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Review of Specific Heat Capacity Determination of Lithium-Ion Battery

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Abstract

This paper reviews different methods for determination of specific heat capacity of lithium-ion batteries. Thermal modelling of lithium-ion battery cells and battery packs is of great importance. The specific heat capacity of the battery is an essential parameter for the establishment of the thermal model, and it is affected by many factors (such as SOC, temperature, etc.). The scientific purpose of this paper is to collect, sort out and compare different measurement methods of specific heat capacity of battery. The advantages and disadvantages of different methods are discussed. The applicability of each measurement method for various battery types and the required experimental conditions are discussed. The factors influencing the specific heat capacity of the battery are also summarized.

Keywords: lithium-ion battery; specific heat capacity; method of measurement; influence factor.

1. Introduction

Applications of lithium-ion batteries are in great demand. Although lithium-ion batteries have low memory effects, high specific energy and power density, the increasing charging and discharging power capability rates of lithium-ion batteries raises safety concerns. High temperatures can shorten life, reduce capacity, and even cause a battery to catch fire or increase the risk of thermal runaway. The non-uniform distribution of battery temperature

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will lead to the inconsistency of internal resistance, capacity and so on, thus reducing the output voltage and available capacity of the whole battery pack. Because of the problems mentioned above, it is very important to build a heat model for the battery pack and design a heat management system, and the specific heat capacity of the battery is one of the essential parameters.

The specific heat capacity of different batteries may vary greatly due to the different materials, internal structures and production processes. In addition, the batteries have complex chemical composition, and complex chemical reactions occur in the battery during charging and discharging and aging, leading to the change of chemical composition and phase structure on its electrodes. Therefore, the specific heat capacity of the battery will be affected by SOC, SOH and temperature and so on.

There are many ways to measure the specific heat capacity of a battery. The results obtained by different measurement methods are different. The scientific purpose of this paper is to collect, sort out and compare different measurement methods of specific heat capacity of battery. The advantages and disadvantages of different methods are discussed. The factors influencing the specific heat capacity of the battery are also summarized.

2. Method of measurement

2.1. Mass-weighted average

The specific heat capacity is of additive quality, so the total specific heat capacity of the battery can be calculated according to the density, volume and specific heat capacity of each material of the battery:

$$\rho C_p = \frac{\sum_i \rho_i c_i v_i}{\sum_i v_i} \tag{1}$$

where ρ, ρ_i: The density of the cell and constituent materials, respectively; C_p, c_i: The specific heat capacity of the cell and constituent materials, respectively; v_i : The volume of constituents. This method is the most straightforward approach but it requires accurate values for both the mass and specific heat capacity for all constituents in the cell. This usually involves either dissecting the test cell or gaining access to proprietary data from the manufacturer. Some researchers use surrogate data cited in existing references without consideration for differences in the batteries. The difference between the computational results and the values measured by ARC calorimeter can be considerable 8.5%[1] .

2.2. adiabatic calorimeter

For batteries, the use of adiabatic calorimeter is the most standard and most appropriate method for measuring specific heat capacity. Heating was carried out on the battery, the measuring cell absorbs heat and it's temperature changes over time, if there is no heat exchange between the system and environment, the specific heat capacity of the battery can be calculated according to the battery quality and heat generation:

$$P = C_p m \frac{dT}{dt} \tag{2}$$

where P : Heating power; m : Mass. T : Battery temperature; t : Time. High vacuum insulation is usually adopted to eliminate the heat transfer of gas, and a radiation screen is installed to reduce the heat leakage of radiation. This method requires complicated equipment for high vacuum, while the data analysis is simple.

2.2.1. Accelerating rate calorimeter(ARC)

The ARC has heater wire in heat shield to ensure that the temperature of the heat shield is kept constant or tracked by the control system to eliminate heat exchange caused by temperature difference. In 2013, Nieto N et al. [2] used ARC to measure the specific heat capacity of 10.5Ah lithium-ion pouch power battery at different temperatures. In 2014, g. Vertiz et al.[1] used ARC to analyze the influence of SOC, SOH, electrolyte content and other factors on the specific heat capacity of the battery.

2.2.2. Heat flow calorimeter

In 2015, Bazinski S J et al.[3] used a hot-flow isothermal calorimeter to measure the specific heat capacity of a 14Ah LFP pouch cell. The battery is sandwiched between two isothermal heat sources and the rest is insulated. The heat power P absorbed by the battery is measured by the thermoelectric reactor. By this method, the specific heat capacity of the electric core at different SOC and temperature was studied.

2.2.3. Differential scanning calorimeter(DSC)

DSC calculates the specific heat capacity of the object by measuring the change in enthalpy at the same temperature rise of the object and the reference. First, two empty plates were heated at a certain temperature rise rate, and the heat flow-temperature curve was measured as the baseline. Then heat the plate containing the object to be measured and the reference (usually a high purity Al_2O_3 sapphire). Then C_p can be calculated as:

$$C_P = \frac{C_{Pr} m_r p}{m p_r} \tag{3}$$

Where p, p_r: Heat flux into the sample and the reference, respectively. The thermal insulation requirements of DSC are not strict, the measurement error can reach less than 1%, and the latent heat of materials' phase change can be measured. The experiment is carried out in nitrogen atmosphere, so convective heat transfer is inevitable, which makes it important to make sure the sample is in the same shape as the reference. Otherwise, there will be a big error[4] . Due to this limitation, it is difficult to measure the entire cell, so the battery is usually taken apart to measure the specific heat of its core. In 2014, Maleki H et al. [5] put the core of the polymer lithium ion pouch battery into an aluminum sealing box to measure the specific heat at different temperatures. In 2016, Loges A et al.[6] measured the specific heat of electrode coating materials of three lithium ion batteries at different temperatures. Many researchers used DSC to measure the specific heat capacity of polymer electrolyte, composite cathode and positive electrode materials [13, 14].

2.2.4. mixing method

According to the principle of heat balance, when objects with different temperatures contact, heat will be transferred from high-temperature objects to low-temperature objects, and the temperature difference between the two will gradually decrease and eventually become the same. In this process, the heat lost by the high temperature cell is equal to the heat absorbed by the low temperature reference. The specific heat is calculated from the equation:

$$C_{p\_cell} = \frac{C_{p\_ref} m_{ref} \left(T_{end} - T_{ref}\right)}{m_{cell} \left(T_{cell} - T_{end}\right)} \tag{4}$$

Where T_{ref}, T_{cell}: The temperature of the cell and the reference material before mixing; T_{end}: The temperature after mixing. This method does not require expensive calorimeter, but can only obtain the specific heat at one temperature point in an experiment. Due to the inevitable heat loss, the calibration experiment should be carried out with the known specific heat such as aluminum and H62 brass. In 2014, Guangfeng Yu et al. [7] measured the specific heat of the lithium thionyl chloride batteries at different temperatures and SOC while brass is used for calibration. In 1999, Maleki H et al. [12] measured the heat capacity of sony-18650 lithium ion battery with different open voltage.

The reference materials used for calibration are mostly metal. However, the thermal conductivity of the battery is much smaller than that of the metal, so it takes more time to reach the same temperature and dissipates more heat during mixing process, so errors still occur. Another calibration method is to reasonably set the experimental conditions so that the heat absorbed by the system to the environment is close to the heat dissipated during the mixing process, which is equivalent to adiabatic. But its operations will be complex.

2.2.5. Heat balance equation method

In 2015, Vega D H et al [19] believed that the temperature rise rate in the discharge process of li-ion batteries was determined by the self-generating heat rate and the rate of heat dissipation into the air, and established a heat balance equation (5). Where, R_0 denotes the battery internal resistance; i_B denotes the discharge current; Q_{loss} denotes the heat dissipation power in the experimental process; h denotes the convection heat transfer coefficient; s denotes the battery surface area. However, this model uses the internal resistance model to calculate the heating power of the battery and ignores the reversible thermal power generated by polarization effect and so on, so errors occur.

$$\begin{cases} mC_p \dfrac{\partial T}{\partial t} = R_0 {i_B}^2 - Q_{loss} \\ Q_{loss} = hs(T - T_{amp}) \end{cases} \tag{5}$$

2.3. parameter optimization method

The temperature distribution of the object under certain excitation is related to thermal parameters. The real value of battery's temperature response is obtained through the experiment, and the calculated value of temperature response is obtained from the heat balance equation. The optimal solution of specific heat can be obtained by optimizing the parameters by least square method so that the calculated value is close to the real value.

Various researchers have proposed equivalent thermal circuit (ETC) models with different complexity for both soft-coated and cylindrical batteries [15, 16, 17, 18]. In 2017, Murashko K et al. [8] insulated two ends of cylindrical lithium-ion batteries and assuming there is no axial heat transfer. It is considered that the cell geometry and temperature field are completely symmetrical, so there is no tangential heat transfer. Thus, a one-dimensional heat transfer model with only radial heat transfer is established, as shown in Fig. 1. The heat balance equation of the battery is as follows:

$$\begin{cases} T = T_0 + \dfrac{1}{C_p \cdot \rho \cdot V} \displaystyle\int_{t_1}^{t_{end}} \dot{Q}(t)\,dt - \dfrac{r}{k} \cdot \mathbf{\Theta} \times \mathbf{S} \\ \dot{Q} = \dfrac{\dot{Q}_{ch} + \dot{Q}_{dis}}{2} = \dfrac{I \cdot (U_{ch} - U_{dis})}{2} \end{cases} \tag{6}$$

Where T_0 : The initial temperature; V : Cell volume; $\dot{Q}$: The self-heating rate of the cell; Radius of the cell; Radial thermal conductivity; The 1×N matrix of temperature coefficient; The N×1 matrix of heat flow rate measured by the heat flow gradient sensor (GHFS) attached to the battery surface; $\dot{Q}_{ch}, \dot{Q}_{dis}$: Self-heating rate during charge and discharge, respectively; U_{ch}, U_{dis} : Terminal voltage during charge and discharge, respectively; I : Current.

The charge and discharge cycle is used to calculate the self-heating rate of the battery. It is assumed that the reversible heat in the process of charge and discharge will cancel each other, thus reducing the error of heat generation rate. The specific heat can be calculated by using least square method.

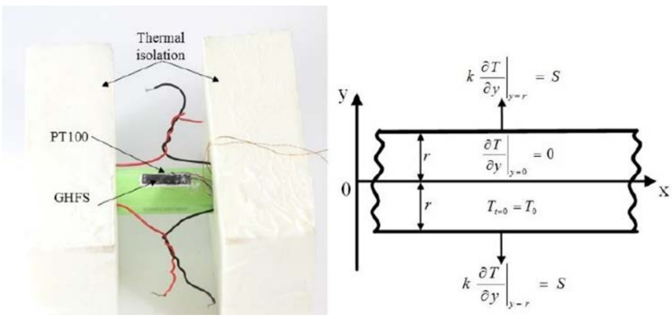

Fig. 1. Radial heat transfer model of cylindrical lithium ion battery[8]

In 2015, Bin Wu et al.[9] studied the thermal parameters of pouch laminated lithium-ion battery. The experimental principle is shown in Fig. 2. A circular ceramic heater was placed between two laminated batteries of the same size. Eight thermocouples are mounted symmetrically on the surface of the battery. The battery is encased in insulating foams and is placed in the approximate vacuum oven in order to reduce the influence of air convection. Two cells' temperature distribution is symmetrical. Power the heating plate and temperature curve over time were obtained. A simplified two-dimensional thermal model was established in COMSOL, and the mass weighted mean values were taken as the initial values to simulate the temperature change. The specific heat and thermal conductivity is obtained by SIMPLEX optimization algorithm.

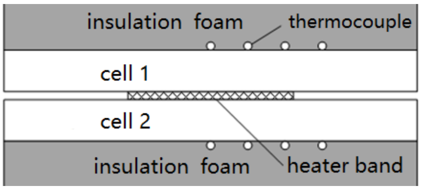

Fig. 2. Experimental principle of parameter optimization method for two-dimensional thermal model

2.4. Equivalent thermal circuit model method

2.4.1. Transient thermal resistance model

2017, H Ruan etc. [10] established an equivalent thermal circuit model of a cylindrical ternary lithium ion battery, as shown in Fig. 3. Where $\dot{Q}_b$ denotes the heat source of the battery itself; C'_p denotes the heat capacity of the cell; T_a denotes the environment temperature; R_T denotes the total thermal resistance from the inside to the outside of the cell. The equilibrium equation of this model is as follows:

$$\dot{Q}_b = C'_p \frac{dT}{dt} + \frac{T - T_a}{R_T} \tag{7}$$

In the experiment, the battery was heated to a certain temperature and then cooled in the air. The temperature of the battery decreased exponentially during cooling, and the measured time constant τ_T can be expressed as:

$$\tau_T = R_T C'_p = \frac{mC'_p}{Ah} = \frac{(T_a - T)dt}{dT} \tag{8}$$

Where A : Surface area of the cell; h : Convective heat transfer coefficient.

Then a 10A, 500Hz current was supplied to self-heat the battery. The heat generation rate was calculated by a first-order RC model. By converting equation (7) into the least square form and associating it with equation (8), the parameters such as thermal resistance, heat capacity and convection heat transfer coefficient can be identified.

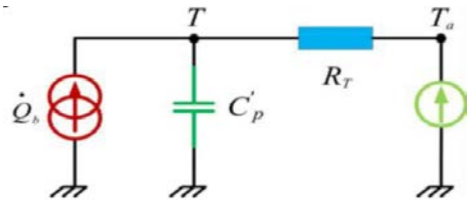

Fig. 3. an equivalent thermal circuit model of a cylindrical ternary lithium ion battery

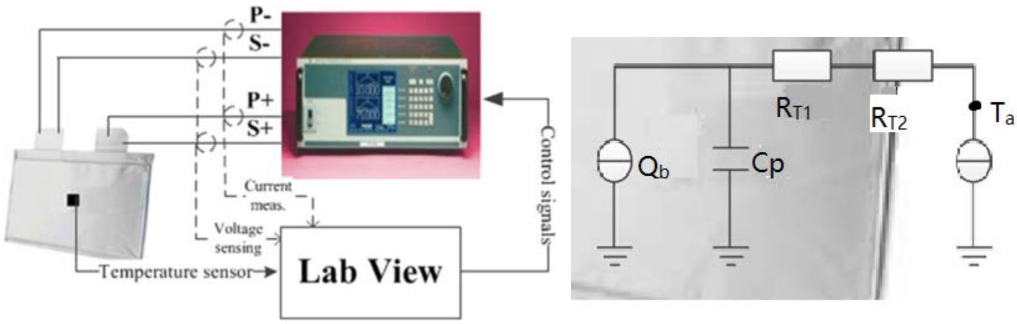

Fig. 4. experimental device and equivalent heat path model of Thermal impedance spectroscopy method[11]

2.4.2. Thermal impedance spectroscopy method

In 2016, Swierczynski M et al. [11] used thermal impedance spectroscopy to analyze the thermal conductivity and specific heat of a 13Ah pouch lithium ion battery. The experimental device and equivalent heat path model are shown as Fig. 4. Where R_{T1} denotes the total thermal resistance from the inside to the outside of the cell; R_{T2} denotes the thermal resistance of the thermocouple. Current of multiple frequency within the range of 0.1mHz to 3mHz was supplied to the cell. In the frequency domain, the thermal impedance spectra are obtained by the ratio of the thermal excitation to the temperature response of the battery surface. The obtained results are presented in the Nyquist plot. Thermal parameters can be computed from the fitted parameters by parameter optimization. In 2013, Matthias Fleckenstein et al. [20] measured the specific heat capacity and thermal conductivity of a cylindrical LFP cell using thermal impedance spectroscopy.

In 2014, wu bin et al.[9] deduced the thermal impedance spectrum model of infinite RC order and extended it to two dimensions, making it more suitable for measuring the thermal parameters of pouch battery.

3. Influence factor analysis

There are several factors that may influence the measurement result of cells' heat capacity.

(1) Electrolyte content. Some measurements require breaking the battery, inserting a temperature sensor into the interior, or taking out the positive and negative electrode-diaphragm coils or laminated structures. In this process, the electrolyte volatilizes, which takes into an error more than 19%[5] .

(2) SOC. During charge and discharge process, lithium-ion move from one electrode to the other one while complex chemical reaction occur occur in the battery. This process changes electrode structure and the chemical composition, and so did the heat capacity. Maleki H[5] et al. found that when OCV increased from 2.75V to 3.75V, the specific heat increased by 14.6%. Guangfeng Yu[7] et al. found that when the battery discharged from SOC=1 to SOC=0, the specific heat capacity decreased by 17.1%.

(3) Temperature. Nieto N[2] found that the cell's specific heat at different temperature changes less than 6%, whileBazinski S J[3] found that the variation can reach 38% within -5℃~55℃.

(4) SOH. The aging of the battery causes changes in its chemical composition and structure, and so did the heat capacity[1] .

4. conclusion

ARC is the most widely used device for measuring the specific heat capacity of lithium-ion batteries. But measurement result of aluminum block shows an error of 9% when the air in the heat chamber is not pumped out. If the gas in the heat chamber is pumped out, the pressure would be too low and the relief valve may break. The measurement accuracy can be improved by measuring the air temperature in the thermal cavity and establishing the thermal correction model.

The thermal parameters of batteries on the electric vehicle may change due to aging, discharging and temperature rising. The strict thermal insulation required by the adiabatic method is difficult to achieve on the vehicle. The parameter optimization method based on FEM software can identify the specific heat capacity and thermal conductivity at the same time. However, this method is more suitable for cylindrical cells and pouch cells, because the aluminum shells of the prismatic cells have high thermal conductivity and little difference in surface temperature. Due to the limitation of instrument precision, the accuracy of the coupled parameters identified by this method is difficult to guarantee. Besides, this method requires a lot of computing resources, and its real-time performance cannot meet the requirements of real-time measurement.

In order to shorten calculation time, equivalent thermal circuit (ETC) models with different degree of complexity are applied. ETC models reduce calculation amount by reducing spatial resolution. It simplified heat transfer process to one dimension, which is only applicable to cylindrical cells with insulation at both ends and thin pouch cells with insulation at four sides. As for the prismatic cells, its structure determines that the in-plane temperature field is not uniform, which leads to the obvious heat transfer on the aluminum shell, so the heat transfer is not one-dimensional. The measurement accuracy may be improved by means of eliminating the influence of aluminum shell or establishing the equivalent thermal path model with multiple branches

Recent research initiated electrothermal impedance spectroscopy as a novel and non-destructive method of identifing the thermal parameters of batteries by defining frequency dependent thermal impedance. This method can be extended to a two-dimensional model by finite element theory and numerical calculation. Therefore, it can be used to measure the thermal conductivity and specific heat capacity of cylindrical cells with assumption of one-dimensional heat transfer and pouch cells. But its application on prismatic hard-case cells still need to be verification and it's measurement time efficiency have yet to be improved.

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References

[1] Vertiz G, Oyarbide M, Macicior H, et al. Thermal characterization of large size lithium-ion pouch cell based on 1d electro-thermal model[J]. Journal of Power Sources, 2014, 272(272):476-484.
[2] Nieto N, Diaz L, Gastelurrutia J, et al. Thermal Modeling of Large Format Lithium-Ion Cells[J]. Journal of the Electrochemical Society, 2013, 160(2):A212-A217.
[3] Bazinski S J, Wang X. Experimental study on the influence of temperature and state-of-charge on the thermophysical properties of an LFP pouch cell[J]. Journal of Power Sources, 2015, 293:283-291.
[4] Liu L, Zhao J, et al. Determination of specific heat of plastics by differential scanning calorimetry[J]. China Rubber/Plastics Technology and Equipment, 2017, 43(18):35-38.
[5] Maleki H, Wang H, Porter W, et al. Li-Ion polymer cells thermal property changes as a function of cycle-life[J]. Journal of Power Sources, 2014, 263(4):223-230.
[6] Loges A, Herberger S, Werner D, et al. Thermal characterization of Li-ion cell electrodes by photothermal deflection spectroscopy[J]. Journal of Power Sources, 2016, 325:104-115.
[7] Yu G, Zhang X, Wang C, et al. Experimental Study on Specific Heat Capacity of Lithium Thionyl Chloride Batteries by a Precise Measurement Method[J]. Journal of the Electrochemical Society, 2013, 160(6):A985-A989.
[8] Murashko K, Mityakov A V, Mityakov V Y, et al. Heat flux based method for determination of thermal parameters of the cylindrical Li-ion battery: Uncertainty analysis[C]// European Conference on Power Electronics and Applications. 2017.
[9] Wu b, Zhang J, et al. Thermal Design Methodology for Traction Lithium-Ion Batteries[D]. Tsinghua University, 2015.
[10] Ruan H, Jiang J, Ju Q, et al. A Reduced Wide-temperature-range Electro-thermal Model and Thermal Parameters Determination for Lithium-ion Batteries [J]. Energy Procedia, 2017, 105:805-810.
[11] Swierczynski M, Stroe D I, Stanciu T, et al. Electrothermal impedance spectroscopy as a cost efficient method for determining thermal parameters of lithium ion batteries: Prospects, measurement methods and the state of knowledge[J]. Journal of Cleaner Production, 2016.
[12] Maleki H, Hallaj S A, Selman J R, et al. Thermal Properties of Lithium-Ion Battery and Components[J]. Journal of the Electrochemical Society, 1999, 146(3):947-954.
[13] Villano P, Carewska M, Passerini S. Specific heat capacity of lithium polymer battery components[J]. Thermochimica Acta, 2003, 402(1):219-224.
[14] Gotcu-Freis P, Cupid D M, Rohde M, et al. New experimental heat capacity and enthalpy of formation of lithium cobalt oxide[J]. Journal of Chemical Thermodynamics, 2015, 84:118-127.
[15] Forgez C, Do D V, Friedrich G, et al. Thermal modeling of a cylindrical LiFePO 4 /graphite lithium-ion battery[J]. Journal of Power Sources, 2010, 195(9):2961-2968.
[16] Lin X, Perez H E, Mohan S, et al. A lumped-parameter electro-thermal model for cylindrical batteries[J]. Journal of Power Sources, 2014, 257(257):1-11.
[17] Ruan H, Jiang J, Ju Q, et al. A Reduced Wide-temperature-range Electro-thermal Model and Thermal Parameters Determination for Lithium-ion Batteries [J]. Energy Procedia, 2017, 105:805-810.
[18] K. A. Murashko, A. V. Mityakov, J. Pyrhonen, V. Y. Mityakov, S. S. Sapozhnikov. Determination of the thermal parameters of high-power batteries by local heat flux measurements. Journal of Power Sources. 2014; 271:48-54
[19] Vega D H, Kelouwani S, Boulon L. Efficient Internal Resistance and Specific Heat Identification of Li-Ion Battery at Low Temperature Conditions[C]// Vehicle Power and Propulsion Conference. IEEE, 2015:1-6.
[20] Fleckenstein M, Fischer S, Bohlen O, et al. Thermal Impedance Spectroscopy - A method for the thermal characterization of high power battery cells[J]. Journal of Power Sources, 2013, 223(223):259-267.