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

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Abstract

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

Full Text

Preamble

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Abstract: This study employs an Accelerating Rate Calorimeter (ARC) combined with a battery charge-discharge cycler to dynamically measure variations in 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 both the pulse period and subsequent rest interval. Battery temperature exceeds that of normal discharge due to the pulse effect, and the temperature rise rate curve also increases sharply at the pulse instant. However, the influence of pulse on temperature and temperature rise rate diminishes as the internal battery temperature increases. Furthermore, due to thermal lag, the battery temperature does not show an immediate significant increase at the pulse instant.

Keywords: lithium titanate battery; discharge; pulse; temperature; temperature rise rate

With increasing concerns over petroleum depletion and atmospheric pollution, new energy vehicles powered by alternative energy sources have attracted growing attention. Among various energy forms, lithium-ion batteries are considered one of the most promising power sources for new energy applications. Lithium-ion batteries offer superior performance characteristics including high voltage, large specific energy, long cycle life, low self-discharge rate, no memory effect, fast charge-discharge capability, and environmental friendliness. In particular, lithium titanate batteries exhibit high thermal safety and stability, making them especially suitable for electric vehicles, hybrid electric vehicles, and energy storage systems. However, pure electric vehicles impose stringent requirements on onboard power batteries. Unlike conventional starter batteries for internal combustion engine vehicles that primarily operate with medium-current continuous discharge, automotive power batteries are characterized by medium-current continuous discharge with intermittent high-current discharge during startup, climbing, or acceleration, and are mainly used in deep-cycle applications. The intermittent high-current discharge conditions of power batteries resemble pulse discharge processes. Previous studies have employed battery structural models to investigate the effects of pulse charge-discharge on internal ion transfer, diffusion, and electrochemical reactions. Bernardi et al. 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 the influence of pulses on temperature during discharge and charge-discharge cycling processes.

This study combines an Accelerating Rate Calorimeter with a battery charge-discharge cycling system to dynamically measure heat generation during cycling of lithium titanate batteries under adiabatic conditions. By comparing temperature and temperature rise rate variations with and without pulse discharge conditions, the thermal behavior of batteries is investigated to provide a basis for thermal management of automotive power batteries.

1. Experimental Samples

The experimental battery is a pouch-type lithium titanate battery shown in [Figure 1: see original paper]. The battery has a capacity of 1000 mAh, a nominal voltage of 2.8 V, and a cut-off voltage of 1.5 V. The battery mass and specific heat capacity are 33.0±0.5 g and 1.0 J/(g·K), respectively. The cathode material is nickel cobalt manganese oxide (LiNixCoyMnzO4), and the anode material is lithium titanate (Li4Ti5O12). The electrolyte consists of lithium hexafluorophosphate dissolved in a 1:1 mass ratio mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), with a molar concentration of 1 mol/L. Detailed experimental parameters are listed in .

2. Experimental Setup and Methods

This study employs a combined Accelerating Rate Calorimeter and battery charge-discharge cycler to measure temperature variations during battery cycling in real time, as illustrated in [Figure 2: see original paper]. The ARC (Accelerating Rate Calorimeter) from Thermal Hazard Technology (UK) provides temperature data and temperature rise rates under adiabatic conditions. The battery cycler is a Land Battery Test System with a voltage range of 0-5 V and current range of 0-1500 mA, capable of constant-current discharge, constant-current charging, constant-voltage charging, rest periods, and cycling operations, while outputting current and voltage data during cycling.

During experiments, a well-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 with alligator clips from the battery test system. After fixing the battery, the chamber lid was closed. The ARC initial temperature was set to 25 °C with a temperature sensitivity of 0.005 °C/min. Using experimental case 1 (0.2 C rate cycling) as an example, the specific test procedure settings for the Land battery test system are shown in .

According to literature, batteries release maximum heat at state-of-charge (SOC) levels between 30%-70%. Following reference [9], pulse discharge was performed at 35% and 65% SOC with a pulse duration of 40 s and a 5-min rest period after each pulse, followed by continued discharge at the initial current (200 mA/500 mA). The pulse condition setup is shown in [Figure 3: see original paper].

3. Results and Discussion

3.1 Voltage-Current Characteristics

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

Differences in voltage curves during pulse stages at various current rates are shown in [Figure 5: see original paper], where red curves represent pulse voltage and black curves represent normal voltage variations, with the second pulse selected for detailed comparison. The shaded areas indicate corresponding voltage changes. The battery terminal voltage can be expressed by Equation (1):

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

The lithium ion insertion/extraction rate at the positive and negative electrodes is closely related to electrochemical overpotential magnitude, which can be expressed by the Butler-Volmer kinetics as follows:

where J is current density, α and β 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 · K)), T is battery temperature in Kelvin, and i_0 is exchange current density.

Concentration polarization at the electrodes reflects the difference in lithium ion concentration within solid electrodes. According to the Nernst equation, lithium concentration at the battery electrodes changes significantly during pulses, causing increased concentration polarization. During pulse discharge, a concentration gradient exists in the electrolyte, and longer pulse durations create larger gradients requiring more time to return to initial concentrations.

Consequently, battery voltage drops sharply during pulses due to increased polarization. For 200 mA discharge pulses, voltage dropped by 0.77 V, while for 500 mA pulses, the drop was 0.58 V. During the 5-min rest period after each pulse, with no current flowing, the electrochemically induced overpotential becomes zero, causing voltage to recover to levels higher than normal discharge voltage at that moment. Voltage increased by 0.12 V after 200 mA pulses and 0.31 V after 500 mA pulses. As shown in the kinetic equation, overpotential magnitude is closely related to current density (current magnitude for a given battery), with larger currents requiring greater kinetic overpotential. Therefore, the voltage plateau at 500 mA cycling is higher than at 0.2 C cycling, and the overpotential generated at 500 mA exceeds that at 200 mA, reasonably explaining the voltage drop and recovery values.

3.2 Temperature Variation at Different Cycling Rates

[Figure 6: see original paper] shows absolute temperature rise curves at different current rates. During five consecutive charge-discharge cycles, temperature exhibits a stepwise increasing trend. Clear temperature inflection points appear at discharge-charge transitions, while charge-to-discharge transitions show gradual changes. During low-rate charging, reversible heat is negative, while during discharge it is positive, corresponding to an exothermic process with significantly greater heat generation than charging. Therefore, after discharge, the temperature rise rate slows and the temperature curve cannot transition smoothly. Figure 6: see original paper shows similar trends, with temperature rising steadily during each charge-discharge cycle.

Heat generation during lithium-ion battery charge-discharge is multifaceted, including Joule heating, electrochemical heat, and chemical reaction heat. However, during normal charge-discharge, internal heat primarily consists of reversible and irreversible heat, with the heat generation relationship expressed by Equation (5). According to Equation (5), internal heat release is positively correlated with current; thus, heat release at 500 mA exceeds that at 200 mA. After four discharge-charge cycles, the 0.5 C battery temperature increased by 23.33 K, 3.09 K higher than the 0.2 C case (20.24 K).

Comparison of Figure 6: see original paper and (b) reveals that at 200 mA, battery temperature exceeds normal discharge conditions due to pulses. At 500 mA, temperature increase during the first discharge pulse exceeds normal discharge conditions because increased concentration and electrochemical polarization during pulses enhance irreversible heat, resulting in higher battery temperatures.

To specifically examine pulse effects on temperature, temperature rise values during discharge processes were compared in [Figure 7: see original paper]. Pulse discharge produces greater temperature increases than non-pulse discharge. However, in an adiabatic environment, as heat accumulates and internal temperature rises, the temperature increase due to pulses becomes less pronounced. At 200 mA, battery temperature under pulse conditions consistently exceeds normal discharge. At 500 mA, the first discharge pulse temperature increase is 1.48 K higher than normal discharge, but this increment decreases as internal temperature rises. Due to the 0-1500 mA current range limitation of the test system, pulse current was set to 1400 mA (7× the 200 mA baseline and 2.8× the 500 mA baseline). The relatively low pulse multiplication factor results in less pronounced temperature rise during 500 mA pulse discharge.

3.4 Temperature Rise Rate Comparison

[Figure 8: see original paper] shows temperature rise rate profiles under different cycling conditions. The temperature rise rate during discharge exceeds that during charging because reversible heat is positive during discharge and negative during charging. According to Equation (5), heat release during discharge exceeds that during charging, corresponding to higher temperature rise rates. Additionally, during the two pulse stages in each discharge process, the temperature rise rate curve shows clear increases above normal discharge levels, returning to baseline after each pulse. As cycling progresses, due to internal heat accumulation and thermal lag of battery materials, the temperature rise rate change caused by pulses diminishes in later discharge cycles. Comparison of Figure 10: see original paper and (b) shows that pulse-induced temperature rise rate changes are smaller at 200 mA than at 500 mA, consistent with the direct proportionality between heat release and current magnitude.

Conclusion

This study employed combined ARC and battery cycler technology to dynamically measure voltage, current, temperature, and temperature rise rate variations during pulse discharge of lithium titanate batteries. The findings are: (1) Due to pulse effects on overpotential, voltage curves drop sharply during pulses, then recover during the subsequent 5-min rest period to levels exceeding normal discharge voltage at that moment; (2) Pulse discharge produces higher temperatures and temperature rise rates than normal discharge, though this influence weakens as internal battery temperature increases; (3) Due to thermal lag, battery temperature does not show an immediate significant increase at the pulse instant. These conclusions enhance understanding of battery heat release behavior during startup and acceleration of electric and hybrid vehicles, providing a basis for battery system thermal management. Additionally, due to current range limitations of the test system, the thermal behavior of lithium titanate batteries at higher pulse rates requires further investigation, as does whether pulse discharge at elevated temperatures could trigger thermal runaway.

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Note: Figure translations are in progress. See original paper for figures.