



Experimental investigation of the thermal and cycling behavior of a lithium titanate-based lithium-ion pouch cell

Florian Hall^{a,1}, Jonas Touzri^a, Sabine Wußler^b, Hilmi Buqa^b, Wolfgang G. Bessler^{a,*}

^a Institute of Energy Systems Technology (INES), Offenburg University of Applied Sciences, Badstrasse 24, 77652 Offenburg, Germany

^b Leclanché GmbH, Industriestraße 1, 77731 Willstätt, Germany

ARTICLE INFO

Article history:

Received 28 June 2017

Received in revised form 9 February 2018

Accepted 19 February 2018

Available online 23 March 2018

Keywords:

Lithium-ion battery

Lithium titanate (LTO)

Lifetime

Ageing

Experiments

ABSTRACT

Lithium-ion pouch cells with lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) anode and lithium nickel cobalt aluminum oxide ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, NCA) cathode were investigated experimentally with respect to their electrical (0.1C . . . 4C), thermal (5 °C . . . 50 °C) and long-time cycling behavior. The 16 Ah cell exhibits an asymmetric charge/discharge behavior which leads to a strong capacity-rate effect, as well as a significantly temperature-dependent capacity ($0.37 \text{ Ah} \cdot \text{K}^{-1}$) which expresses as additional high-temperature feature in the differential voltage plot. The cell was cycled for 10,000 cycles inbetween the nominal voltage limits (1.7–2.7 V) with a symmetric 4C constant-current charge/discharge protocol, corresponding to approx. 3400 equivalent full cycles. A small ($0.192 \text{ m}\Omega/1000$ cycles) but continuous increase of internal resistance was observed. Using electrochemical impedance spectroscopy (EIS), this could be identified to be caused by the NCA cathode, while the LTO anode showed only minor changes during cycling. The temperature-corrected capacity during 4C cycling exhibited a decrease of 1.28%/1000 cycles. The 1C discharge capacity faded by only 4.0% for CC discharge and 2.3% for CCCV discharge after 10,000 cycles. The cell thus exhibits very good internal-resistance stability and excellent capacity retention even under harsh (4C continuous) cycling, demonstrating the excellent stability of LTO as anode material.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years the demand for electrochemical storage systems for portable, mobile and stationary applications grew rapidly [1,2]. For stationary energy storage in industrial or private applications, high calendaric and cyclic lifetime is of particular importance [3].

The ageing of lithium-ion batteries is today considered to be strongly driven by the graphite negative electrode, which is subject to formation of the solid electrolyte interphase (SEI) and can suffer from lithium plating when being charged at high current and/or low temperature [4,5]. An alternative negative electrode material is lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) [6]. LTO is considered a “zero strain material”, that is, it shows negligible volume change during cycling and hence exhibits almost no mechanical aging [7–9]. In addition, due the comparatively high half-cell voltage (1.55 V vs. Li/Li⁺) as compared to graphite (0.05–0.3 V vs. Li/Li⁺), SEI formation (0.8 V vs. Li/Li⁺ [10]) and plating (0 V vs. Li/Li⁺) are effectively

suppressed. Consequently, high cyclic lifetime of LTO electrodes has been demonstrated [11]. High half-cell voltage and low specific capacity (1.55 V vs. Li/Li⁺ and $180 \text{ Ah} \cdot \text{kg}^{-1}$ [6], compared to 0.2 V vs. Li/Li⁺ and $370 \text{ Ah} \cdot \text{kg}^{-1}$ [12] for graphite) reduce the cell-level specific energy considerably (57 Wh/kg for the cell considered in the present work), which however is not a key issue for stationary applications.

Various commercial lithium-ion cells have been subject of experimental investigations for assessing performance and lifetime under controlled laboratory environments. Graphite/LiFePO₄ cells (C/LFP, high-power, 2.3 Ah, 26650) have been tested by Groot et al. [13], showing 20% capacity loss after 4200 cycles at 100% DOD, 1C, 20 °C. C/LFP cells (high power, 8 Ah, cylindrical) were also investigated by Lewerenz et al. [14], demonstrating a 25% capacity loss at 100% DOD, 1C, 40 °C after 4000 cycles. A graphite/nickel manganese cobalt oxide cell (C/NMC, high energy, 2.05 Ah, 18650) was tested by Ecker et al. [15], where cycling at 100% DOD, 1C and 35 °C showed a capacity fade of 20 % after only 500 cycles. In contrast, significantly higher lifetime was observed for cells with LTO anode. Hang et al. [16] observed a capacity fade of 12% after 5000 cycles at 100% DOD for high-power LTO/LCO (lithium cobalt oxide, 4 Ah) cells. Zaghbi et al. showed negligible capacity fade for

* Corresponding author.

E-mail address: wolfgang.bessler@hs-offenburg.de (W.G. Bessler).

¹ Present affiliation: Leclanché GmbH, Willstätt, Germany.

an LTO/LFP (18650 laboratory) cell after 20,000 full cycles [11]. Takami et al. [17] have investigated two prototype cells: An LTO/LMO (lithium manganese oxide) cell (3 Ah, high power, pouch) showed 4% capacity fade after 30,000 cycles with 10C rate at 100% DOD, 25 °C; and an LTO/NMC cell (20 Ah, high energy, prismatic) showed 14% capacity fade after 6000 cycles at 3C, 100% DOD, 25 °C. Yan et al. have investigated both C/LMO and LTO/NMC high-power cells using a dynamic hybrid electric vehicle cycling profile, where the LTO based cell showed significant higher cyclic lifetime than the graphite-based cell [18]. As all cells discussed here have different chemistries and format, a quantitative comparison is not possible. However, generally cells with an LTO negative electrode were observed to provide high cyclic lifetime.

In this present work we investigate the electrical, thermal and cycling behavior of commercial LTO/NCA cells designed for stationary energy storage. Continuous cycling at 4C (maximum rate) was performed for 10,000 cycles inbetween the nominal voltage limits (1.7–2.7 V). Internal resistance measurements and electrochemical impedance spectroscopy (EIS) carried out as checkup every 1000 cycles were used to support the identification of aging mechanisms. The experimental setup and used methods will be described in Section 2. In Section 3 electrical and thermal characteristics of the cell will be shown and discussed, followed by the results of the long-term cycling. In Section 4, capacity fade will be discussed and EIS spectra will be interpreted using an equivalent circuit.

2. Experimental setup

2.1. Investigated cells

Large-format full-cell measurements were carried out using commercial (Leclanché) lithium-ion pouch cells consisting of LTO as negative electrode, NCA as positive electrode, an aluminum oxide ceramic laminated type separator (produced by Leclanché), and copper and aluminum current collectors. The cells (163 × 174 × 12 mm³, 641 g) have a nominal capacity of 16 Ah, nominal voltage of 2.3 V, and nominal specific energy of 57 Wh/kg. The cells can be continuously charged and discharged at a maximum 4C-rate. Details of the electrode preparation and materials haven been published before [19] and are not repeated here for conciseness. The electrodes are balanced such that the NCA electrode is capacity-limiting towards low SOC, while the LTO electrode is capacity-limiting towards high SOC; LTO is operated within its plateau region for the complete SOC region below approx. 95% (cf. half-cell discharge curves in Ref. [19]). It is interesting to note that the LTO electrode can be seen as pseudo reference electrode, providing a constant (with respect to SOC, not with respect to temperature or C-rate) half-cell potential. The data shown here were collected from a total of four nominally identical individual cells.

2.2. Experimental setup and characterization

The cells were cycled using a BaSyTec XCTS cell test system. This system has a resolution of 0.1 mV/0.2 mA. Temperature on the cell surface was measured at the center of the cell face using an NTC element, as provided with the BaSyTec system. The cells were placed in a CTS Type T –40/200 climate chamber using custom-made cell holders. Temperature inside the climate chamber was measured using a PT100 sensor which enables a temperature stability of ±0.3 K. EIS measurements were conducted using a Gamry Reference 3000 device.

Fresh cells as obtained from the manufacturer were characterized before long-term cycling tests were started. Charge/discharge curves using a constant current/constant voltage (CCCV) protocol

for both charge (2.7 V/0.1C cutoff) and discharge (1.7 V/0.1C cutoff) were recorded at different symmetric C-rates (0.1, 0.2, 0.5, 1, 2, 4C) and ambient temperatures (5, 20, 35, 50 °C). The rest time between charge and discharge was 30 min. We selected a symmetric CCCV protocol for the following reasons: (i) the full capacity range can be accessed, in particular with respect to the asymmetry of the discharge/charge behavior at low SOC (cf. below, Section 3.1); (ii) the data will be used in future for validating physicochemical models, where again a particular focus will need to be put on validating the behavior at low SOC [19]. Given the strong capacity-rate effect of the cell (cf. below, Section 3.1), CCCV discharge may also be relevant in applications; it is interesting to note that the cell is specified (data sheet) for symmetric 4C discharge and charge operation. Internal resistance R_i was measured using a current step from $I_1 = 1.6$ A (0.1C) to $I_2 = 16$ A (1C) after discharging the cell (1C, 2 h rest) to the desired state of charge (SOC), defined based on the capacity measured at 1C/20 °C (varying with ageing time). From the measured voltage dynamics, R_i was calculated according to

$$R_i = -\frac{U_2(t_2) - U_1(t_1)}{I_2(t_2) - I_1(t_1)}, \quad (1)$$

for a typical time step of

$$\Delta t = t_2 - t_1 = 3\text{ s}. \quad (2)$$

EIS measurements were performed in galvanostatic mode ($I_{ac} = 0.16$ A, C/100) within a frequency range from 1 mHz to 10 kHz. From 10 kHz to 1 Hz ten data points per decade were registered, from 1 Hz to 1 mHz three data points per decade. We used Gamry Echem Analyst to fit an equivalent circuit model to the data.

For the cyclic ageing tests, the investigated cells were cycled for a total of 10,000 cycles between the nominal cutoff voltages of 1.7 V and 2.7 V with 4C, for both charge and discharge, without CV phase and without rest time in between cycles. This protocol was chosen to represent harsh cycling conditions. Note that the lack of the CV phase leads to considerably lower cycle depth (approx. 5.5 Ah cycled capacity corresponding to approx. 34% DOD). As will be further discussed below, it is mainly the low-SOC regime that is omitted with this cycling protocol.

After each 1000 cycles checkup measurements were carried out consisting of charge/discharge curves, internal resistance, and EIS at SOC = 50 %. The cells were cycled at an ambient temperature of 20 °C.

3. Results

3.1. Electrical and thermal characterization

Fig. 1 shows results of symmetric charge/discharge measurements (voltage vs. capacity) for different conditions. Fig. 1a) compares different C-rates at 20 °C ambient temperature. The cell shows the typical increasing discharge and charge overpotentials with increasing current. As consequence, although the cells were cycled with a CCCV protocol, the CC discharge part of the capacity is considerably rate-dependent. More noteworthy, the cell shows a distinct asymmetry in the discharge/charge behavior towards low SOC (above approx. 13 Ah discharged capacity). The asymmetry is present even at low C-rates. We have previously shown that this behavior is due to the NCA positive electrode and can be caused by a two-step adsorption/intercalation mechanism [19]. At high C-rates an “overshoot” of the voltage at the beginning of the charging phase is observed. This effect may be related to the two-step mechanism or may have additional causes such as self-heating.

Fig. 1b) and c) compare the behavior at different temperatures. The cell exhibits a significant temperature dependence of overpotential, discharge capacity, and asymmetry. It is noteworthy that

Download English Version:

<https://daneshyari.com/en/article/7539906>

Download Persian Version:

<https://daneshyari.com/article/7539906>

[Daneshyari.com](https://daneshyari.com)