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Overcharge durability of $Li_4Ti_5O_{12}$ based lithium-ion batteries at low temperature

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ABSTRACT

The decrease in capacity at low temperature limits further application of lithium-ion batteries. This paper introduces an approach to compensating the capacity loss of $Li_4Ti_5O_{12}$ (LTO) based lithium-ion batteries at low temperature by increasing the charging cut-off voltage. The impact of this approach on battery durability is examined afterwards, and a "tipping point" voltage for degradation is observed. Cut-off voltages over the tipping point (3.2 V) cause severe degradation, while those beneath the tipping point do not. The degradation mechanisms are studied with incremental capacity (IC) curve analysis, a prognostic and mechanistic (P&M) model and Scanning Electron Microscope/X-Ray Energy Dispersive Spectrometer (SEM/EDS) tests. Analysis show that the potential of the LTO anode first drops below 1 V when the battery is overcharged to 3.2 V. The electrolyte exceeds the reduction potential and decomposes on the LTO surface, forming Solid Electrolyte Interface (SEI) film with gas generation. The anode potential then gradually rises to above 1 V as we continue to charge the battery. However, the cathode potential exceeds 4.6 V, resulting in electrolyte oxidation and active material loss in the cathode. Overall, enhancing the cut-off voltage from 2.7 V to 3.2 V is effective to enlarge the charging capacity (9.5%) of the LTO batteries at −20°C with slight degradation.

1. Introduction

Lithium-ion batteries are excellent candidates for the energy storage system in electric vehicles given their high power density and long cycle life. However, the durability and safety problems at low temperature restrict their further applications [1–4]. The performance of lithium-ion batteries can be greatly improved by changing carbon anodes to $Li_4Ti_5O_{12}$ (LTO). LTO anodes display good properties such as structural stability during cycling, no Solid Electrolyte Interphase (SEI) film formation and no lithium plating, due to its zero-strain characteristic and high operating potential around 1.55 V [5–8]. Lithium-ion batteries with LTO anodes show outstanding cycle stability at normal operating conditions with slight capacity degradation usually caused by the $Li[Ni_{1-m-n}Co_mMn_n]O_2$ (NMC) cathodes [9,10].

However, batteries with LTO anodes have their unique problem of low energy density due to high operating potential of LTO, especially when cycled at low temperature [7,11]. The conductivity of Li^+ declines and the polarization of the electrode increases as temperature falls. Thereby, battery voltage at low temperature rises fast to the cut-off voltage, resulting in significant loss of charging capacity and energy density. To solve this problem, many efforts have been made to enhance the Li^+ conductivity in the manufacture process, such as doping, reducing the particle size of the electrodes and incorporating conductive agents [12–14].

This paper proposes a novel approach to compensating the capacity loss of LTO batteries at low temperature by enhancing the charging cut-off voltage (ECCV), which is useful in application of large format LTO batteries. However, the feasibility of this approach, especially the impact on the battery durability, needs to be verified.

Many studies have focused on the impact of ECCV on battery durability at room temperature. The aging mechanisms are mainly categorized into three modes: loss of lithium-ions inventory (LLI), loss of active material (LAM) and Ohm resistance increase (ORI) [9,15,16]. ECCV at room temperature results in overcharge of the batteries and usually causes substantial capacity loss [17–20]. Studies suggest that the potential of the LTO anode drops sharply when the charging cut-off voltage is enhanced from 2.8 V to 3.6 V, resulting in electrolyte decomposition at the anode surface, gas generation and battery capacity loss [17,19]. Thus, LAM in the LTO anode, LLI and ORI are the main reasons for battery degradation when the batteries are overcharged at

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room temperature. However, the impact of different charging cut-off voltages on the battery durability and the battery degradation behavior at low temperature still remain unclear. The side reaction rate decreases as temperature falls [18,21,22], and there may exist a moderate charging cut-off voltage that can enhance charging capacity with slight degradation.

In this study, the capacity charged into LTO batteries when ECCV to different level at low temperature is examined. The impact of overcharge voltages on the battery durability is then studied. The degradation mechanisms are analyzed with incremental capacity (IC) curves [23–25], a prognostic and mechanistic (P&M) model [26–28], and Scanning Electron Microscope/X-Ray Energy Dispersive Spectrometer (SEM/EDS) tests [29–31]. A tipping point at the voltage of 3.2 V is observed. Setting cut-off voltage beyond the tipping point (3.2 V) leads to distinct degradation after a few cycles, whereas setting that below the tipping point does not. Electrolyte reduction/oxidation due to abnormal electrode potential mainly causes the battery degradation. Studies show that ECCV from 2.7 V to 3.2 V can enlarge the charging capacity at −20℃ by 9.5% with little capacity degradation. Thus, there exists a moderate overcharge voltage of 3.2 V at low temperature, and the ECCV approach can be useful to enhance low temperature charging capacity in application of large format LTO batteries.

2. Experiments

2.1. The commercial 20 Ah lithium-ion batteries with LTO anodes

Commercial 20 Ah lithium-ion batteries with NMC cathodes and LTO anodes were tested in this study. The batteries were manufactured by TOSHIBA Co., Ltd and showed outstanding cycling stability according to our previous research. The capacity remained more than 85% after 1000 cycles at 55℃ [32].

2.2. The reference performance tests

The reference performance test (RPT) was conducted to measure the basic performance of the batteries and evaluate the degradation mechanisms. The RPTs were conducted in temperature chambers at 25℃, including three consequent tests: the standard capacity test, the hybrid pulse power characterization (HPPC) test and the low-current test. An entire RPT is shown in Fig. 1(a).

The standard capacity test included three cycles between 1.5 V and 2.7 V. The cell was first charged to 2.7 V at 1C rate, followed by a constant-voltage process to 1 A, and then discharged to 1.5 V at 1C rate. The HPPC test was carried out to measure the resistance of the batteries at different states of charge (SOC) [33,34]. During the HPPC test, a series of pulse power sequences were conducted with SOC intervals of 10%. Low-current test was conducted at the rate of 1/20C, and the test results were used to calculate the IC curves at quasi-equilibrium status.

2.3. The low temperature overcharge tests

2.3.1. The charging performance tests

The charging performance tests were used to examine the impact of ECCV on the charging capacity and resistance at low temperature (−20℃). The battery was charged at constant 1C rate. The charging process terminated once the battery was charged to the standard capacity of 20 Ah to ensure safety. Pulse current interruption was superimposed to measure the resistance during the ECCV process, as shown in Fig. 1(b).

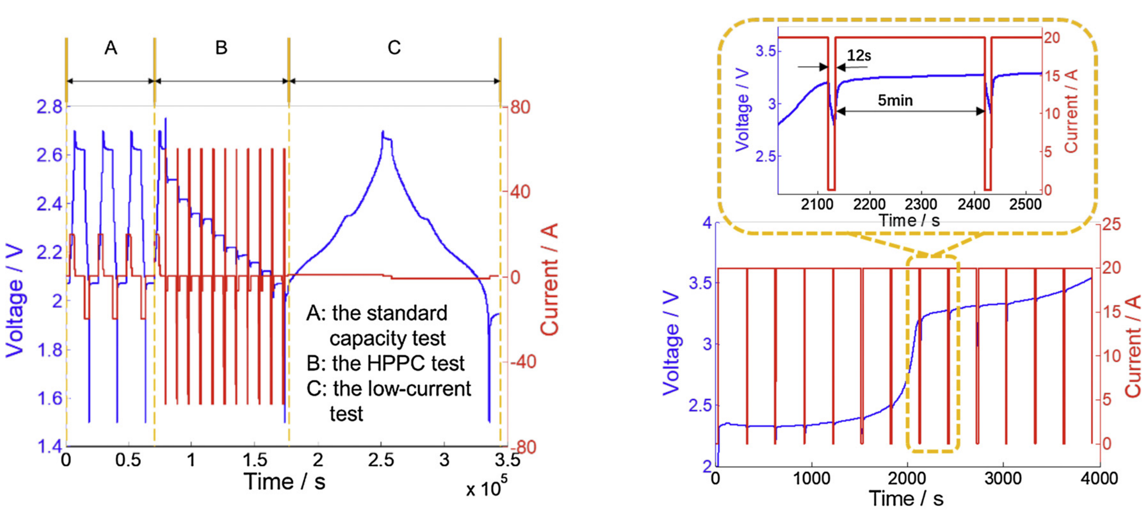
2.3.2. The cycling test with enhanced cut-off voltages

The cycling test with enhanced cut-off voltages, conducted at −20℃ in an explosion-proof thermal chamber made by DG BELL®, was utilized to examine the impact of ECCV on battery aging. In a low temperature cycle, the battery was first charged to different cut-off voltages at 1C rate. After a rest to stabilize the voltage, the battery was then discharged to 1.5 V. The RPT was conducted after several low temperature cycles. The number of the cycles between two adjacent RPTs was adjusted according to the degradation rate. The cycling test terminated once the capacity measured in the RPT dropped below 80% of its initial value or the cycle number reached 50.

Table 1 summarizes the cycling tests conducted in this study. A fresh cell without cycling (Cell No.0), Cell No.1, and Cell No.3 were dissembled to compare the battery components characteristics before and after the cycling tests.

2.4. The half-cell tests

Coin cells with NMC or LTO cathodes and Li metal anodes were assembled to investigate the electrochemical properties of the electrodes. The electrode materials of the coin cells were cut from a



(a) The reference performance test at 25℃

(b) The resistance test using pulse power method

Fig. 1. Basic information of the performance tests.