Understanding the trilemma of fast charging, energy density and cycle life of lithium-ion batteries

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HIGHLIGHTS

- Temperature-dependent aging behavior of Li-ion battery is studied numerically.
- Overall aging rate depends on the competition of lithium plating and SEI growth.
- The optimal temperature for cycle life increases with charge rate & energy density.
- Raising charging temperature is an effective method to eliminating lithium plating.

GRAPHICAL ABSTRACT
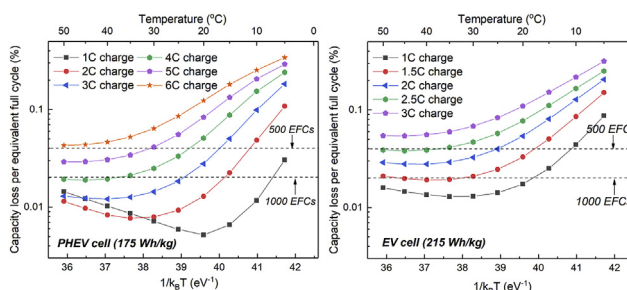
ABSTRACT

Increasing energy density of Li-ion batteries (LiBs) along with fast charging capability are two key approaches to eliminate range anxiety and boost mainstream adoption of electric vehicles (EVs). Either the increase of energy density or of charge rate, however, heightens the risk of lithium plating and thus deteriorates cell life. The trilemma of fast charging, energy density and cycle life are studied systematically in this work utilizing a physics-based aging model with incorporation of both lithium plating and solid-electrolyte-interphase (SEI) growth. The model is able to capture the key feature of temperature-dependent aging behavior of LiBs, or more specifically, the existence of an optimal temperature with the longest cycle life. We demonstrate that this optimal temperature is a result of competition between SEI growth and lithium plating. Further, it is revealed that either the increase of charge rate or of energy density accelerates lithium plating induced aging. As such, the optimal temperature for cell life increases from ∼20 °C for a high-power cell at 1C charge to ∼35–45 °C with the increase of charge rate and/or energy density. It would be beneficial to further increase the charge temperature in order to enable robust fast charging of high energy EV cells.

1. Introduction

With the rapid drop in the cost of Li-ion batteries (LiBs) by 80% in the past seven years, the world is now truly embracing electric vehicles (EVs). Numerous countries has announced their timelines to phase out diesel/gasoline vehicles and more than 10 major automakers launched their future EV plans in 2017. Should these plans fructify, we are foreseeing 400 EV models and sales of 25 million units by the year 2025. Despite the promising future, the EV market, as of 2017, still only accounts for 1.7% of annual vehicles sales. Range anxiety, the fear that an EV may run out of juice on the way has long been cited as the key reason keeping consumers from EVs [1]. To tackle this barrier, automakers are targeting higher battery capacities of over 60 kWh that could offer a driving range of ∼200 miles on a single charge, along with

boosting the number of fast charging stations with charging power up to 350 kW, capable of charging a 60 kWh battery in 10–15 min [2].

A critical barrier to fast charging is the issue of lithium plating [3,4]. Most EV batteries utilize graphite as the anode material whose equilibrium potential is fairly close to the reversible potential of lithium deposition/dissolution. At harsh charging conditions when there is large anode polarization, the anode potential could fall below 0 V vs Li/Li$^+$ and triggers lithium plating, leading to drastic capacity loss and even to safety hazards. Extensive efforts have been made to explore the bottlenecks of fast charging [5–9] and to optimize charge protocols [10–14]. It is widely acknowledged that lithium plating is prone to occur at high charge rates and/or low temperatures.

Recent studies showed that lithium plating could be a serious issue in high energy cells even at moderate charge rate and temperature. A typical approach to increase the energy density of LiBs is to increase the areal loading of active materials, which makes the anode thicker, denser and more tortuous [15], leading to larger anode polarization and thus higher risk of lithium plating. Gallagher et al. [16] revealed that the maximum charge rate of LiBs drops with the increase of areal loading. In their study, a cell with 3.3 mAh/cm^2 areal loading had stable capacity retention upon cycling with 1C charge at 30 °C but rapid capacity fade with 1.5C charge. A cell with 4.4 mAh/cm^2 areal loading could not even survive 1C charge at 30 °C. A large amount of metallic lithium was observed after dismantling the aged cells, confirming the occurrence of lithium plating in these high energy cells, though the charge rate and temperature are moderate. Malifarge et al. [17] recently presented a detailed analysis of the voltage losses in graphite anodes with different areal loading (2–6 mAh/cm^2) and porosity (0.1–0.45) and revealed that the large electrolyte-phase overpotential and the associated non-uniform state of charge (SOC) across the anode are the key reasons yielding lithium plating. Most recently, Spingler et al. [18] confirmed through thickness measurement, voltage relaxation method and post-mortem imaging that a high energy cell (190 Wh/kg, 98 μm-thick anode) suffered serious lithium plating with only 1.5C charge at 25 °C.

The impacts of fast charging and energy density on cell life are more complicated when considering temperature effects. In the early stage of literature, it was typically believed that cell aging is faster at higher temperatures due to the faster growth of solid-electrolyte-interphase (SEI) [19]. Waldmann et al. [20] conducted a comprehensive study of temperature effects on LiB aging via cycling of 1.5Ah graphite/NMC 18650 cells with 1C charge at different temperatures. Interestingly, it was found that the cell at 25 °C had the longest cycle life; either higher or lower temperatures resulted in faster degradation. Plotting the aging rate against reciprocal temperature, the authors found that the aging rate follows Arrhenius law and there is a transition of activation energy, from a positive value at T > 25 °C to a negative value at T < 25 °C, indicating a transition of the dominant aging mechanism, which is believed to be SEI growth at T > 25 °C and lithium plating at T < 25 °C. Shimpe et al. [21] tested a set of 3Ah graphite/LFP 26650 cells with 1C charge and also found that the 25 °C cell had the best cycle life. Further, it is worth noting that the cycle life at 10 °C was only about half of that at 25 °C. Ecker et al. [22] also reported that the cycle life of a 53Ah high power graphite/NMC cell dropped sharply with the reduction of temperature at 0.85C charge, from ∼4000 cycles at 20 °C to ∼2000 cycles at 10 °C and only ∼40 cycles at 0 °C. Similarly, the work of Matadi et al. [23] showed that a 16Ah graphite/NMC cell which could sustain 4000 cycles at 25 °C lost 75% capacity in only 50 cycles at 5 °C. These results indicate that lithium plating could be a serious issue even at cool temperatures. To that end, it would be beneficial to charge a cell at high temperatures, which, on the other hand, accelerates SEI growth. The best scenario would be charging a cell always at its optimal temperature where the combined aging rate of SEI growth and lithium plating reaches the minimum. An interesting question is that: is room temperature always the best for cell charging?

A fundamental understanding of the temperature-dependent aging

behavior of LiBs is thus of vital significance for extending the lifetime of EVs. Previous studies on this subject were mostly based on the last-generation high power cells designed for plug-in hybrid electric vehicles (PHEVs) with relatively low areal capacity (< 2 mAh/cm^2) and thin electrodes (< 50 μm) and at moderate charge rates. As the world is targeting higher energy density and faster charging, there is an urgent need to understand the impacts of energy density and charge rate on the temperature-dependent aging behavior. Indeed, recent studies have shown that cycle life is not always the best at room temperature. Matsuda et al. [24] tested commercial 18650 cells in 25 °C and 45 °C (Fig. S1a). At 1C charge, the cycle life was better at 25 °C than at 45 °C. At 2C charge, however, the 45 °C cell had much longer life than the 25 °C cell. Friesen et al. [25] tested high energy cells with thick anode (74–80 μm) at 1C charge and found that the cycle life at 45 °C was 3x longer than at 20 °C (Fig. S1b). Similarly, Rieger et al. [26] cycled high energy cells (77-μm thick anode) with 1C charge and found that the cells at 25 °C lost 30% capacity in 250–400 cycles whereas the cells at 40 °C lost only 5% capacity after 400 cycles (Fig. S1c). The above results indicate that the optimal temperature for LiBs could shift with the change of charge rate and energy density.

The objective of the present work is to gain a systematic understanding of the impacts of fast charging and energy density on the temperature-dependent aging behavior of LiBs. A physics-based aging model with incorporation of SEI growth and lithium plating is utilized to predict the aging rate of LiBs at different temperatures with various charge rates and areal loadings. Special attention is paid to the competition between SEI growth and lithium plating and to the variation of optimal temperature with charge rate and energy density. Directions for enabling temperature-independent, fast, and healthy charging of high energy cells are also presented.

2. Model description

The aging model that we recently developed for modeling of lithium plating induced aging of LiBs [27] is adopted in this work. A key feature of the model is that it accounts for both SEI growth and lithium plating. Further, the model considers the reduction of anode porosity due to continuous SEI growth, which results in onset of lithium plating and thereby in transition from linear to nonlinear capacity fade after prolonged cycling. A brief summary of the model is given below and further details could be found in our previous work [27].

A total of three electrochemical reactions are considered to occur in the anode, including lithium intercalation into graphite (Eq. (1a)), SEI formation (Eq. (1b)), and lithium plating (Eq. (1c)):

$$C_6 + Li^+ + e^- \leftrightarrow LiC_6 \tag{1a}$$

$$2C_2H_4CO_3 + 2e^- + 2Li^+ \rightarrow (CH_2OCO_2Li)_2 + C_2H_4 \tag{1b}$$

$$Li^+ + e^- \rightarrow Li(s) \tag{1c}$$

The total volumetric current density in the anode is the sum of current density of the above three individual reactions, as:

$$j_{tot} = j_{gr} + j_{SEI} + j_{Li} \tag{2}$$

where the subscripts *tot*, *gr*, *SEI* and *Li* denote total, graphite, SEI formation and lithium plating, respectively. The current density of graphite is calculated via the following Butler-Volmer equation:

$$j_{gr} = a i_{0,gr} \left\{ \exp\left(\frac{\alpha_a F}{RT} \eta_{gr} \right) - \exp\left(-\frac{\alpha_c F}{RT} \eta_{gr} \right) \right\} \tag{3}$$

where a is specific surface area, i_o the exchange current density, α_a and α_c the anodic and cathodic charge transfer coefficients, and η_{gr} the overpotential of Li$^+$ intercalation into graphite.

The current density of SEI formation is calculated via the following Tafel equation: