Analysis of Thermal Behavior of Lithium-Ion Batteries During Pulse Discharge: Postprint

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Abstract

This study employs the combined technique of an accelerating rate calorimeter and a battery charge-discharge cycler to real-time measure the variations in voltage, current, temperature, and temperature rise rate of lithium titanate batteries during pulsed discharge. The voltage curve exhibits a sharp initial decrease followed by a subsequent increase during the pulse and the following rest period. Owing to the presence of pulses, the battery temperature is higher than that during normal discharge, and the temperature rise rate curve also shows a sharp increase at the pulse instant; however, as the internal battery temperature increases, the influence of pulses on both temperature and temperature rise rate diminishes. Furthermore, due to the thermal lag effect, the battery temperature does not exhibit a significant increase at the pulse instant.

Full Text

Preamble

The Thermal Response of Lithium Titanate Battery during Pulse Discharge

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Abstract

This study employs an Accelerating Rate Calorimeter (ARC) combined with a battery charging/discharging cycler to dynamically measure the voltage, current, temperature, and temperature rise rate of lithium titanate batteries during pulse discharge. The voltage curve exhibits an initial sharp drop followed by a recovery during the pulse and subsequent rest period. Battery temperature remains higher during pulse discharge compared to normal discharge, and the temperature rise rate increases sharply at the pulse instant. However, the influence of pulse on temperature and temperature rise rate diminishes as the internal battery temperature increases. Additionally, due to thermal lag, no immediate temperature rise is observed at the pulse instant.

Keywords: Lithium titanate battery; discharge; pulse; temperature; temperature rising rate

Introduction

With increasing concerns over petroleum depletion and atmospheric pollution, new energy vehicles powered by alternative energy sources have attracted significant attention. Among various energy forms, lithium-ion batteries are considered one of the most promising power sources for new energy vehicles due to their high voltage, large specific energy, long cycle life, low self-discharge rate, absence of memory effect, capability for fast charging/discharging, and environmental friendliness. In particular, lithium titanate batteries exhibit high thermal safety and stability, making them especially suitable for electric vehicles (EVs), hybrid electric vehicles (HEVs), and energy storage systems. However, EVs impose stringent requirements on onboard power batteries, which differ from starter batteries in conventional internal combustion engine vehicles. EV batteries primarily operate through medium-current continuous discharge, occasionally interrupted by high-current discharge events during vehicle startup, hill climbing, or acceleration, and are characterized by deep cycling usage. These high-current discharge scenarios resemble pulse discharge processes in batteries.

Previous studies [5-8] have employed battery structural models to investigate the effects of pulse charging/discharging on internal ion transfer, diffusion, and electrochemical reactions. Bernardi et al. [9] analyzed the electrochemical behavior of batteries during pulse and subsequent rest periods through mathematical modeling. However, few studies have examined the thermal behavior of batteries during pulse discharge and post-pulse rest periods, or investigated how pulses affect temperature throughout the discharge and cycling processes. This research gap is particularly significant for understanding thermal management requirements in EV applications.

In this study, we combine an Accelerating Rate Calorimeter with a battery charging/discharging cycler to dynamically measure heat generation in lithium titanate batteries under adiabatic conditions during cycling. By comparing temperature and temperature rise rate variations between pulse and non-pulse discharge conditions, we investigate the thermal behavior of these batteries to provide a basis for thermal management of onboard power batteries.

1. Experimental Samples

The experimental samples were pouch-type lithium titanate batteries, as shown in [Figure 1: see original paper]. The battery specifications are as follows: capacity of 1000 mAh, nominal voltage of 2.8 V, cut-off voltage of 1.5 V, mass of 33.0$±$0.5 g, and specific heat capacity of 1.0 J/(g·K). The positive electrode material was nickel-cobalt-manganese oxide (LiNixCoyMnzO4), while the negative electrode material was lithium titanate (Li4Ti5O12). The electrolyte consisted of lithium hexafluorophosphate (LiPF6) at a concentration of 1 mol/L dissolved in a solvent mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a mass ratio of 1:1.

Detailed experimental parameters are listed in .

2. Experimental Apparatus and Methods

This study employs a combined technique using an Accelerating Rate Calorimeter (ARC) and a battery charging/discharging cycler to measure temperature variations in lithium titanate batteries during cycling in real time, as illustrated in [Figure 2: see original paper]. The ARC (manufactured by Thermal Hazard Technology, UK) provides temperature data and temperature rise rates under adiabatic conditions; its structure and operating principle are described in reference [10]. The battery cycler is a LAND battery testing system with a voltage range of 0-5 V and current range of 0-1500 mA, capable of performing constant-current discharge, constant-current charging, constant-voltage charging, rest periods, and cycling operations while outputting current and voltage data throughout the process.

During experiments, a properly conditioned lithium titanate battery was secured inside the ARC reaction chamber. Two nickel strips wrapped with insulating tape were connected at one end to the battery tabs and passed through holes in the explosion-proof chamber to connect at the other end to the alligator clips of the battery tester. After securing the battery and closing the chamber, the experimental setup was complete as shown in [Figure 2: see original paper]. The ARC initial temperature was set to 25 °C with a temperature sensitivity of 0.005 °C/min. Taking experimental case No. 1 (cycling at 0.2 C rate) as an example, the specific test procedure settings for the LAND battery testing system are detailed in .

According to reference [11], batteries generate the most heat when the state of charge (SOC) is between 30% and 70%. Therefore, following reference [9], we selected SOCs of 35% and 65% for pulse discharge tests. The pulse discharge duration was 40 s, followed by a 5-min rest period before resuming discharge at the initial current (200 mA or 500 mA). The pulse condition setup is shown in [Figure 3: see original paper].

3. Results and Discussion

3.1 Voltage-Current Characteristics

The differences in voltage-current behavior between pulse discharge and normal discharge for lithium titanate batteries in the ARC are illustrated using the 0.2 C rate case in [Figure 4: see original paper]. Figure 4: see original paper shows the voltage-current curve during 0.2 C cycling. During discharge, the voltage decreases; after discharge ends, the voltage instantly recovers due to overpotential, with larger recovery amplitudes observed at higher discharge currents. In the subsequent charging process, the voltage continues to rise until reaching the cut-off voltage, followed by constant-voltage charging until the current drops to 20 mA. After a 1-min rest period, the next cycle begins. Figure 4: see original paper shows the corresponding voltage-current pulse variations at 0.2 C rate.

The voltage variations during pulse stages at different current rates are compared in [Figure 5: see original paper], where the red curve represents pulse voltage and the black curve represents normal voltage variation. Both curves show the second pulse during partial discharge, with the shaded area indicating corresponding voltage changes. The battery terminal voltage can be expressed by equation (1):

$$U = E - i\eta$$

where $i\eta$ represents the battery overpotential caused by polarization. Based on different polarization mechanisms, overpotential can be classified into three types: (1) electrochemical polarization, (2) concentration polarization, and (3) resistance polarization, with the first two being more significant.

The electrochemical polarization is closely related to the rate of lithium ion intercalation/deintercalation at the positive and negative electrodes, which can be expressed by the Butler-Volmer kinetics [12] as:

$$J = J_0 \left[\exp\left(\frac{\alpha_a F \eta_{act}}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta_{act}}{RT}\right)\right]$$

where J is the current density, α_a and α_c are transfer coefficients (between 0 and 1), F is the Faraday constant (96,487 C/mol), R is the gas constant (8.3143 J/(mol $\cdot$ K)), T is the battery temperature in Kelvin, and J_0 is the exchange current density.

Concentration polarization at the electrodes reflects the difference in lithium ion concentration within the solid electrode. According to the Nernst equation, the lithium concentration at the electrode surface changes significantly during the pulse instant, causing concentration polarization to increase [5]. Additionally, a concentration gradient of lithium ions exists in the electrolyte solution during the pulse, and longer pulse durations create larger concentration gradients that require more time to return to initial concentrations [5].

Consequently, various polarization effects increase during the pulse process, causing the battery voltage to drop sharply. For pulses at 200 mA, the voltage dropped by 0.77 V, while for 500 mA pulses, the drop was 0.58 V. During the 5-min rest period after the pulse, no current flows through the battery, so electrochemically induced overpotential becomes zero. Therefore, the battery voltage during the rest period is higher than that during normal discharge at the same moment, resulting in voltage recovery. The voltage increased by 0.12 V for 200 mA pulses and 0.31 V for 500 mA pulses. As shown in equation (3), kinetic overpotential magnitude is closely related to current density (current magnitude for a given battery), with larger currents requiring greater kinetic overpotential. Therefore, [Figure 5: see original paper] shows that the voltage plateau at 500 mA cycling is higher than at 0.2 C rate, and the overpotential generated at 500 mA exceeds that at 200 mA, which reasonably explains the voltage drop and recovery values observed during pulsing according to equation (1).

3.2 Temperature Variations at Different Cycling Rates

[Figure 6: see original paper] shows the absolute temperature rise curves at different current rates. As seen in Figure 6: see original paper, during five consecutive charge-discharge cycles, the temperature curve exhibits a stepwise increasing trend. Clear temperature inflection points appear at the transition between discharge and charge processes, while the transition from charge to discharge shows a gradual change. This occurs because reversible heat is negative during low-rate charging but positive during discharge [13], making the discharge process clearly exothermic with significantly greater heat generation than charging. Consequently, the temperature rise rate slows after discharge, preventing smooth temperature transitions. Figure 6: see original paper shows essentially the same trend, with temperature curves rising steadily within each charge-discharge cycle.

Heat generation during lithium-ion battery charging and discharging arises from multiple sources, including Joule heating, electrochemical heat, and chemical heat from internal reactions. However, during normal charge-discharge cycling, the primary heat sources are reversible and irreversible heat. The heat generation relationship can be expressed as:

$$Q = Q_{rev} + Q_{irrev} = I(T\frac{dE}{dT} - E + U)$$

where I is the current, T is temperature, E is the open-circuit voltage, and U is the terminal voltage. Equation (5) shows that internal heat release is positively correlated with current. Therefore, heat release during 500 mA cycling exceeds that during 200 mA cycling. After four discharge-charge cycles, the battery temperature increased by 23.33 K at 0.5 C rate, which is 3.09 K higher than the 20.24 K increase observed at 0.2 C rate.

Comparing Figure 6: see original paper and (b) reveals that at 200 mA, battery temperature during pulsed cycling exceeds that during normal cycling. At 500 mA, the temperature increase during the first discharge pulse is greater than in normal cycling conditions. This occurs because concentration polarization and electrochemical polarization increase during pulsing, leading to greater irreversible heat generation [5, 9] and consequently higher battery temperatures.

To specifically examine pulse effects on battery temperature, [Figure 7: see original paper] compares temperature increases during discharge processes. The results show that temperature rise during pulse discharge exceeds that during non-pulse discharge. However, in an adiabatic environment, as heat accumulates and internal temperature rises, the additional temperature increase due to pulsing becomes less pronounced. For 200 mA discharge, battery temperature remains higher under pulse conditions throughout cycling. For 500 mA discharge, the first pulse produces a temperature increase 1.48 K higher than normal cycling, but this pulse-induced temperature increment decreases as internal temperature rises. Due to the 0-1500 mA current limitation of our battery cycler, the pulse current was set to 1400 mA, which is only 7 times the 200 mA baseline and 2.8 times the 500 mA baseline. This relatively low pulse ratio results in less pronounced temperature rise during 500 mA pulse discharge.

3.4 Temperature Rise Rate Comparison

[Figure 8: see original paper] presents temperature rise rate profiles under different cycling conditions. Both Figure 8: see original paper and (b) show that temperature rise rates during discharge exceed those during charging because reversible heat is positive during discharge and negative during charging. According to equation (5), heat release during discharge is greater than during charging, corresponding to higher temperature rise rates. Additionally, the temperature rise rate curves show clear increases during the two pulse stages in each discharge process, rising above the normal discharge temperature rise rate curve and returning to baseline after the pulse. As cycling progresses, the pulse-induced temperature rise rate variation diminishes due to heat accumulation and the thermal lag of internal materials. Comparing Figure 10: see original paper and (b) reveals that pulse-induced temperature rise rate changes are smaller at 200 mA than at 500 mA, which is consistent with the direct proportionality between heat generation and current magnitude.

Conclusion

This study employs a combined ARC and battery cycler technique to dynamically measure voltage, current, temperature, and temperature rise rate variations in lithium titanate batteries during pulse discharge. The key findings are: (1) Due to pulse effects on battery overpotential, voltage curves drop sharply during pulses and recover to values higher than normal discharge voltage during the subsequent 5-min rest period; (2) Battery temperature and temperature rise rate during pulse discharge exceed those during normal discharge, though these pulse effects weaken as internal battery temperature increases; (3) Due to thermal lag, no immediate temperature rise is observed at the pulse instant. These conclusions enhance understanding of battery heat release behavior during vehicle startup and acceleration, providing a basis for battery system thermal management. Additionally, due to the limited current range of our battery cycler, the thermal behavior of lithium titanate batteries at higher pulse rates requires further investigation, as does the potential for pulse discharge at elevated temperatures to trigger thermal runaway.

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