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An electrochemical-thermal coupled overcharge-to-thermal-runaway model for lithium ion battery

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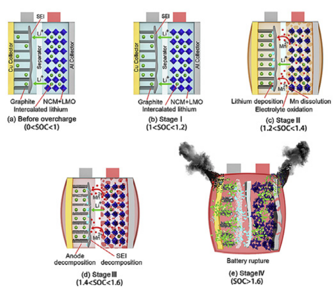
HIGHLIGHTS

- An electrochemical-thermal coupled overcharge-to-thermal-runaway model is built.
- Adiabatic overcharge tests were conducted using EV-ARC to validate the model.
- The overcharge-to-thermal-runaway model can fit well with the experiment.
- The model help to quantify the heat generation rates of each heat sources.
- Modeling analysis of the parameters helps find solutions for overcharge problem.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents an electrochemical-thermal coupled overcharge-to-thermal-runaway (TR) model to predict the highly interactive electrochemical and thermal behaviors of lithium ion battery under the overcharge conditions. In this model, the battery voltage equals the difference between the cathode potential and the anode potential, whereas the temperature is predicted by modeling the combined heat generations, including joule heat, thermal runaway reactions and internal short circuit. The model can fit well with the adiabatic overcharge tests results at 0.33C, 0.5C and 1C, indicating a good capture of the overcharge-to-TR mechanism. The modeling analysis based on the validated model helps to quantify the heat generation rates of each heat sources during the overcharge-to-TR process. And the two thermal runaway reactions including the electrolyte oxidation reaction and the reaction between deposited lithium and electrolyte are found to contribute most to the heat generations during the overcharge process. Further modeling analysis on the critical parameters is performed to find possible solutions for the overcharge problem of lithium ion battery. The result shows that increasing the oxidation potential of the electrolyte, and increasing the onset temperature of thermal runaway are the two effective ways to improve the overcharge performance of lithium ion battery.

1. Introduction

Under the pressure of energy crisis and environmental pollution, new energy vehicles, especially the electric vehicles (EVs)

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Nomenclature

Variables

A_x	the frequency factor for the reaction with reactant x (s^{-1})
C_{anode}	the capacity of anode (Ah)
$C_{cathode}$	the capacity of cathode (Ah)
$C_{cathode,0}$	the initial value of $C_{cathode}$ (Ah)
C_p	the specific heat capacity ($J\cdot kg^{-1}\cdot K^{-1}$)
c_x	the normalized concentration of reactant x (1)
$c_{x,0}$	The initial value of c_x (1)
$E_{a,x}$	the activation energy for the reaction with reactant x ($J\cdot mol^{-1}$)
F	the Faraday constant ($C\cdot mol^{-1}$)
I	the overcharge current (A)
i_0	the exchange-current for lithium deposition reaction (A)
i_{Li}	the rate of lithium deposition reaction (A)
$k_{cathode}$	the proportion factor for the cathode decomposition reaction (1)
k_{Mn}	the proportion factor for the Mn dissolution reaction (1)
$k_{electrolyte}$	the proportion factor for the electrolyte oxidation reaction (1)
k_{Li}	the proportion factor for the reaction between deposited lithium and electrolyte (1)
k_Q	the proportion factor for the cathode capacity (1)
M	the mass of the battery (kg)
m_x	the mass of reactant x (g)
n_{Li}	the amount of deposited lithium (mol)
Q	the heat generation rate (W)
Q_e	the heat generation rate originated from massive internal short circuit (W)
Q_{ohm}	the joule heat generation rate (W)
Q_p	the heat dissipation rate (W)
Q_r	the heat generation rate by chemical reaction (W)
Q_{rev}	the reversible entropic heat generation rate (W)
Q_x	the heat generation rate of the reaction with reactant x (W)
R	the ideal gas constant ($J\cdot mol^{-1}\cdot K^{-1}$)
r_{bat}	the internal resistance of the battery (Ω)
r_{SEI}	the resistance caused by the SEI (Solid Electrolyte Interface) film (Ω)
$r_{cathode}$	the resistance caused by the film formed on the cathode surface (Ω)
SOC	the battery state of charge (1)
SOC_{TR}	the battery SOC when thermal runaway happens (1)
T	the battery temperature (°C)
T_0	the initial value of battery temperature (°C)
$T_{onset,TR}$	the onset temperature of thermal runaway (°C)
$T_{onset,x}$	the onset temperature of the reaction with reactant x (°C)
V_{anode}	the anode potential (V)
$V_{cathode}$	the cathode potential (V)
$V_{electrolyte,ref}$	the oxidation potential of the electrolyte (V)
$V_{Mn,ref}$	the dissolution potential of Mn^{3+} (V)
V_{sim}	the simulated battery voltage (V)
x	the lithium content in Li_xC_6 (1)
x_0	the initial value of x (1)
y	the lithium content in the cathode (1)
y_0	the initial value of y (1)
ΔH_e	the total electrical energy released during massive internal short circuit (J)
ΔH_x	the enthalpy for the reaction with reactant x ($J\cdot g^{-1}$)
Δt	the average short circuit time (s)
ΔV	the battery voltage change during the interruption of the charging current (V)

Greek letters

K_x	the rate of the reaction with reactant x (s^{-1})
α_a	the transfer coefficient for the lithium deposition reaction (1)
α_c	the transfer coefficient for the lithium deposition reaction (1)
$\alpha_{electrolyte}$	the transfer coefficient for the electrolyte oxidation reaction (1)
α_{Mn}	the transfer coefficient for the Mn dissolution reaction (1)
ν_{Li}	the proportion factor for the calculation of the amount of deposited lithium (mol)

Subscripts

x	denotes that the variable is for reactant x, as listed in Table 2

become increasingly popular throughout the whole world. Lithium ion batteries are the most widely used power sources for electric vehicles, given their high energy, power density and extended cycle life. However, potential safety problems of lithium ion batteries, especially those associated with thermal runaway, have aroused much attention [1–6].

The thermal runaway of lithium ion batteries can be induced by unexpected abuse conditions, such as crush [7], short circuit [8], overheat [9,10] or overcharge [11,12]. Overcharge, as one of the most common field failure, usually occurs when the charge current is forced through after the battery reaches its nominal cut-off voltage [4,13]. The overcharge can be caused by the malfunction of the charger or the inappropriate design of battery management system [14].

The overcharge failure mechanism for lithium ion batteries has been investigated by some researchers [4,11,12,15–22]. Generally, when a battery is overcharged, its temperature quickly rises up due to a large amount of heat generation, including joule heat and the heat generated by a series of side reactions at both cathode and anode [11,22]. The cathode active material suffers from irreversible structural change when over-delithiated [23–25], followed by transitional metal ion (Mn^{2+} etc.) dissolution and active material decomposition [26–29]. The electrolyte will also be oxidized when the cathode potential surpasses the electrolyte oxidation potential [27,30]. The anode potential drops down to below 0 V with full intercalation of lithium, resulting in metallic lithium deposition [27,31–33]. The deposited lithium will react with the electrolyte and thicken the SEI (Solid Electrolyte Interface) film [27,34]. Moreover, those side reactions will also release a large amount of gas, such as CO_2 and H_2O, leading to severe swelling of the battery [15,35,36].

Thermal runaway models were built based on the experimental works to simulate the thermal and electrochemical responses and explore the failure mechanisms of lithium ion batteries under