



# Hysteresis and current dependence of the thickness change of lithium-ion cells with graphite anode



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## ABSTRACT

The charging process of a lithium-ion cell causes the graphite anode to expand due to the intercalation of lithium ions in the graphite layers. This leads to an increased cell thickness, which is entirely reversible when moderate charging currents are applied. This paper measures the cell thickness using a dial indicator on the surface of a commercial nickel–cobalt–manganese/graphite pouch cell during the charging and discharging process. By comparing the measurements to the theoretical thickness calculated from published layer parameters, information can be acquired about the insertion and extraction processes in the graphite anode for the charging and discharging directions. One of the peculiarities of the measured thickness during discharging is that the theoretical maximum is exceeded in a specific SOC range. A current dependence of the graphite thickness can also be observed for insertion and extraction. The thickness hysteresis between charging and discharging is analyzed considering different intercalation variants for the same SOC. In addition, it is shown that moving between the discharging and charging curve is possible without a complete charge or discharge of the cell.

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## 1. Introduction

A cell thickness measurement helps to better understand structure changes within the electrode material as well as the electrical behavior of lithium-ion cells with graphite anode. Important applications include determining the state of charge (SOC) and the early detection of lithium plating. Most of the change in thickness results from the graphite anode due to the intercalation and deintercalation of lithium-ions in the graphite layers [1–9].

Graphite has different insertion variants for lithium-ions [10]. The so-called stages depend on the number of lithium-ions in each graphite layer and are characterized by different layer distances. The graphite thickness at a specific SOC results from a mixture of one or more different stages.

To detect lithium plating, Bitzer et al. [3] measured the cell thickness change using a dial indicator on the surface of a pouch cell. As the measurement was taken, a hysteresis effect was identified between charging and discharging [3,8,9]. Rieger et al. [9] used three different methods to investigate the change in cell

thickness of a commercial lithium-cobalt oxide/graphite pouch cell. Bauer et al. [8] made initial theoretical calculations of the thickness with different graphite intercalation compositions to describe the relaxation behavior associated with different SOCs.

This paper presents the thickness change of a commercial nickel–cobalt–manganese (NMC)/graphite pouch cell for different charge and discharge currents. The thickness curves for low currents provide insight into the insertion and extraction processes. When high current values are applied, the cell thickness curve becomes current dependent but remains stable over time. To classify the measured cell thickness curves, the theoretical maximum and minimum cell thickness are calculated for each SOC from the literature values of the different intercalation stages. The thickness hysteresis effects between charging and discharging are also analyzed using measured partial charging and discharging curves.

## 2. Theory

Different stages are run through during the intercalation of lithium in graphite. These stages are listed in Table 1. At full charge, the lithium-ions in the graphite layer create a volumetric increase in thickness of up to 10.4% [11,12]. The cathode material used, on

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**Table 1**

Properties of graphite intercalation stages:  $j$  is the index,  $x_j$  the normalized quantity of lithium and  $d_j$  the reported thickness value.

$j$	Stages	$x_j$	SOC/%	$d_j/\text{Å}$	Lit.
1	LiC <sub>6</sub>	1.0	100	3.70	[12,14]
2	LiC <sub>12</sub>	0.5	50	3.51	[12,16]
3	LiC <sub>18</sub>	0.3	33.3	3.53	[12]
4	LiC <sub>36</sub>	0.16	16.6	3.45	[15]
5	LiC <sub>72</sub>	0.083	8.3	3.40	[15]
0	C	0	0	3.35	[12,16]

the other hand, is volumetrically stable up to 4.15 V vs. Li/Li<sup>+</sup> and its change in thickness is negligible [13].

The values cited in the literature for the graphite layer distances of Li<sub>*x*</sub>C<sub>6</sub> were measured by X-ray diffraction [12,14–16]. All test samples were formed through the direct reaction between graphite and lithium in the respective proportions under high-temperature conditions. Therefore all measured graphite stages were very homogeneously distributed, with each graphene layer containing the same quantity of lithium. The existence of discrete stages at lower SOC is still discussed in literature. Recent in situ neutron diffraction measurements show no discrete stages but so-called liquid stages [17,18] or a two-phase transformation from lithiated graphite to LiC<sub>6</sub> [19]. In the following theory, the discrete stages are used.

Table 1 shows the six homogeneous SOC<sub>s</sub> found by X-ray diffraction. At SOC levels between these fixed values, different stages must exist simultaneously. An anode SOC of 100% means that the hexagonal structure of the graphite is completely filled with lithium and can be represented as LiC<sub>6</sub>. For any given quantity of lithium in the graphite anode the SOC  $x$  ( $0 \leq x \leq 1$ ) can be formally described as Li<sub>*x*</sub>C<sub>6</sub>.

In Table 1, the lithiation degree of the respective stage is represented by  $x_j$ , which specifies the relative quantity of lithium per layer. The fraction of carbon atoms that is occupied with structure  $j$  is represented by  $c_j(x)$ . Since the anode has a finite quantity of carbon atoms the following equation holds:

$$\sum_{j=0}^5 c_j(x) = 1 \quad (1)$$

The product  $x_j \cdot c_j(x)$  describes the contribution of stage  $j$  to the total anode SOC. Any given SOC  $x$  is therefore characterized by the sum of all existing stages  $j$ :

$$\sum_{j=0}^5 x_j \cdot c_j(x) = x \quad (2)$$

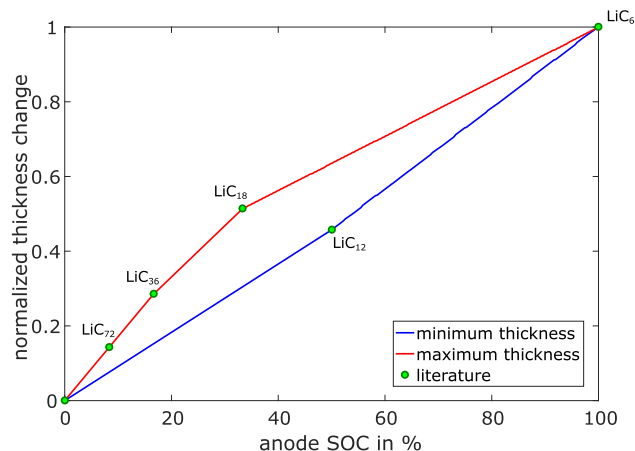
A given anode SOC can be realized with different combinations of the respective stages. The individual  $c_j$  values are therefore not unambiguously defined. The thickness  $d(x)$  of a given combination is then

$$d(x) = \sum_{j=0}^5 d_j \cdot c_j(x) \quad (3)$$

assuming that only the six different stages from Table 1 exist. Here,  $d_j$  represents the literature value of the thickness for stage  $j$  as listed in Table 1. The product  $d_j \cdot c_j(x)$  describes the contribution of stage  $j$  to the anode thickness.

For each SOC the minimum and maximum thickness can be determined by calculating all possible combinations of the six existing  $c_j$  using Eqs. (1)–(3). The values can then be normalized using the minimum and maximum values  $d_0$  and  $d_1$  from Table 1:

$$d_{norm}(x) = \frac{d(x) - d_0}{d_1 - d_0} \quad (4)$$



**Fig. 1.** Calculated normalized minimum (blue line) and maximum (red line) thickness of the mixed structures of Li<sub>*x*</sub>C<sub>6</sub> along with the literature values (green dots) as a function of anode SOC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 1 shows the minimum theoretical thickness in blue and the maximum theoretical thickness in red. The literature values for homogeneous distribution from Table 1 are included as green dots.

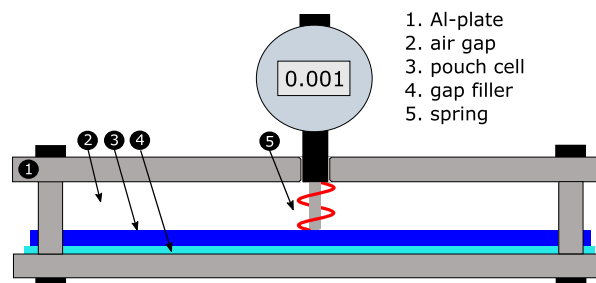
The minimum thickness curve is the path with the lowest slope touching LiC<sub>12</sub> and then continuing toward LiC<sub>6</sub> (100% anode SOC). The maximum thickness curve connects the points LiC<sub>72</sub>, LiC<sub>36</sub>, LiC<sub>18</sub> and LiC<sub>6</sub>. Note that the maximum and minimum thickness have been calculated by trying all combinations of up to six stages.

The measured thickness change is expected to be within the theoretical window of minimum and maximum thickness depicted here.

### 3. Experimental

Fig. 2 illustrates the experimental setup for measuring the cell thickness change as reported earlier [3]. The pouch cell is fixed to the lower aluminum plate using a thermally conductive adhesive to achieve a good thermal connection and mechanical stability. The measurement setup is placed in a climatic chamber during the test procedure to ensure a constant ambient temperature. The upper aluminum plate is mounted with a gap respective to the cell to provide enough room for the cell expansion and air to transfer the heat generated during charging and discharging. The dial indicator with a spatial resolution limit of 1 mm is attached to the upper plate and measures the expansion at the center of the cell. A spring is mounted around the measuring point to displace any evolution of gas near the measurement position. The lithium-ion cell used has an NMC cathode and a graphite anode. More properties of the used high-energy cell are listed in Table 2.

A BaSyTec XCTS battery tester is used to perform the charging and discharging operations.



**Fig. 2.** Measurement setup for quantifying the cell thickness change with a spatial resolution limit of 0.001 mm.

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