



Performance tuning of lithium ion battery cells with area-oversized graphite based negative electrodes

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HIGHLIGHTS

- Area-oversizing of negative electrodes increases specific capacity losses.
- Capacity loss in overhang area (negative electrode) due to trapped active lithium.
- Kinetically trapped, but thermodynamically active lithium can be reactivated.
- Duration in charged state irreversibly increases losses of active lithium.
- Cycle life can be electrochemically improved by periodic discharge modifications.

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ABSTRACT

The accuracy for positional alignment of the positive electrode vs. the negative electrode is of great importance for the quality of assembly of lithium ion cells. Area-oversized negative electrodes increase the tolerance for electrode alignment. In this study, the impact of area-oversizing of the negative electrode on the specific capacity losses during charge/discharge cycling is systematically investigated by using electrochemical and analytical methodologies. It is shown, that with a higher degree of area-oversizing more active lithium is kinetically trapped in the outer negative electrode areas (“overhang”), causing performance-deteriorating losses in usable specific capacity. Nevertheless, most of this “lost” specific capacity is of reversible nature as the trapped active lithium can be electrochemically recovered, which is analytically proven by inductively coupled plasma-optical emission spectrometry (ICP-OES) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Given this relation, a periodic application of a short constant voltage step after discharge results in a significant performance increase. In contrast, holding the cell in the charged state is detrimental for cells with area oversized negative electrodes as the amount of reversible and irreversible trapped active lithium increases. Based on the obtained insights, the influence of variations of the electrochemical conditions on charge/discharge cycling performance is discussed.

1. Introduction

The steadily increasing demand for alternative energy sources and electro-mobility necessitates adequate electrochemical energy storage devices [1–7]. Among different systems, batteries, particularly the lithium ion batteries (LIBs) are the state-of-the-art (SOTA) benchmark technology [8–10]. In view of commercial claims, issues with respect to specific energy, energy efficiency, cycle life, safety and even recycling still require further research and development efforts [11–13], which

remains challenging given the complexity of a LIB cell during operation [14–17].

The charge/discharge cycling performance of a LIB cell sensitively depends on a wide range of parameters regarding not only the active and inactive materials (including their composition and balancing aspects) [18–25], but also the design of cell geometry [26,27,45]. An example for the influence of the latter is a cell with geometrically oversized area of the negative electrode relative to the area of the positive electrode. This design has practical benefits as it minimizes the

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risk of lithium plating at the edges of graphite electrode sheets during charge [28]. However, a deteriorating relation between the performance and the oversized area of the negative electrode is reported by Son et al. [29]. It is claimed that the outer areas (overhang) of the negative electrode additionally utilize active lithium for the formation of the solid electrolyte interphase (SEI) [30–32], resulting in increased irreversible specific capacity losses. However, these conclusions made on the interpretations of Coulombic efficiencies (CEs) did not consider possible kinetic origins, which can have a significant impact on the observed phenomena, as well [33]. In fact, recent reports point to an even reversible character of the apparently “lost” specific capacity by revealing changes in the lithium amount in the negative electrode overhang depending on the state of charge and discharge [34–37].

In this work, the reversible and irreversible specific capacity losses are thoroughly investigated by applying electrochemical and analytical measures for varying degrees of the overhang. Given the practical importance of the overhang usage [27,38,39], the goal of this work is not only to clarify but also to circumvent the origin of the accompanied losses in specific capacity.

2. Experimental

Single side coated electrodes for the LIB pouch cells were in house made, based on mesocarbon microbeads (MCMB, Osaka) and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111, Cellcore) active materials for negative and positive electrodes, respectively. The electrodes were locally separated by an electrolyte soaked Freudenberg 2190 separator. The electrolyte was based on 1 M LiPF_6 in ethylene carbonate (EC):dimethyl carbonate (DMC) 1:1 wt% (LP30, BASF). The electrolyte amount, which can impact the performance upon variation, was excessed in all cells [40]. The LIB pouch cells were assembled in the dry room (dew point of at least -60°C).

The determined practical delithiation capacity of the MCMB graphite based negative electrodes was $296 \pm 10 \text{ mAh}\cdot\text{g}^{-1}$ and of the NMC111 based positive electrodes was $142 \pm 2 \text{ mAh}\cdot\text{g}^{-1}$, when cycled at 0.1 C in three-electrode lithium half cells in the range of 0.02 V and 1.5 V vs. Li/Li^+ and 4.2 V and 2.5 V vs. Li/Li^+ , respectively. Providing an active material mass loading of $9.2 \text{ mg}\cdot\text{cm}^{-2}$ and $14.2 \text{ mg}\cdot\text{cm}^{-2}$, respectively, the negative electrode was oversized in capacity in a ratio of 1.3:1. Different negative to positive electrode area ratios were studied. Whereas the positive electrode had the area size of $30 \text{ mm} \times 30 \text{ mm}$, the negative electrode area sizes were varied from $30 \text{ mm} \times 30 \text{ mm}$ – $33 \text{ mm} \times 33 \text{ mm}$, $40 \text{ mm} \times 40 \text{ mm}$, and $55 \text{ mm} \times 55 \text{ mm}$, respectively (Fig. 1(a)–(d)). Similar mass loading of the overhang (as apparently “inactive” area) was chosen. (With increasing overhang, the amount of “inactive” materials increases, increasing the overall mass and volume of the cell, finally decreasing energy density/specific energy) [41].

The full cells were cycled according to the electrochemical conditions in Table 1. Five constant current (cc) formation cycles (as default cycles for reasons of SEI optimization) were followed by one constant current/constant voltage (cc/cv) charge, cc discharge acclimation cycle at 1C/0.05C (6th cycle). The 7th cycle included a self-discharge (SD) experiment (i.e., a rest step of 120 h) with subsequent cc discharge at 1C. After the SD experiment, cells were cycled in cc/cv charge, cc

Table 1

Charge/discharge cycling procedure includes five constant current (cc) formation cycles, a self-discharge experiment and subsequent constant current/constant voltage (cc/cv) charge/cc discharge cycling. The criterion of 0.05C for cv steps implies a cut-off when the detected current during the cv step drops below the threshold value of 0.05C.

Cycle	Mode	Charge	Discharge
1	Formation	cc: 0.05C	cc: 0.1C
2–5	Formation	cc: 0.1C	cc: 0.1C
6	Cycling	cc/cv: 1C/0.05C	cc: 1C
7	Cycling + SD	cc/cv: 1C/0.05C 120 h rest	cc: 1C
8–19	Cycling	cc/cv: 1C/0.05C	cc: 1C
20	Cycling + dcV	cc/cv: 1C/0.05C	cc/cv: 1C/0.05C
21- ...	Cycling	cc/cv: 1C/0.05C	cc: 1C

cc: constant current.

cv: constant voltage.

1C: 1C corresponds to charge or discharge rate of $142 \text{ mAh}\cdot\text{g}^{-1}$.

SD: A rest step of 120 h is applied after charge.

dcv: constant voltage step during discharge.

discharge mode. The discharge of the 20th cycle comprised a low rate (0.05C) constant voltage step during discharge (dcv). LIB pouch cells were cycled between 4.2 V and 3.0 V.

Four different charge/discharge cycling procedures were used to investigate long term cycling according Table 2. The standard procedure contains 5 formation cycles and 494 cycles of cc/cv charge with subsequent cc discharge at 2C. After the 20th, 120th, 220th, 320th, and 420th charge and discharge was a rest step of 50 min, respectively. The second procedure includes a SD experiment (120 rest step after conventional cc/cv charge) after the 7th, 107th, 207th, 307th and 407th charge. The third procedure includes a dcV step to the standard procedure after the 20th, 120th, 220th, 320th, and 420th discharge. The fourth procedure includes both, SD and dcV experiments.

For analytical investigations, cells with 78% oversizing of the negative electrode were investigated (Fig. 1 (c)). Two cells were cycled with the procedure depicted in Table 1 till the 6th, 7th or 20th cycle, respectively. In addition to the discharged cells, two uncycled cells were transferred into the glove box (water and oxygen content of less than 0.2 ppm), disassembled and electrodes were washed with DMC.

For Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements, six 4 mm \varnothing discs were punched out of the negative electrode overhang for each cell. ICP-OES measurements were performed using a Spectro ARCOS ICP-OES (Spectro Analytical Instruments) instrument with axial plasma viewing. A standard Fassel type torch (Spectro Analytical Instruments) was employed. For sample introduction, the system's peristaltic pump with a cross flow nebulizer and a double-pass spray chamber (Scott type) was used. Element emission was detected at different individual emission lines simultaneously. Operating conditions for ICP-OES measurements are shown in Table 3 [42]. This method was used to determine the lithium content of the discharged electrode according the literature [42].

For Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), 20 mm \times 20 mm rectangles were punched out of a corner of the 40 mm \times 40 mm negative electrodes. The ^7Li signal (cps = counts per second) was recorded using 184 transient signals per

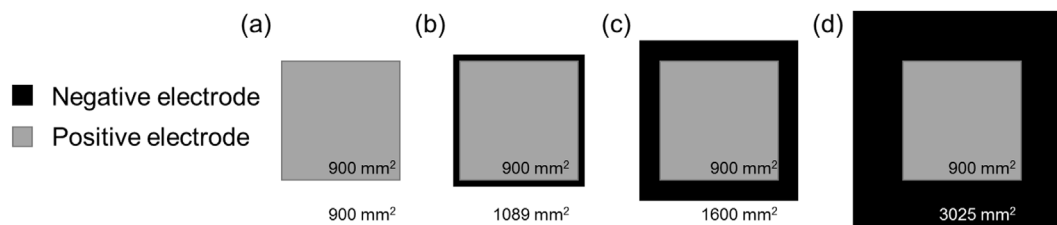


Fig. 1. Cells with varying oversized negative electrode area: (a) 0%, (b) 21%, (c) 78% and (d) 236%.

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