiPF_6$/EC: EMC: DMC (1:1:1, by volume) as electrolyte, respectively. The LIB has a capacity of 10 Ah, cut-off voltage of 2.8–4.2 V, a length of 70 mm, width of 32 mm and height of 56 mm.

The LIB pack is shown in Fig. 2, and it consists of three LIBs. The three LIBs were bound together with a gap of 1 mm, and fixed by a LIB clamp, which is designed autonomously. The clamp was made of steel, and the wall thickness was 5 mm. Six thermocouples were used to measure the surface temperatures of the LIB pack, and their locations were marked by number 1–6. The number 1, 2 and 3 were on the negative side, and the number 4, 5 and 6 were on the positive side.

2.1. Electrochemical model

In this work, Newman's model was applied to analyze electrochemical properties [18,24,25]. The mass balance for the LIB is shown as the following [26].

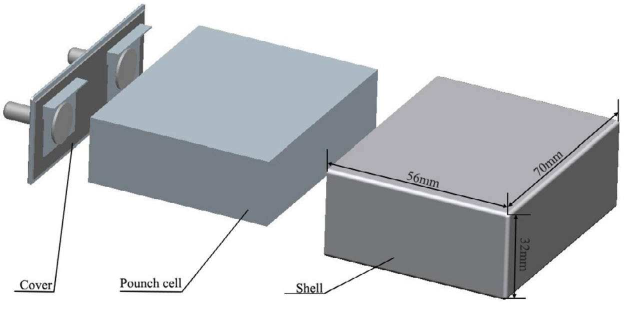

Fig. 1. LIB used in this work.

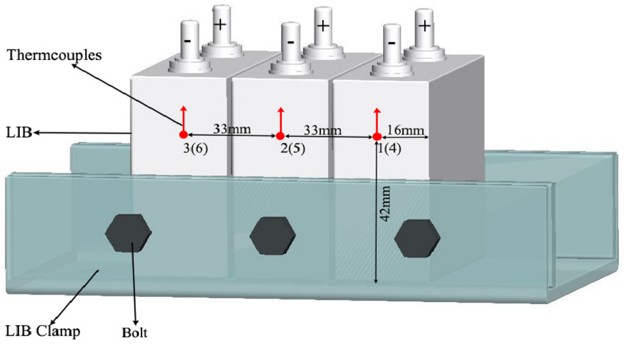

Fig. 2. Battery pack used in this work.

$$\varepsilon_{ele}\frac{\partial C_{ele}}{\partial t} = \nabla\cdot(D_{ele}\nabla C_{ele}) + aj_n(1-t_0^+) \tag{1}$$

$$\frac{\partial C_s}{\partial t} = \frac{D_s}{r_2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_s}{\partial r}\right) \tag{2}$$

Eqs. (1) and (2) are the mass balance of electrolyte phase and solid phase, respectively, where, ε_{ele} denotes volume fraction of electrolyte, C_i denotes the volume-averaged lithium concentration in phase i, D_i denotes lithium diffusion coefficient, a is the active area per unit volume, t^+ is transference number of lithium ion, j_n denotes the local charge transfer current density in solid phase, R is ideal gas constant, r is the average radius of the positive active particle, T is Kelvins temperature and F is Faraday constant.

Based on the Butler-Volmer equation, the local charge transfer current density can be calculated by Eq. (3) [25].

$$j_n = i_{ex}\left[\exp\left(\frac{0.5F}{RT}\eta_{s,k}\right) - \exp\left(-\frac{0.5F}{RT}\eta_{s,k}\right)\right] \tag{3}$$

$$i_{ex} = F(k_a)^{0.5}(k_c)^{0.5}(C_{\max}-C_s)^{0.5}(C_s)^{0.5} \tag{4}$$

$$\eta_{s,k} = V_{ca} - V_{an} - U_k \tag{5}$$

where i_{ex} is exchange current density and $\eta_{s,k}$ is over potential, k_a and k_c denote the reaction rate of positive electrode and negative electrode, respectively, U_k is open circuit potential, C_{max} denotes the maximum concentration of lithium in solid phase, C_s is the concentration of lithium ion in solid phase, V_{ca} is the potential of positive electrode, V_{an} is the potential of negative electrode. The detail descriptions of V_{ca} and V_{an} can be referenced in the Ref. [14].

In order to introduce the concept of overcharge, the state of charge (SOC) was defined as follows.

$$SOC = C_s/\alpha C_{\max} \tag{6}$$

When LIB was charged, the lithium ion was transferred from the positive electrode to the negative. The amount of lithium ion in the negative electrode can only reach 70–80% of its maximum when LIB reached the cut-off voltage [27]. The SOC was determined by the initial concentration of lithium ion and the charging time. Therefore, the adjustment factor α was introduced to the model to calculate the initial concentration of lithium ion and SOC.

The electrochemical model parameters are listed in Table 1.

2.2. Thermal abuse model

The thermal energy conservation equation governs the thermal behaviors during the overcharge process and is given as follows [32].

$$\frac{\partial(\rho C_p T)}{\partial t} = \nabla\cdot\lambda\nabla T + Q_{gen} - Q_{dis} \tag{7}$$