



Graphitic carbon anode temperature excursions reflect crystallographic phase transitions in lithium-ion cells



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HIGHLIGHTS

- Anode temperature (T_a) is sensitive to phase transitions in graphitic carbon.
- Transitions in T_a matches with lithiation-induced phase transitions in graphitic carbon.
- At all rates of charging, T_a also exhibits a unique maximum at 61% SoC.
- Surface temperature is a poor indicator of internal temperature.
- T_a is a reliable parameter for adaptive charging to safely reduce charging time.

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ABSTRACT

Surface temperature measurement of lithium-ion cells provides a limited view of internal physical processes during charging. Using a recently developed non-invasive battery internal temperature sensor, we now demonstrate that anode temperature reflects physically-based dynamics at the anode that were previously obscured by cell-surface measurements. First, using automated segmentation with a maximum-likelihood piecewise-linear statistical model, we show that features in the anode temperature reproducibly coincide with phase transitions into Stages IVd, IV and I of graphitic carbon lithiation at various charging rates. Second, we show that anode temperature peaks around 61% state of charge, intermediate between Stages II and I of the lithiated graphitic carbon. Third, we demonstrate a sharp and sustained increase in anode temperature at variable state of charge above 85%. These findings open the possibility for improved state-of-charge estimation and adaptive charging profiles that safely reduce charging time.

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1. Introduction

Rechargeable lithium-ion (Li-ion) batteries were first introduced to the consumer market in 1991 [1–3]. Over the intervening two decades, charging has remained one of the riskier steps in Li-ion battery usage due to the possibility of thermal runaway, that can lead to battery fires [4]. Slow charging rates can guard against thermal runaway. For batteries in electrical utility systems and electric vehicles, slow charging rates and risk of thermal runaway [5] present major barriers to widespread adoption of Li-ion battery technology. An added challenge is that batteries with higher energy density require slower charging rates to avoid thermal runaway or

other irreversible damage. [6–15].

Anode temperature is fundamental to battery safety because thermal runaway starts with temperature-dependent chemical processes at the anode [11]. During charging, the temperature of the graphitic carbon anode increases. At 80 °C, graphite reacts exothermally with commonly used cell electrolytes [16–19], irreversibly modifying the anode properties [11]. Such exothermic reactions at the anode generate heat that increases the cell's global internal temperature, including the anode, cathode and electrolyte. This global temperature rise initiates other cascading exothermic reactions, including electrolyte decomposition above 120 °C and cathode decomposition above 250 °C [20]. Uncontrolled rises in global temperature above 120 °C result in venting, combustion, and explosion. The primary safeguard against thermal runaway during charging is to maintain the anode temperature well below 80 °C.

The physical basis for anode temperature changes during

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charging is a sequence of phase transitions in the crystal structure of graphite at the anode. The graphitic carbon anode acts as the host for lithium to form lithium-intercalated carbon (LiC_x) in a process called lithiation. Penetration of lithium into the anode increases the van der Waals distance between adjacent graphite layers. During charging, LiC_x proceeds in fixed order through four discernible lithiation phases (Stages), beginning with IV and ending with I [21–23]. Each Stage is defined by a characteristic periodicity between Li-occupied and unoccupied graphite layers. As lithiation proceeds from 0% to 100% state of charge (SoC), the LiC_x stoichiometry is initially undefined, i.e., dilute Stage IVd at 10% SoC. At 20% SoC, the first distinguishable phase (IV) is structured with every fourth layer occupied, resulting in an approximate stoichiometry of LiC_{30} . Next in order are Stage III (34% SoC; every third layer occupied; LiC_{18}), Stage II (50% SoC; every other layer occupied; LiC_{12}) and Stage I (100% SoC; every layer occupied; LiC_6) [22].

Transitions between these Stages of lithiation are accompanied by thermal energy changes at the anode. One contributory factor to the thermal energy is a decrease in entropy associated with restructuring of lithium and carbon at the anode [25,26]. Another source of thermal energy is resistive heating, caused when lithium passes from the electrolyte into the anode [27]. A third source of thermal energy is a change in the stacking, which defines the relative positions of the graphite layers [28,29]. Each of these sources contributes thermal energy to a variable extent as a function of SoC.

The relationship between thermal energy and structural changes has almost always been established in half cells containing a graphite anode and a lithium foil auxiliary electrode [25,26]. Until now, the capability of existing techniques has precluded researchers from demonstrating this association between temperature and structure in full, dynamically charging Li-ion cells. Instead, structure-related thermal energy release has been typically inferred through steady-state electrochemical potential measurements on graphite-only half-cells, together with the Nernst equation [21–26]. In functional Li-ion cells, physically co-located cell-internal temperature measurements of the anode would be confounded by proximity of possible sensor locations to thermal energy sources from the cathode and the electrolyte. Cell-surface temperatures, measured from thermocouples or thermal imaging, are also confounded by non-anode sources of thermal energy, and additionally influenced by thermal inertia of the cell and thermal noise from the surrounding environment.

Recently, we developed a non-invasive battery-internal-temperature sensor (NIBITS) technology to directly measure anode temperature (T_a) [30–32]. This method builds on the previously established correlation between anode electrical impedance and temperature [33,34]. The NIBITS technology includes a calibration curve relating phase shift (ϕ) at any single frequency in the 40 Hz–100 Hz range to the anode temperature. For the cell used in this paper, the corresponding calibration curve and the empirical equation that relates ϕ to T_a are provided in Fig. 1. Unlike cell-surface temperature (T_s) measurements that can be distorted by the environmental thermal noise and the cell's thermal inertia, the T_a measured by the NIBITS approach is free from those influences over a wide range of charging rates.

In this paper, we apply NIBITS to provide the first dynamic characterization of anode temperature during charging as it relates to the various Stages of lithiated graphite and the corresponding SoC. First, we show that reproducible features in the anode temperature coincide with lithium-intercalated graphite phase transitions into Stages IVd (7.8–10.0% SoC), Stage IV (16.7–23.2% SoC) and Stage I (80–90% SoC) for charging at less than 1C rate. Second, we show that anode temperature reliably peaks around 61% SoC, regardless of charging rate. Third, we demonstrate a sharp and

sustained increase in anode temperature at variable SoC above 85%, as lithiated graphite is converted to Stage I. We discuss these findings in the context of future strategies to decrease charging time while maintaining safety through dynamic, closed-loop current control.

2. Experimental section

2.1. Li-cells and charging profile

Five Swing 5300 Li-ion cells (manufacturer: Boston Power, Boston, MA, USA), at different stages of their cycle life between 5 and 75 charge–discharge cycles were used in the study. Each cycle corresponded to 70%–99% depth of discharge. Each cell consisted of graphitic carbon anode and lithium manganese dioxide cathode. The cell's nameplate capacity was 5.3-Ah. However, the actual capacity of a new cell cycled less than 10 times was close to 5.5-Ah, and a cell cycled up to 75 times was 5.43-Ah.

We use the conventional battery terminology to describe charging rate. The rate of charge is defined as charging current divided by the theoretical current required to charge the cell in one hour, and it is expressed in terms of C rate (hour^{-1}). For example, a 0.5C charging rate (h^{-1}) would charge a battery to half its capacity in one hour.

Each Swing 5300 cell was first discharged at 0.5C-rate to 2.7 V. After 4 h of rest, the cell depolarized, and cell voltage relaxed to 3.1 V. It was discharged again at C/50 rate to 2.7 V, and then set to rest for 12 h before recharging. At the start of recharging, the cell voltage (E_{cv}) was between 2.7 and 2.8 V. Charging was taken to completion through the “Constant Current–Constant Voltage” (CC–CV) protocol, and the charge capacity obtained at the end of charging was used in calculating SoC shown in all the figures. Anode temperature (T_a) was measured only during the CC-part of the charging protocol. The CC-part of the protocol ended when E_{cv} reached 4.2 V. Lower C-rates took longer time to reach 4.2 V; nevertheless, achieved higher percent of SoC. The time to charge a Li-ion battery from 0% to 100% SoC depended upon the C-rate in the CC-part of the charging protocol: 255 min at 0.25C-rate, 115 min at 0.7-C rate, 85 min at 1C-rate, and 48 min at 2C-rate.

2.2. Measurement of anode temperature using impedance phase angle

Fig. 1(A) provides a schematic of our phase shift measurement apparatus. First, impedance phase angle is measured as the phase shift at a fixed frequency between a small-amplitude alternating current signal applied at the positive and negative terminals of a Li-ion cell and the resulting alternating voltage measured across the same terminals. Next, anode temperature (T_a) is estimated using an empirical relationship between phase shift (ϕ) and T_a at a fixed frequency, specific to the Swing 5300 cell, and documented in Fig. 1(B). In our experiment, the fixed frequency was set at 69.95 Hz to avoid interference with 60 Hz line noise and harmonics, and phase shift was averaged over 210 cycles.

The use of another cell would require calibration against data specific to that cell, with experiments to confirm stability of the ϕ vs. T_a relationship over multiple charge–discharge cycles. In our setup, no sensor is inserted into the cell. More generally, the applied current can be chosen from a frequency ranging from 40 to 200 Hz to measure T_a . Similarly, a 5–20 Hz range of input current can be used to measure cathode temperature (T_c) [30–32]. The estimated anode or cathode temperatures based on phase shift can be measured dynamically, while the cell is being charged, discharged or at rest.

In this work, the applied current is a 50-mA rms sinusoidal

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