



## Short communication

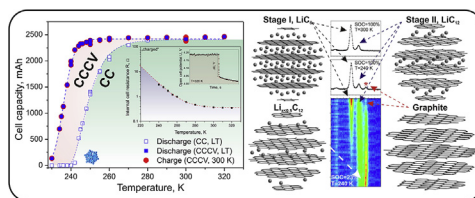
## Low-temperature performance of Li-ion batteries: The behavior of lithiated graphite

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## HIGHLIGHTS

- Combined *in operando* electrochemical and neutron powder diffraction study at low temperatures.
- Reduction of cell capacity along with an increase of the internal cell resistance.
- Structural indications for anomalous behavior of lithium intercalation into graphite at low temperatures.
- Quasicontinuous  $\text{LiC}_{12}$ -to-C transition pathway breaks at low temperatures.
- Anomalous temperature behavior of  $\text{LiC}_6$  (stage I) intercalated graphite.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Safety issues along with the substantially reduced energy and power capabilities of Li-ion cells, operated at low temperatures, pose a technical barrier limiting their use in electric vehicles and aerospace applications. A combined *in situ* high-resolution neutron powder diffraction and electrochemical study on Li-ion cells of the 18650-type over a temperature range from 230 K to 320 K is reported with a focus on the graphite anode and the low temperature performance of the cell. Instead of a quasi-continuous behavior as observed at ambient temperatures, an anomalous behavior occurs upon discharge at low temperature, primarily reflected in the abrupt character of the  $\text{LiC}_{12}$  – to – graphite phase transformation and the unusual temperature dependence of the amount of  $\text{LiC}_6$ . An instability of lithiated graphite phases at temperatures below 250 K is observed, which affects the performance of Li-ion batteries at low temperatures.

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## 1. Introduction

Lithium ion batteries are considered as the major energy storage technology in the field of portable electronics and electric vehicles primarily due to their high power/energy density, good cycle life and excellent storage characteristics. Despite their overall success, further research on Li-ion batteries towards higher energy/power

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density, lighter weight, safer and lower cost rechargeable batteries is of high scientific and technological relevance. There is also another aspect to be addressed: the stability of the Li-ion cells over a broad range of environmental conditions, where operating temperature is one of the most important criteria. According to the recommended range of Li-ion battery operation (253 K–333 K) their use in countries with moderate and frigid climate in winter time becomes quite bounded. Limited low temperature performance of Li-ion batteries turns out to be even more critical in aerospace applications, where stable energy storage and conversion under more extreme environmental conditions is demanded over a long period of time. Therefore broadening the temperature range of stable battery performance and characteristics is an emergent research task. In this context the lower temperature region of operation has obviously higher priority compared to the high temperature one.

Electrochemical aspects related to a poor performance of Li-ion batteries at low temperatures have extensively been studied in recent years. A majority of research was devoted to the boost of electrolyte performance towards lower freezing point and higher conductivity by using different solvent mixtures, admixtures and novel electrolytes [1–7]. The poor performance of Li-ion cells is usually ascribed to effects like low electrolyte conductivity, slow kinetics of charge transfer, increase of the SEI (solid-electrolyte interphase) resistance, slow lithium diffusion or to a combination of these factors. Another possible reason for the restricted Li-ion cell performance at low temperatures is the low carbon electrode activity in form of either poor transport through the SEI [8,9], high charge transfer resistance, low lithium diffusivity [8–13] or substantial loss of lithiation capacity. Using a combination of galvanostatic intermittent titration and impedance spectroscopy authors [9] reported that “the poor low-temperature performance of the graphite insertion anodes results from a low lithium insertion capacity because polarization or overpotential is higher than the stage transformation plateau potential.” This declared statement might be reflected in the map of the phase transitions supplementing the lithium de/intercalation into the electrode materials and consequently result in deviations from established schemes [14–17]. On the other hand low-temperature impedance spectroscopy studies [18,19] on Li-ion cells with reference electrode revealed an increase of the cell impedance at subambient temperatures to the interfacial resistance (primarily charge transfer) of the cathode/electrolyte interface. A formation of lithium plating at low temperatures is widely discussed in literature as another reason for limited cell performance [20,21]. But to our knowledge its experimental *in situ* evidence (e.g. by means of diffraction methods) has not been presented so far.

Although diverse and somewhat contradictory opinions about the origin of the poor performance of Li-ion batteries at low temperatures and the role of the electrode materials in this process are reported in literature, no comprehensive electrochemical and structural studies of lithium ion batteries at low temperatures were found. However, they could potentially resolve existing controversies and shed more light on the role of the electrode structure regarding cell performance. This is maybe due to the fact that despite the relatively simple principle of operation modern Li-ion batteries are sophisticated electrochemical devices possessing numerous degrees of freedom and complicated interactions dependent on chemistry, morphology, packing density *etc.* Their accurate identification and study requires experimental approaches capable to give information about processes occurring “live” inside the battery thus eliminating the risks of possible materials oxidation, electrolyte evaporation and battery state-of-charge (SOC) changes. Among different experimental methods capable to probe the structure of Li-ion cell constituents under real operating

conditions neutron scattering is already a well-established tool having numerous advantages [22]. The most prominent one is the high penetration depth of thermal neutrons enabling non-destructive studies of commercial Li-ion cells, which usually possess very low production spread and therefore good reproducibility of their characteristics. Cells of the most common design (18650-type, based on LiCoO<sub>2</sub> as positive and graphite as negative electrode) were chosen. As previously reported [16,23–25] a combined cell characterization by means of high-resolution neutron powder diffraction and electrochemistry was performed on the cells, which have a nominal capacity of 2600 mAh.

## 2. Experimental section

### 2.1. Electrochemical studies at low temperatures

A Li-ion cell (18650-type, LiCoO<sub>2</sub> cathode, graphite anode, nominal capacity 2600 mAh) was mounted in a top-loading closed cycle refrigerator. Helium 4.6 was used as a heat transmitter. The instantaneous temperature was controlled by a temperature controller LakeShore 470 and measured using a combination of a thin film resistance cryogenic temperature sensor Cernox and a resistance thermometer PT 100. Experiments were performed in a temperature range from 230 K to 320 K (shown in Fig. S1). The SOC control has been realized using a SP-240 potentiostat from BioLogic via constant current/constant voltage protocol using 400 mA current in the voltage window from 3.0 V to 4.2 V (Fig. S2). The cutoff value for the current in the constant voltage mode was set to 25 mA. In order to avoid cell failure and minimize state-of-health changes no low temperature charge was applied, i.e. the Li-ion cell was always charged at 300 K and discharged at the desired temperature.

### 2.2. High – resolution neutron powder diffraction

The neutron powder diffraction experiment has been performed at the instrument SPODI at the neutron source FRM II (Garching b. München, Germany). All measurements were performed in Debye–Scherrer geometry with an incident neutron beam having a rectangular cross section at the sample position of 40 × 30 mm<sup>2</sup>. In order to reduce the background and to improve the transmission characteristics of the sample its plastic cover has been removed prior to mounting it on the sample table of the diffractometer. As a certain amount of fatigue was introduced to the cell during the studies carried out without neutrons a “fresh” Li-ion cell of the same batch has been chosen for the *in situ* neutron measurements. The cryostat with the 18650 – type cell inside was mounted on the sample table and diffraction data were collected “live” with 30 min time discretization. “Long” (ca. 5 h integration time) neutron powder diffraction data were collected *in situ* during the rest phase in discharged and charged state at 300 K and at 320 K, 270 K, 250 K, 240 K, 235 K and 230 K, respectively. “Short” (ca. 30 min integration time) powder diffraction datasets were collected during the CCCV discharge process. A comparison of potention/galvanostatic measurements performed with and without neutron diffraction in parallel indicated their identity.

### 2.3. Crystal structure analysis

Monochromatic neutrons with a wavelength of 1.54832(4) Å were chosen from the 551 reflection of a vertically focused composite germanium monochromator. High resolution neutron powder diffraction data were collected in the 2 $\theta$  range from 1.0° to 151.9°. Data analysis was performed by a combination of the full profile Rietveld method and single profile decomposition using the FullProf program package. The Thompson-Cox-Hastings pseudo-

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