



Numerical study on lithium titanate battery thermal response under adiabatic condition



Qiujuan Sun^a, Qingsong Wang^{a,b,c,*}, Xuejuan Zhao^a, Jinhua Sun^a, Zijing Lin^d

^a State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230026, PR China

^b Collaborative Innovation Center for Urban Public Safety, Anhui Province, Hefei 230026, PR China

^c CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei 230026, PR China

^d Hefei National Laboratory for Physical Sciences at the Microscale and Department of Physics, University of Science and Technology of China, Hefei 230026, PR China

ARTICLE INFO

Article history:

Received 6 April 2014

Accepted 7 December 2014

Keywords:

Lithium titanate batteries

Electrochemical–thermal model

Thermal runaway

Heat generation

ABSTRACT

To analyze the thermal behavior of 945 mA h lithium titanate battery during charging and discharging processes, the experimental and numerical studies are performed in this work. The cathode and anode of the 945 mA h lithium titanate soft package battery are the lithium nickel–cobalt–manganese-oxide and lithium titanate, respectively. In the experiment, an Accelerating Rate Calorimeter combined with battery cyclers is employed to investigate the electrochemical–thermal behavior during charge–discharge cycling under the adiabatic condition. In numerical simulation, one electrochemical–thermal model is adopted to predict the thermal response and validated with the experimental results. From both experimental and simulated results, the profile of potential and current, the heat generation, the temperature, the temperature changing rate and the temperature distribution in the cell are obtained and thermal runaway is predicted. The analysis of the electrochemical and thermal behavior is beneficial for the commercial application of lithium titanate battery in the fields of electric vehicles and hybrid electric vehicles.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Recently, the fog and haze has spurred worldwide interest in the development of clean and fuel-efficient vehicles. As the fossil fuels combustion in the traditional vehicles could cause air pollution, especially from the particulate matter in air less than 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$) pollution. Lithium ion batteries are thought as one key to make today's Electric Vehicles (EVs) and Hybrid Electric Vehicles (HEVs) a success, owing to its non-toxicity, and remarkable thermal stability [1].

Commercially available lithium ion battery is mainly composed of negative electrode, electrolyte, and positive electrode [2]. The thermal stabilities of cathode materials, such as LiCoO_2 , LiMn_2O_4 , LiFePO_4 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM), anode materials of graphite and lithium titanate have been studied. Viswanathan et al. used the electrochemical thermodynamic measurement to investigate the entropy for various cathodes and anodes. They found that LiCoO_2 based electrode has a much larger entropy change than electrodes based on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and LiFePO_4 , while $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) based anodes have lower entropy change compared to

graphite anodes [3]. LTO has advantages in safety and cycle life when compare with graphite, in particular when paired with the cathodes materials [4].

Lithium-titanate batteries have become an attractive option for electric vehicles and hybrid electric vehicles [5]. However, most researches focused on the batteries with LiFePO_4 cathode, rather than NCM cathode, and the anode materials is graphite rather than lithium titanate. Furthermore, relatively limited literature concentrates on thermal analysis under a series of charge–discharge cycles [6–8]. Therefore, this work is to study the thermal behavior of the lithium titanate battery, i.e. NCM cathode, 1.0 M $\text{LiPF}_6/\text{EC} + \text{DEC} + \text{DMC}$, and LTO anode. Furthermore, one-dimensional electrochemical model coupled into three-dimensional thermal model with finite element method was used to analysis the thermal behavior of lithium titanate pouch cell under charge–discharge cycles and to simulate thermal runaway. Besides, the numerical results were validated with the experimental results measured by an Accelerating Rate Calorimeter (ARC).

2. Modelling

2.1. Lithium titanate battery

Commercially available lithium titanate batteries consist of three primary functional components, i.e. negative electrode,

* Corresponding author at: State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230026, PR China. Tel.: +86 551 6360 6455; fax: +86 551 6360 1669.

E-mail address: pinew@ustc.edu.cn (Q. Wang).

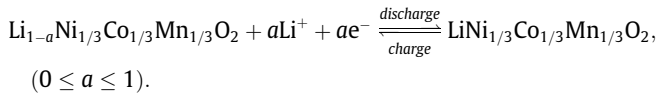
Nomenclature

a_s	specific interfacial area of the electrode, m^{-1}	κ	electric conductivity, S m^{-1}
c	lithium concentration, mol m^{-3}	ε	volume fraction of a phase
C_p	heat capacity, $\text{J kg}^{-1} \text{K}^{-1}$	η	activation over-potentials of an electrode reaction, V
D	diffusion coefficient of Lithium ion, $\text{m}^2 \text{s}^{-1}$	ρ	effective density of the active battery material, kg m^{-3}
E	cell potential, V		
$\partial E_{OC}/\partial T$	temperature derivative of equilibrium potential, V K^{-1}	Subscripts	
f	mean molar activity coefficient of the electrolyte	e	the electrolyte phase
F	Faraday's constant, $96,485 \text{ C mol}^{-1}$	neg	negative electrode
i_0	exchange current density of an electrode reaction, A m^{-2}	pos	positive electrode
J	transfer current resulted from the intercalation or deintercalation of Lithium, A m^{-3}	sep	electrolyte
k	electrochemical reaction rate constant, m s^{-1}	neg_cc	negative current collector
K	thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$	pos_cc	positive current collector
L	thickness of the different layers of the cell, m	i	different layer of active battery material, i.e. neg, pos, sep, neg_cc, pos_cc.
R	the gas constant, $8.3143 \text{ J mol}^{-1} \text{K}^{-1}$	s	the solid phase
r_s	radius of the spherical particle, m	eff	effective
T	absolute temperature, K	oc	open circuit
t_+^0	transport number	rev	reversible
α	charge transfer coefficients	rxn	irreversible
		j	X, Y, Z-direction

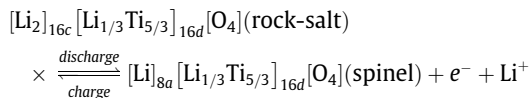
electrolyte, and positive electrode. During charging, lithium ions deintercalate from the positive electrode and intercalate into the negative electrode, and the reverse takes place in the process of discharge. Schematic of lithium titanate cell is shown in Fig. 1, and the orderly accumulation of the CoO_2 , NiO_2 , and MnO_2 layers were selected as the structural model of lithium nickel–cobalt–manganese-oxide material [9].

The electrochemical reactions during the charge/discharge can be expressed as:

At positive electrode,



At negative electrode, structurally, the lithium ion insertion into LTO spinel results in the displacement of the lithium ions originally located at the tetrahedral site 8(a) into the octahedral 16(c) sites that also accommodate the newly inserted lithium ions according to the following scheme [4]:

**2.2. Mathematical model**

During charging and discharging processes, there are various chemical and electrochemical reactions as well as other physical phenomena. The Butler–Volmer equation, concentrated solution theory, porous electrode theory, solid potential equation, potential equation, and current equation were applied to describe the electrochemical behavior of the battery. Accompanied with the electrochemical reaction, the heat is released and followed with the temperature increase of the lithium ion battery.

According to the proposed theories [10–15], the equations in the electrochemical reactions, the heat equilibrium equation and corresponding boundary conditions are listed in Table 1, and the expressions for the required parameters are listed in Table 2.

2.3. Numerical method

The finite element method (FEM) was employed to solve the 1D electrochemical model and 3D thermal model [16–19]. The above mentioned governing equations are discretized by the FEM. COMSOL Multiphysics® was employed as the solver to simulate the thermal behavior of the NCM–LTO cells, while the NCM–LTO battery model in this work was developed with Matlab®. For computational efficiency, the layered-structure of the cells is taken as a homogenous material. The computational mesh used in the simulation is shown in Fig. 2. In order to ensure the numerical accuracy and save the computing time, a half model with geometrical symmetry is created. There are 358 elements in the 1D electrochemical model. There are 24,860 tetrahedral elements, 10,490 triangular elements, and 776 edge elements in the 3D thermal analysis. Moreover, the grid independence study to verify the accuracy of the simulation results was carried out. The numerical results are found to be accurate within 2% when the grids are refined threefold. Time increment satisfying the stability criteria for the constant current discharge was calculated as 10 s.

3. Experimental

A commercial 945 mA h lithium titanate soft package battery was used in the experiment. Before the experiments, CR2032 coin cells, with lithium foil as counter electrode and 1 M LiPF_6 in EC:DEC:DMC (1:1:1 in mass) as electrolyte, were assembled. The equilibrium potential of the LTO anodes, NCM cathodes and the open circuit potential curves of the lithium titanate battery at different states of charge were measured and shown in Fig. 3. The entropy change is described as $\Delta S = nF\partial E_{OC}/\partial T$, where n equals the number of electrons per reaction, n is taken to be equal to 1 for lithium battery. The entropy changes of lithium titanate based anodes and lithium nickel–cobalt–manganese-oxide cathodes were adopted from [3]. Viswanathan et al. [3] computed the entropy change of the full cell for NCM–LTO battery from individual electrode data. According to $\partial E_{OC}/\partial T = \Delta S/nF$, the temperature coefficient $\partial E_{OC}/\partial T$ as a function of state of charge (SOC) is plotted in Fig. 4.

Besides, ARC experiments were carried out to analyze the thermal behavior of lithium titanate battery under adiabatic

Download English Version:

<https://daneshyari.com/en/article/7163172>

Download Persian Version:

<https://daneshyari.com/article/7163172>

[Daneshyari.com](https://daneshyari.com)