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Charging protocols for lithium-ion batteries and their impact on cycle life—An experimental study with different 18650 high-power cells

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ABSTRACT

This paper presents an overview on charging strategies for lithium-ion batteries. Moreover, a detailed assessment of charging strategies is performed, based on an extensive experimental study with three different cell types.

The experimental results reveal that the impact of charging currents and charging voltages on cycle life can vary markedly among different lithium-ion batteries. In general, the cycle life is influenced more by high charging currents than by high discharging currents. Different boost charging protocols have disclosed that high charging currents can deteriorate cycle life not only at high state of charge (SoC), but also at very low SoC. Our investigations on pulse charging show that lithium-ion cells withstand charging pulses of high current or high voltage without any deterioration in cycle life, when the duration of the pulses remains short and the mean current and voltage values are considerably lower. For pulses of less than 1 s, cycle life has been similar for pulsed and continuous charging with the same mean charging currents and identical cycle depths.

This paper also presents the impact of charging currents and charging voltages on capacity utilization, charging time, and efficiency to support the development process of optimized charging protocols for practical applications.

1. Introduction

Lithium-ion batteries provide higher energy and power densities than other commercial rechargeable battery technologies. Thus, they are used in various mobile applications, such as notebooks, cellular phones, cordless tools, and electric vehicles. To maximize battery life, the methods of operation have to be optimized. The optimization potential for the discharging processes is usually very limited, as the discharging depends largely on the users' ways of operating the devices. The charging processes, however, can be influenced substantially by the manufacturers: by implementing a specific charging protocol, adjustments between charging time, capacity utilization, and cycle life can be realized.

The standard charging protocol for lithium-ion batteries is constant current constant voltage (CCCV) charging. In addition to this, several alternative charging protocols can be found in literature. Section 2 will provide an overview on the different categories of charging protocols and their specific characteristics. Many of the alternative charging protocols claim to increase the amount of charge stored, improve efficiency, or reduce the charging duration without deteriorating cycle life. However, there are often only few measurement data presented to verify these claims. Moreover, the experimental procedures vary among the different publications, which impedes a direct comparison. As the experiments are usually performed with only one specific cell type, no interdependencies between charging protocol and cell type are revealed. Some charging protocols are even derived solely from simulation without any experimental validation. Consequently, it is difficult to compare the performance of the various charging protocols and assess them for specific practical applications.

To overcome these shortcomings, we present an extensive experimental study on charging protocols: for three high-power 18650 lithium-ion cell types from different manufacturers and with different cell chemistries, several charging protocols are examined with key parameters varied. Moreover, we have conducted a cycle life study, where the lithium-ion cells have been cycled with various charging protocols under identical environmental conditions. This enables an objective comparison

Abbreviations: BC, boost charging; CC, constant current; CCCV, constant current constant voltage; CCPC, constant current + pulsed charging; CV, constant voltage; EIS, electrochemical impedance spectroscopy; EoL, end of life; LFP, $LiFePO_4$, lithium iron phosphate; MSCC, multistage constant current; OCV, open circuit voltage; PC, pulse charging; SoC, state of charge.

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and evaluation of the different charging strategies. It also reveals the crucial parameters for optimizing the charging procedure for lithium-ion batteries.

2. Charging protocols for lithium-ion batteries

In general, optimized charging procedures aim to provide a short charging time, a good capacity utilization, and a high energy efficiency, while maintaining a long cycle life [1,2]. Before introducing the different categories of charging protocols, the basic limitations for charging lithium-ion batteries are presented as described in Ref. [3]: the charging process of lithium-ion cells is mainly limited by two factors: lithium plating on the anode and oxidation of the electrolyte solution due to high potentials at the cathode [4,5]. Both undesired side reactions lead to an irreversible loss of cyclable lithium. Moreover, they consume electrolyte components and promote the growth of resistive surface layers [4,6,7].

Lithium plating describes the reduction of Li^+ ions, which are dissolved in the electrolyte, to metal lithium at the surface of the anode's active material. This reactions takes place instead of the regular intercalation of lithium into the lattice structure of the active material [8]. It can originate from limitations in charge transfer or lithium solid diffusion [9,10]. Lithium plating can occur, when the anode potential drops below the standard potential of Li^+/Li [9]. Some of the plated lithium later reacts irreversibly with the electrolyte and forms insoluble side products [6,7]. Graphite anodes, which are used in most lithium-ion cells, are very prone to lithium plating due to their low equilibrium potential, especially at high state of charge (SoC) [11]. As a general trend, lithium plating increases with higher SoC, higher charging current, and reduced temperature [9,12]. Moreover, the intercalation of lithium into the graphite anode causes volume changes and mechanical stress, which can lead to battery aging [13,14]. As shown in Ref. [15], aged cells can become more susceptible to lithium plating. All in all, the charging currents for graphite-based lithium-ion cells are mainly limited by the intercalation kinetics at the anode [16].

The charging voltage is limited by the oxidation of electrolyte solvents, which occurs at high cathode (over)potentials [4,5]. Overcharging a lithium-ion cell promotes heat generation and causes irreversible damage to the cathode's crystallographic structure, when the cathode material is completely delithiated [17]. This leads to further oxidative side-reactions that can entail gas evolution, overpressure inside the cell, an opening of the cell's safety vent, and leakage of electrolyte. As the organic electrolytes of lithium-ion batteries are highly flammable, this can cause a fire or lead to an explosion of the cell [18]. Thus, complying with the maximum cell voltage, specified by the manufacturer, is essential.

Consequently, any charging procedure for lithium-ion batteries has to consider these fundamental limitations to achieve safe operation and good cycle life. The following subsections present different categories of charging protocols for lithium-ion batteries and their specific characteristics.

2.1. Constant current constant voltage (CCCV) charging

The standard charging protocol for lithium-ion cells is CCCV charging [19]. Fig. 1a illustrates the two phases of CCCV charging: at first, the cell is charged with a constant current I_{ch}, until the cell voltage reaches the specified charging voltage V_{ch}. Then, the cell voltage is kept constant at V_{ch}, entailing a continuous reduction of the charging current. This constant voltage (CV) phase is terminated, when the charging current drops below a predefined threshold value I_{end} or when a predefined maximum charging time t_{max} is exceeded. The speed of the charging process is mainly influenced by I_{ch}; the capacity utilization is determined by V_{ch} and I_{end}. As demonstrated in Ref. [20], higher charging voltages and higher charging currents can deteriorate cycle life considerably. Thus, it is necessary to choose I_{ch} and V_{ch} appropriately to minimize lithium plating and electrolyte decomposition.

Setting $I_{end} = I_{ch}$ results in sole constant current (CC) charging, which is considered as a special case of CCCV charging within this paper. Due to the missing CV phase, the capacity utilization for sole CC charging is generally lower. High capacity utilization with sole CC charging can only be achieved with very low charging currents. As this extends charging times massively, CCCV charging is usually preferred to CC charging.

2.2. Multistage constant current (MSCC) charging

In MSCC charging (Fig. 1b), the CV phase of the CCCV protocol is replaced by a series of CC periods with monotonic decreasing charging currents ($I_{ch1} > I_{ch2} > \ldots > I_{chN}$) [21,22]. Each time the cell voltage reaches the charging voltage V_{ch}, the charging current is

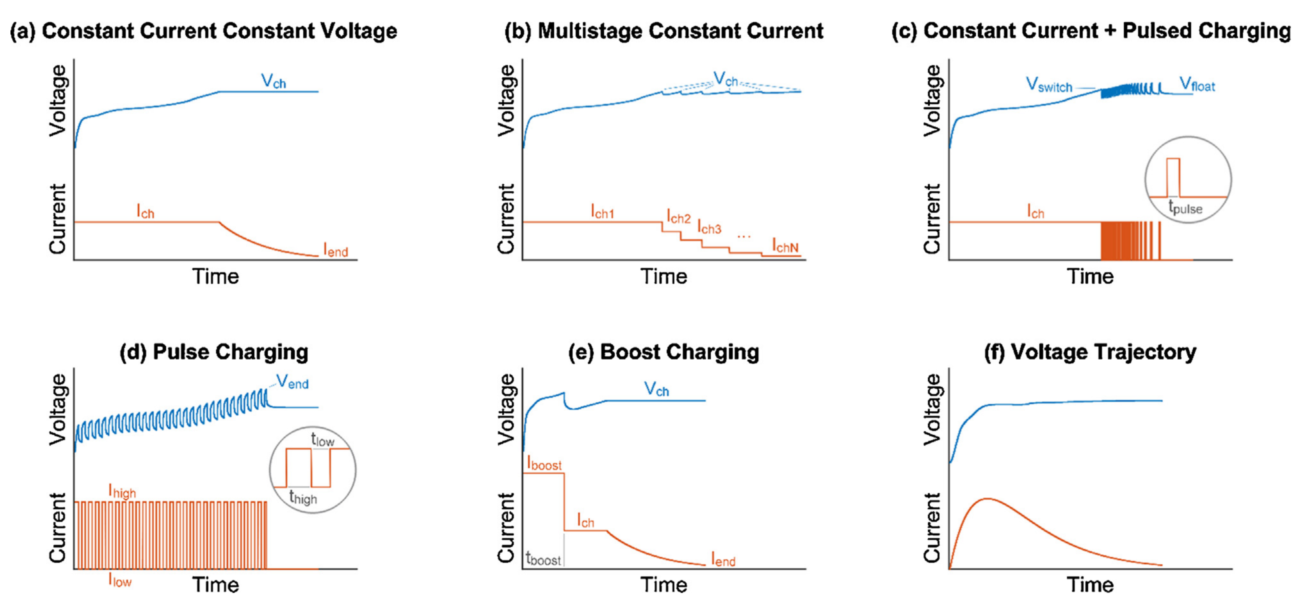

Fig. 1. Schematic illustration of different charging protocols: (a) CCCV, (b) MSCC, (c) CCPC, (d) PC, (e) BC, and (f) charging with a predefined voltage trajectory.