Research on Lithium-Ion Battery with New Flexible Electrode Materials

Qifei Du *
National Demonstration Center for Experimental Engineering Training Education, Tianjin Polytechnic University, Tianjin, 300387, China

* Corresponding author email: duqifei@tiangong.edu.cn

Abstract. The thesis studied the thermal characteristics and influencing factors of the flexible electrode material lithium-ion power battery during the charging and discharging process through a combination of experiment and simulation. Studies have shown that the charge and discharge rate, ambient temperature, and state of charge will affect the battery's thermal characteristics. The greater the charge-discharge rate, the lower the environment, and the lower the state of charge, the greater the battery's healing power. The higher the temperature rise of the battery. As the discharge rate increases, the proportion of ohmic heat in the total heat increases, and the proportion of polarization heat and reaction heat in the total heat decreases: In the case of high-rate discharge, ohmic heat and polarization heat play a major role: environment the lower the temperature, the greater the total internal resistance of the battery, so that the greater the healing power of the battery, the faster the temperature rise of the battery. Besides, the paper proposes an internal heat source model suitable for lithium-ion batteries. The simulation results show that the proposed model can better reflect the battery's internal temperature field during the discharge process. Simultaneously, the model is used to simulate the temperature rise of the battery when the battery is working under harsh conditions and the influence of different convective heat transfer coefficients on the battery's thermal characteristics. The simulation shows that increasing the convective heat transfer coefficient is beneficial to lower the battery's temperature.

Keywords. Lithium battery, flexible electrode material, discharge transient thermal behavior, state of charge.

1. Introduction
With the energy crisis and global climate warming, lithium-ion power batteries have quickly become a research hotspot due to their long cycle life, high energy density, and high working voltage. At present, the types of batteries mainly include lead-acid, nickel-cadmium, nickel-metal hydride, and lithium-ion batteries. Flexible electrode materials, lead-acid and nickel-cadmium batteries appeared relatively early, but as people pay more attention to environmental issues, they are gradually eliminated. Although nickel-hydrogen battery does not have environmental pollution and its performance is better in all aspects, it is compared with the lithium-ion battery. The performance of NiMH batteries is still poor. For example, a lithium-ion battery's operating voltage is about three times that of a nickel-hydrogen battery.
battery, compared with a nickel-hydrogen battery of the same capacity. The volume of lithium-ion batteries can be reduced by 30%, and the weight can be reduced by 50%. Because of their good chemical properties, lithium-ion batteries, which are flexible electrode materials, have achieved rapid development as soon as they came out and have quickly become a research focus.

Many researchers have carried out related studies to solve the core problem of applying this working condition. For example, the inductance active balancing system of lithium-ion power battery for electric vehicles developed by literature. Literature has developed a new single-stage multi-input DC/DC boost converter circuit that can be used for flyback charging from a single cell to a battery pack, and other researchers have carried out exploratory research on the balance problem. Simultaneously, the SOC of the battery as an important balance basis has been widely applied research and method exploration. Based on this, the paper proposes an internal heat source model suitable for lithium-ion batteries. The simulation results show that the proposed model can better reflect the battery's internal temperature field during the discharge process [1]. Simultaneously, the model is used to simulate the temperature rise of the battery when the battery is working under harsh conditions and the influence of different convective heat transfer coefficients on the battery's thermal characteristics. The simulation shows that increasing the convective heat transfer coefficient is beneficial to lower the battery's temperature.

2. Lithium battery performance and structure

2.1. The structure of the lithium-ion battery
Cylindrical lithium-ion batteries include electrodes, separators, organic electrolytes, and shells. The schematic diagram of the structure is shown in Figure 1 below.

![Figure 1. Schematic diagram of the structure of a cylindrical lithium-ion battery](image)

2.1.1. Electrode. The electrode is the core of the battery, which is composed of active material and conductive skeleton. The positive and negative active materials are the source of electric energy. It is an important part of determining the basic characteristics of the battery. Active material refers to the material in which the positive and negative electrodes participate in the flow reaction, generating electrical energy through chemical reactions during discharge. The conductive skeleton is usually called a conductive current collector, which acts to conduct current and evenly divide the electrode surface's current potential [2]. The positive electrode material mainly includes lithium iron phosphate, lithium cobalt oxide, lithium manganate, etc. The negative electrode material is mainly graphite or a carbon material with a structure close to graphite.
2.1.2. **Diaphragm.** The diaphragm is located between the two poles of the battery, and its main function is to prevent the positive and negative active materials from contacting and avoid short circuits inside the battery. The characteristic of the diaphragm is to allow ions to pass through but not to conduct electricity.

2.1.3. **Organic electrolyte.** The electrolyte is a material with high ion conductivity, which transfers charge between the positive and negative electrodes inside the battery. Sometimes the electrolyte also participates in the flow reaction. The electrolyte choice is not based on the conductivity but also the stability between the electrolyte and the active material, high and low-temperature characteristics, and other factors.

2.1.4. **Shell.** The battery case is the container of the battery and plays the role of protecting the electrodes and the battery's reacting substances. The battery case needs to have good mechanical strength, vibration resistance, high and low-temperature resistance, and electrolyte corrosion resistance. Commonly used shells are steel shells, aluminum shells, nickel-plated iron shells, and so on.

2.2. **The working principle of lithium battery**

In this paper, a large-capacity LiFePO4 power battery is selected. The positive electrode material of the battery is LiFePO4, and the negative electrode material is layered graphite. The chemical reaction expression is:

\[
(-)C_6|LiPF_6 - EC + DEC|LiFePO_4(+) \quad (1)
\]

In the formula, the left part represents the negative electrode of the battery. The material is layered graphite; the right part represents the positive electrode of the battery, the material is lithium iron phosphate (LiFePO4); the middle part represents the electrolyte, the solute is lithium hexafluorophosphate (LiPF6), the solvent is a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The charge and discharge reaction of the battery is:

\[
\text{Charging: } LiFePO_4 + 6C \rightarrow Li_{1-x}FePO_4 + Li_xC_6 \quad (2)
\]

\[
\text{Discharging: } Li_{1-x}FePO_4 + Li_xC_6 \rightarrow LiFePO_4 + 6C \quad (3)
\]

The lithium-ion battery is a kind of rechargeable battery, mainly relying on the reciprocating movement of lithium ions between the positive and negative electrodes. The charging and discharging process of the battery is essentially \( Li^+ \) moving between the positive and negative electrodes (as shown in Figure 2). When the battery is charged, \( Li^+ \) is released from the positive electrode compound and inserted into the negative electrode lattice through the electrolyte. In this way, the negative electrode will be in a low-potential lithium-rich state, and the positive electrode will be in a high-potential lithium-poor state, while electrons pass through the outside the circuit enters the carbon negative pole so that the negative pole is in charge balance. When the battery is discharged, the opposite is true [3]. The \( Li^+ \) extracted from the negative electrode is inserted into the positive electrode through the electrolyte, making the positive electrode in a lithium-rich state. To maintain charge balance, electrons pass through an external circuit and enter the positive electrode. In the normal charge and discharge process, lithium ions are only inserted and extracted between the carbon material of the negative electrode layered crystal structure. The oxide of the positive electrode layered crystal structure without destroying the material's structural characteristics. Therefore, it can be considered that the chemical reaction of the bonded ion battery during the charge and discharge process is reversible.
2.3. Heating mechanism of lithium-ion battery

Under normal working conditions, the heat generated inside a lithium-ion battery is mainly composed of two parts: the heat generated by the battery's internal resistance when the current flows inside the battery and the heat generated by the chemical reaction during the working process. The battery's internal resistance includes ohmic internal resistance and polarization of internal resistance. The internal ohmic resistance refers to the resistance of the electrode material inside the battery, the resistance experienced by ions when moving in the electrolyte, the resistance of the diaphragm, the resistance of the current collector, and the contact resistance between various parts of the battery. Polarization internal resistance includes internal resistance caused by concentration polarization and internal resistance caused by electrochemical polarization [4]. The heat generated by the battery's internal resistance during the entire battery charging and discharging process is always positive. The heat of chemical reaction is the heat generated by the chemical reaction between the battery working process components. The chemical reaction that occurs inside the battery may be either an endothermic reaction or an exothermic reaction. The heating power of the battery during operation can be expressed by formula (4):

$$\dot{Q} = \dot{Q}_c + \dot{Q}_p + \dot{Q}_r$$  \hspace{1cm} (4)

In the formula, $\dot{Q}$ represents the total heating power of the battery, W; $\dot{Q}_c$ represents the power generated by the chemical reaction, W; $\dot{Q}_p$ represents the heating power during electrode polarization [5], W; $\dot{Q}_r$ represents the heating power of the ohmic resistance during battery operation, W.

3. Research on the transient thermal characteristics of lithium battery discharge

Table 1 is the battery temperature change curve with time when the battery is charged at a rate of 0.5 °C, 0.75 °C, 1 °C, and 1.5 °C, respectively. It can be concluded that the temperature as whole drops first, then rises, and then drops. This is mainly because the battery's chemical reaction heat in the initial stage of discharge is an endothermic reaction. Although the internal resistance of the battery generates heat, when the charging current is relatively small, the heating power of the internal resistance is less than the endothermic power of the chemical reaction, so the battery will be absorbed. The internal heat of the battery causes the temperature inside the battery to decrease, so there will be a trend of temperature drop at the beginning of the discharge; as the discharge progresses, although the chemical reaction is still an endothermic reaction, the endothermic power is gradually reduced (measured from the back).
seen from the change law of entropy), and the internal resistance of the battery gradually increases, making the heating power of the internal resistance gradually increase, so the total heating power inside the battery is a process from negative to positive, so the battery temperature reaches a certain level Will gradually increase: When entering the constant voltage charging stage, the heating power is gradually reduced due to the gradual decrease of the current, which is less than the heat dissipation power of the battery, so that the battery temperature will gradually decrease [6]. It can also be obtained that in the constant current charging stage, the greater the charging rate, the greater the battery's healing power, and the greater the overall temperature rise of the battery.

Table 1. The relationship between charging time and charging capacity before the temperature rise

| Charging rate (c) | 0.5 | 0.75 | 1 | 1.5 |
|-------------------|-----|------|---|-----|
| Charging time (s) | 500 | 350  | 234 | 42  |
| Charging capacity (Ah) | 0.7 | 0.73 | 0.65 | 0.18 |

Under normal temperature, when the battery is charged at a rate of 0.2℃, 0.5℃, 1.0℃, and 2.0℃, the terminal voltage of the battery varies with the charging time. From the figure, it can be concluded that the smaller the charging current, the longer the charging time. This is mainly because the battery's capacity is fixed, and the capacity is the product of current and time. Therefore, the smaller the current, the longer the charging time; the higher the current, the higher the voltage. The higher, the faster. This is mainly because the battery's ohmic internal resistance is approximately constant during charging. The greater the current, the greater the ohmic voltage. Besides, the Tafel equation shows that the polarization voltage increases with the increase of current. Therefore, the sum of ohmic voltage and polarization voltage will increase with the increase of current, and the total battery terminal voltage will increase faster with the increase of current. In the initial and final stages of constant current charging, the voltage rises quickly [7]. This is mainly due to the internal resistance of the battery. In the early stage of charging, the battery will generate internal voltage due to the internal resistance, which causes the battery voltage to rise rapidly in the initial stage. The later period was mainly because the polarization became stronger, and the polarization potential increased, which caused the battery terminal voltage to rise sharply. As shown in Figure 3.

![Figure 3. The curve of the terminal voltage of the battery with the discharge capacity](image)

When the batteries are charged in different environments, the battery temperature varies with the charging time. It can be seen from the figure that when the ambient temperature is -20℃, -10℃, 0℃, 10℃, 20℃, the time required to charge the battery is 1.34h, 2.03h, 2.32h, 2.15h, 2.85h respectively, that
is, the lower the ambient temperature, the longer the charging time. This is mainly because of the lower ambient temperature, the lower the ion transfer rate inside the battery, which makes the charging time longer.

4. Conclusion

In this paper, the estimated value is used as the balance reference value. Based on the single unbalance degree calculation, a real-time active balancing method for on-board battery packs is proposed. Based on this method and balancing strategy, an on-board battery management system is developed for dynamic balance adjustment of battery pack SOC: It is verified by actual simulation operation test that this method can achieve a better balance effect, can realize the dynamic battery balance adjustment of the battery, and ensure its Safety in working condition.

References

[1] Zhou, G., Li, F., & Cheng, H. M. Progress in flexible lithium batteries and future prospects. Energy & Environmental Science, 7(4) (2014) 1307-1338.

[2] Meng, Y., Wu, H., Zhang, Y., & Wei, Z. A flexible electrode based on a three-dimensional graphene network-supported polyimide for lithium-ion batteries. Journal of Materials Chemistry A, 2(28) (2014) 10842-10846.

[3] He, J., Wang, N., Cui, Z., Du, H., Fu, L., Huang, C., & Li, Y. Hydrogen substituted graphdiyne as carbon-rich flexible electrode for lithium and sodium ion batteries. Nature communications, 8(1) (2017) 1-11.

[4] Lee, S. Y., Choi, K. H., Choi, W. S., Kwon, Y. H., Jung, H. R., Shin, H. C., & Kim, J. Y. Progress in flexible energy storage and conversion systems, with a focus on cable-type lithium-ion batteries. Energy & Environmental Science, 6(8) (2013) 2414-2423.

[5] Huang, X., Sun, B., Li, K., Chen, S., & Wang, G. Mesoporous graphene paper immobilised sulfur as a flexible electrode for lithium–sulfur batteries. Journal of Materials Chemistry A, 1(43) (2013) 13484-13489.

[6] Qiu, W., Jiao, J., Xia, J., Zhong, H., & Chen, L. A Self-Standing and Flexible Electrode of Yolk-Shell CoS2 Spheres Encapsulated with Nitrogen-Doped Graphene for High-Performance Lithium-Ion Batteries. Chemistry–A European Journal, 21(11) (2015) 4359-4367.

[7] Zheng, Z., Retana, M., Hu, X., Luna, R., Ikuhara, Y. H., & Zhou, W. Three-dimensional cobalt phosphide nanowire arrays as negative electrode material for flexible solid-state asymmetric supercapacitors. ACS Applied Materials & Interfaces, 9(20) (2017) 16986-16994.