



Fast-charging to a partial state of charge in lithium-ion batteries: A comparative ageing study



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ARTICLE INFO

Article history:

Received 16 May 2017

Received in revised form 4 July 2017

Accepted 5 July 2017

Available online 31 August 2017

Keywords:

Fast-charging

Charging to partial SOC

Non-destructive analysis

Lithium-ion battery ageing

Battery management

Charging protocol

ABSTRACT

At electric vehicle fast-charging stations, it is generally recommended to avoid charging beyond ~80% State-of-Charge (SOC) since topping-off to full capacity disproportionately increases the charging time. This necessitates studying its long-term impact compared to slower rate charging to full capacity typical of home or residential charging. Here we present the long-term ageing effects on commercial 18650 NMC-LMO/graphite cell cycled between 2.6–4.2 V at three different charging protocols: 1.5 C-rate fast-partial charging (to 82.5% SOC), 0.5 C-rate slow standard charging without or with a constant-voltage step (to 93% or 100% SOC). Quantitative discharge-curve and postmortem analyses are used to evaluate ageing. The results show that ageing rate increases in the order: fast-partial charging < standard charging < standard charging with constant-voltage period, indicating that higher SOC-range near full capacity is more detrimental to battery life than fast-charging. The capacity fade is totally dominated by cyclable-lithium loss. The ~8% NMC-LMO active material loss has negligible impact on the cell capacity fade due to the electrodes excess material in the fresh cell and its moderate loss rate with ageing compared to the cyclable-lithium. Similar ageing modes in terms of capacity fade and impedance rise are found irrespective of the charging protocol.

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1. Introduction

Wide spread market adoption of electric vehicles depends to a large extent on meeting consumer expectations of comfort similar to conventional vehicles which include the ability to travel long distance or make unplanned trips. Fast charging receives increased attention as a means to meet these expectations by decreasing the time to recharge a battery. However, the higher current in the fast charging may cause detrimental effects to the battery durability [1–3]. Hence, it becomes crucial to understand the effects of fast charging on battery components and identify the conditions that lead to the accelerated battery ageing. This is vital in developing durable batteries with fast-charging capability through better material design and battery management.

An optimized fast charging protocol aims for short charging time, high charge efficiency, high energy efficiency, and safe operation with minimal effect on the battery cycle life [4]. To avoid local overcharging processes that can lead to gas evolution, structural damage, and lithium plating, the cell is generally

charged at lower currents towards higher state of charge (SOC), i.e. close to full charge of the cell [5,6]. As the cell impedance usually tends to increase at high SOC, the use of lower currents also decreases the polarization losses, energy losses from joule heating and risks of excessive temperatures in the cell [7]. For these reasons, the standard and commonly used fast charging protocol for lithium-ion batteries is constant current – constant voltage (CCCV) protocol [8,9]. In this method, the battery charges at constant current (CC) until the voltage reaches the predetermined cut-off limit (for example 4.2 V) followed by a constant voltage (CV) charging at the same voltage until the current drops to some pre-determined minimum value. The CC stage is required to charge the battery rapidly at high current rate while the CV stage is required to fully charge the battery with continuously decaying current. Because of such a decaying current, electric vehicle (EV) charge station owners recommend users not to charge beyond ~80% SOC during fast charging since the subsequent low rate charging to 100% SOC inefficiently doubles the total charging time [10,11]. From the perspective of battery durability, however, this fast charging to a partial SOC (ex ~80% SOC) brings about the coupled effect of high charging rate and narrower state of charge range as compared to the standard low rate charging to full capacity. Hence,

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it becomes important to compare the battery cycle life performance and ageing process of fast charging to a partial SOC with a standard low rate charging to full capacity, and decouple influence of cycling parameters of SOC range (Δ SOC) and charging rate.

The effects of charging rate and Δ SOC on the battery durability have been reported previously [3,12–16]. Generally, both high charging rate and wider Δ SOC are detrimental to the battery life [5]. High charging rate can accelerate lithium plating especially at high SOC, surface film formation and mechanical stress leading to capacity fade and impedance rise [3,5]. Moreover, wide Δ SOC and longer floating time at high SOC has been shown to have negative impact on the battery life [5,12,14]. For instance, higher SOC in high voltage lithium-ion batteries such as NMC/graphite accelerate electrolyte oxidation, SEI formation and growth, and binder decomposition [5]. The detrimental effect of high SOC has furthermore been shown to be non-linear. Bendikt et al. [15] have reported ageing rates which shows accelerated and non-linear ageing (factors of 1.6 at 40 °C and 2.5 at 60 °C per +100 mV) above 90% SOC (4.04 V) for NMC cells. Therefore, the generally opposite effects of high charge rate and a narrower Δ SOC on the battery life may result in a different coupled effect in fast-partial charging compared to the standard rate full charging depending on which factor is dominating in the battery ageing.

In this work we report the long-term (3.5 months effective time) degradation effects of 1.5-C rate fast charging to a partial SOC (80%, fast-partial) and compares it to the standard 0.5-C rate charging to a partial and full charge on commercial NMC/LMO (Ni-Mn-Co-Oxide, Mn-Oxide)/graphite cell all cycled between 2.6–4.2 V. Capacity loss has been tracked periodically by measuring the cell capacity at 1C and C/24 rates during cycling. A mathematical cell discharge-curve fitting analysis has been performed to non-destructively analyze the capacity fade in terms of cyclable lithium and material losses [17–19]. Electrodes harvested from opened cells have been electrochemically analyzed to confirm any material loss and identify the source of impedance rise. Scanning electron microscopy (SEM) was used to study the surface morphology of the harvested electrodes.

2. Experimental

2.1. Cells and cycling protocols

A commercial power optimized 18650 cylindrical lithium-ion cell containing mixed NMC (Lithium-Nickel-Manganese- Cobalt Oxide) and LMO (Lithium-Manganese Oxide) as the positive electrode and graphite as the negative electrode is used in this study. According to the manufacturer, the cell can be used for applications such as PHEVs (plug-in hybrid vehicles), scooters and power tools. It has a nominal capacity of 1.5 Ah. All C-rates mentioned henceforth are based on this nominal capacity where 1C rate corresponds to 1.5 A current. Table 1 lists the specification of the cell as given by the manufacturer.

Table 1
Cell specification.

Item	Specification
Nominal capacity	1500 mAh
Charging voltage	4.2 \pm 0.05 V
Nominal voltage	3.6 V
Charging method	CCCV (100 mA cut-off)
Charging current	Standard charge: 0.75 A Rapid charge: 4 A (max)
Max. discharge current (continuous)	23 A (at 25 °C), 60% at 250 cycle
Discharge cutoff voltage	2.5 V
Cell weight	45.0 g (max)
Operating temperature (surface temperature)	Charge 0 to 50 °C Discharge: –20 to 75 °C

In order to select a current value for the fast-charging protocol, a test cell was first discharged at 1C rate to 2.6 V and rested for 5 min before charged at different constant current values until the cell voltage reached 4.2 V without a follow-up constant voltage charging. A current of 1.5C was found to charge 80% of the cell capacity in approximately 30 min (4.638 Wh charging energy), in accordance with charging stations operation of fast-charging [10,11], and thus was selected as the fast charging protocol (fast-partial) for cycle ageing. In order to serve as a baseline to study the effect of fast charging, cells were cycled using the standard protocol recommended by the manufacturer (CCCV-standard): a constant C/2 rate until the cell voltage reached 4.2 V followed by a constant voltage trickle charge at 4.2 V until the current dropped to 0.1 A. For comparison, additional cells were charged at C/2 rate until 4.2 V without the follow-up constant voltage charging (CC-standard) with the aim to get further information about the relative effects of charging rate and Δ SOC on the battery degradation. In all protocols, discharging was done at 1C rate and 5 min rest period was used at the end of each charge and discharge period. In a real life scenario, however, the discharging is done in a complex profile depending on the drive cycle and the vehicle spends most of the time parked at rest (calendar ageing). The complete charging protocols used and the corresponding maximum cell skin temperature which occurs at the end of charging is shown in Table 2. As can be seen in Table 2, the fast-partial, CC-standard, and CCCV-standard charging protocols take approximately 30, 110, and 165 min to charge to 2.5–82.5%, 2.5–93% and 2.5–100% SOC respectively. It can be noted here that the capacity returned by the constant voltage (CV) stage of the CCCV-standard technique is approximately 7% but requires 55 extra minutes as compared to the CC-standard technique (the charging time during CV stage of 1.5C charging would take more than 70 min). Furthermore, the lower SOC reached at 4.2 V when charging at 1.5C compared to C/2 is due to higher overpotential at higher current as shown in Fig. 1.

Duplicate cells were cycled in each case to check the reproducibility of the ageing trend until the capacity retention in all cases fell below 93% of the beginning of life (BOL) capacity. One cell from each protocol was further cycled until capacity retention of approximately 85% of the BOL capacity. The effective test times to reach approximately 85% capacity retention were 82, 106 and 101 days for the fast-partial, CC-standard and CCCV-standard cells respectively. Cell aging to a similar capacity retention value is important to investigate the path dependence of ageing modes induced by using different protocols since the ageing mode varies with the capacity retention. Keithly 2800 current source and Keithly 2700 differential multimeter (DMM) all configured and controlled by LabVIEW program were used for cycling in the fast-partial and CC-standard protocols. Solatron SI 1286/1287 potentiostat was used for cycling in the CCCV-standard protocol. All tests were performed inside a temperature controlled climate chamber set at 25 °C. Reference performance tests (RPT) consisting of 1C and C/24 discharge capacities after CCCV-standard charging were measured in the beginning and periodically during cycling.

2.2. Characterization of harvested electrodes

After the cycling protocols, the cells were discharged at C/24 rate until 2.5 V and potentiostatically held at 2.5 V for 3 h before they were carefully disassembled in argon filled glovebox (O_2 and H_2O <1 ppm). A calendar-aged cell was used as a baseline for comparison to cycle-induced ageing. This cell had been kept at 50% SOC and room temperature for 7 months and can be used as a baseline since calendar ageing induces very little ageing at room temperature [20–23]. For post-mortem analysis, small electrode

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