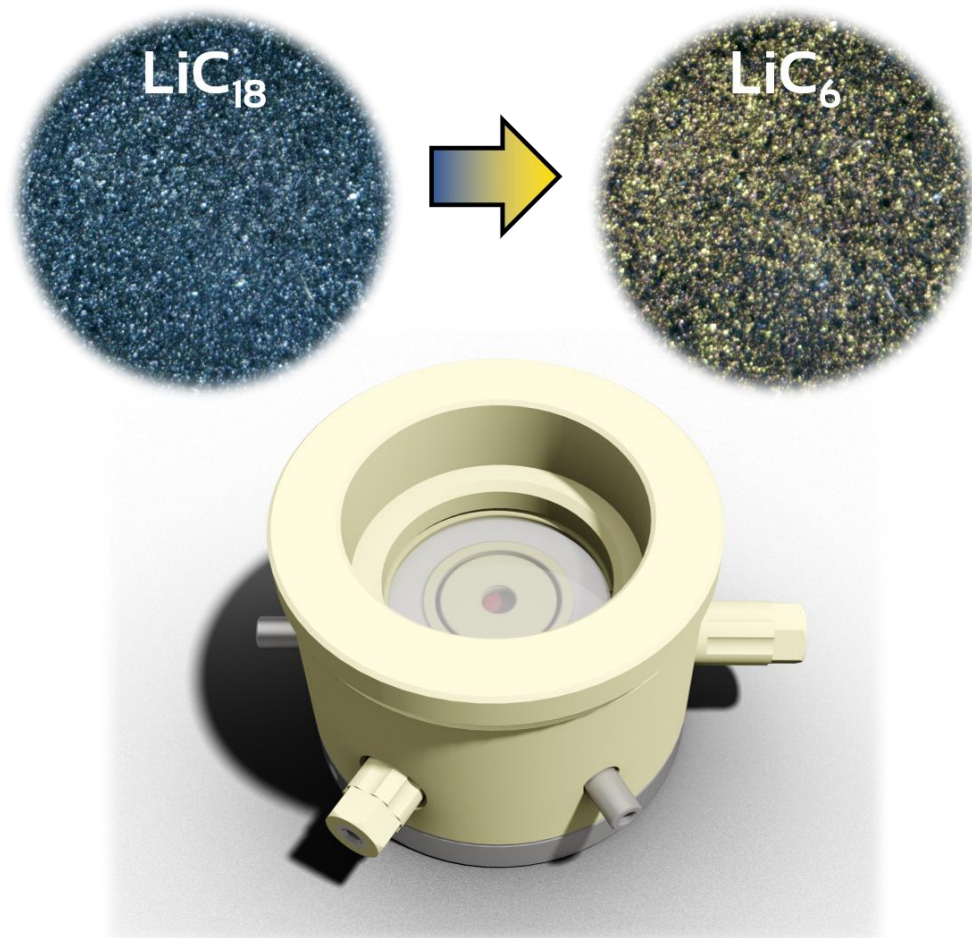


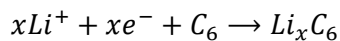
# Application note

## Optical Monitoring of the Lithiation of Graphite *in situ*



## Introduction

Graphite has the ability to intercalate lithium ions between its graphene layers at a potential of around 0.1 V vs  $\text{Li}^{0/+}$ :



where  $x$  is the extent of lithiation ( $0 \leq x \leq 1$ ). The high number of lithium ions that can be reversibly intercalated leads to a very high specific capacity, which in combination with the low potential leads to a high specific energy when employed as anode material in a lithium-ion battery (LIB). The fact that graphite has been used in almost all commercial LIBs for the past 30 years highlights the importance of this reaction to the field of energy storage [1]. Nevertheless, the details of the lithium intercalation mechanism in graphite are still under debate [1, 2]. Ongoing research efforts attempt to elucidate the reactions and side-reactions occurring in this process, as well as to improve the performance of graphite-based LIBs [1, 2].

The main species of lithiated graphite are listed in Table 1. As the graphite lithiation reaction progresses, these species are formed in various ratios depending on factors like the applied current (C-rate), graphite type and quality, electrode coating homogeneity, etc. When two types of lithiated species (phases) exist simultaneously in equilibrium, the potential is fixed. A potential plateau in the charge/discharge curve thus corresponds to a transition between two species. A multitude of less lithiated species also exist at the beginning of the lithiation, but they

are in general less defined and will not be discussed here. Intercalation stage 1 (and 2) refers to lithium being intercalated into every (and every second, respectively) layer in the graphite structure, while stage 2D is a diluted form of stage 2 [1].

Table 1. Main lithiated graphite species.

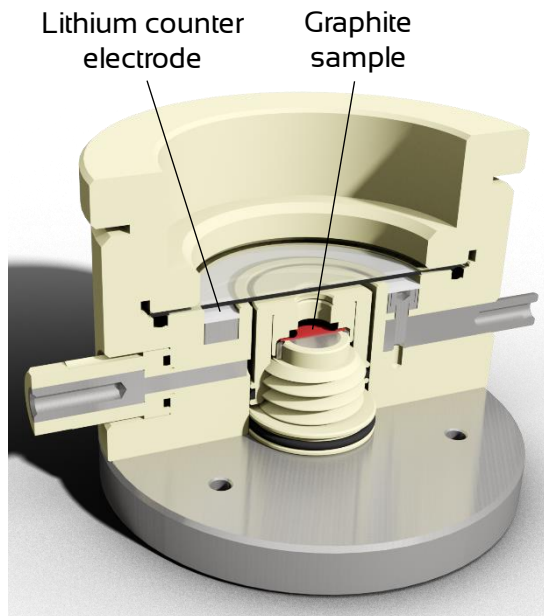
$x^a$	Formula <sup>b</sup>	Intercalation stage	Color
1/3	$\text{LiC}_{18}$	Stage 2D	Blue
1/2	$\text{LiC}_{12}$	Stage 2	Red
1	$\text{LiC}_6$	Stage 1	Gold

<sup>a</sup> See reaction above. <sup>b</sup> Normalized to 1 Li.

As indicated in Table 1, the visible color of graphite changes depending on the amount of intercalated lithium, *i.e.* its state-of-charge (SOC) in a LIB. While pristine graphite is grey, it turns deep blue as  $\text{LiC}_{18}$  is formed, then red with the formation of  $\text{LiC}_{12}$ , and finally golden in the fully lithiated  $\text{LiC}_6$  state. Optical microscopy can therefore be used to assess the progress of the lithiation reaction and the SOC across a graphite electrode [2, 3, 4]. Several setups have been demonstrated for this purpose, in particular using either a “side-by-side” or a “top-down” configuration of the working (WE) and counter electrodes (CE) [2, 3, 4].

In this application note we describe the optical monitoring of the graphite lithiation process *in situ* in a top-down configuration, using a cell with an optical window (Figure 1), a lithium CE, and a lithium reference electrode (RE). The graphite WE is visible from above, as is the ring-shaped

CE. This cell design ensures a homogenous current distribution and planar lithium diffusion to and from the WE, mimicking the situation in a LIB.



**Figure 1.** Cross section of the cell, showing the working electrode sample in red and the ring counter electrode in light gray, both of which can be viewed through a sapphire window. The reference electrode can be seen on the left side.

## Experimental

Circular samples (8 mm  $\varnothing$ ) of a graphite electrode (4.2 mAh/cm<sup>2</sup>; artificial graphite on copper foil) were punched out using an OAB Cutter (rhd instruments GmbH & Co. KG) and vacuum dried (60 °C, 12 hours).

The “Optical Cell M” (rhd instruments GmbH & Co. KG, **Figure 1**) was assembled in a glove box as follows: Lithium foil (0.7 mm thickness) was cut into 4 mm wide strips and pressed into the CE cavity. A small piece of lithium foil was punched out directly onto the RE. A graphite electrode sample was gently

pressed onto the stainless-steel WE current collector with an O-ring (4 mm inner  $\varnothing$ ). The area defined by the O-ring (12.6 mm<sup>2</sup>) was taken as the active area, leading to a nominal capacity of 0.528 mAh. Note however that in practice also some of the graphite outside of this area is electrochemically active. The cell was closed and filled with a 1 M LiPF<sub>6</sub> carbonate-based commercial battery electrolyte before being taken out of the glove box for measurements.

A Biologic SP-200 potentiostat/galvanostat controlled by EC-Lab 11.52 (Bio-Logic SAS) was used for the charge/discharge experiments in three-electrode mode. The tests were carried out at room temperature (20 °C) without active temperature control. After an initial 12-hour rest period, the graphite WE was reduced (lithiated) at a constant current (CC) of C/10 until 0.01 V vs Li<sup>0/+</sup>, followed by a constant voltage (CV) stage until C/20. After a 2.5-hour rest period, the graphite was oxidized (de-lithiated) at C/10 until 1.5 V vs Li<sup>0/+</sup>.

During the charge/discharge experiment, a DST-1028 digital microscope (Bresser GmbH) recorded one image (micrograph) of the graphite electrode surface every 5 minutes. The brightness of the micrograph figures shown here was increased by 40% to enhance visibility.

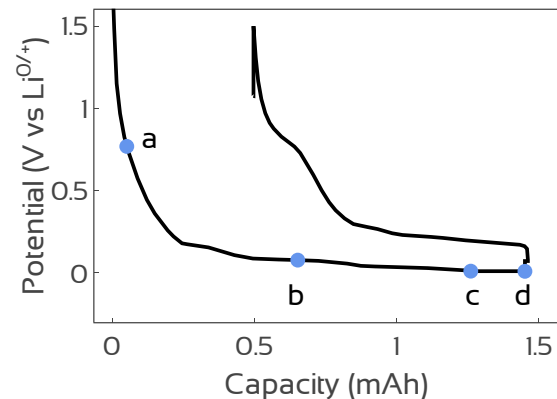
To analyze the color changes during cycling, each raw image (frame) was first converted to the hue/saturation/brightness (HSB) color space, with each HSB

component represented by a number in the range 0 – 255. A filter was then applied to only consider “colorful” pixels, by removing very dark (brightness < 80) as well as very desaturated (saturation < 30) pixels. The color composition of the frame was then determined by counting the portion of filtered pixels that fell in certain ranges of hue values. The specific ranges used were chosen to correspond to the colors of the different lithiation stages of graphite (Table 1) as follows: Blue (125 – 175), red (0 – 20 & 240-255), and gold (20 – 60).

Edelweiss (rhd instruments GmbH & Co. KG) was used to create the plots in this application note.

## Results and Discussion

The charge and discharge curves in Figure 2 reveal the potential plateaus of the lithium (de)intercalation, as detailed above. Both the charge and discharge capacity were larger than expected from the nominal active area, showing that a larger portion of the electrode was in fact participating in the electrochemical reaction. The graphite coating was thus porous enough to allow electrolyte to soak into a larger area, making an exact determination of the active area difficult. Furthermore, there was a large irreversible capacity loss during this first cycle, which in part could stem from the same cause. Partially, however, this originates from the solid-electrolyte interface (SEI) formation process, which consumes some charge to form a protective layer on the graphite surface.



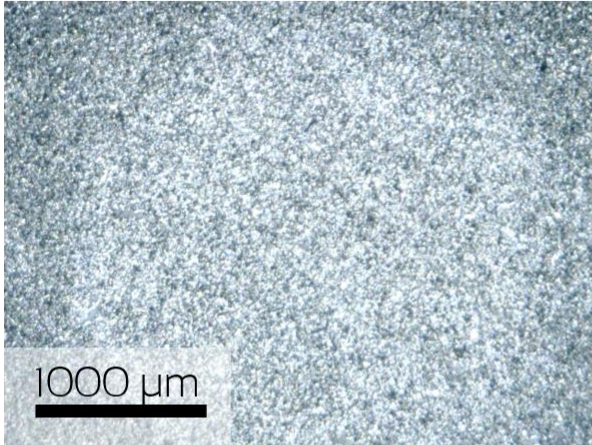
**Figure 2.** Graphite charge/discharge curves (WE vs RE potential, first cycle). Blue points (a – d) indicate when the micrographs in Figure 3 were recorded.

Micrographs recorded *in situ* during the lithiation of graphite are shown in Figure 3. The complete recording including all frames can be seen in a video available online [5]. In the beginning, the grey graphite surface was rather light and colorless (Figure 3a). The image had a slightly blue tone due to the LED lights used to illuminate the surface. During the early stages of lithiation, the graphite surface became darker, with an increasingly deep blue color (Figure 3b). As the lithiation progressed, some grains turned red and then gold (Figure 3c,d). The darkening of the surface might be associated with the SEI formation, while the blue, red, and gold colors come from the  $\text{LiC}_{18}$ ,  $\text{LiC}_{12}$ , and  $\text{LiC}_6$  species, as discussed above (Table 1). Figure 3c shows that at that point during the experiment, all of these species co-existed in the graphite electrode. When the charge step was complete, all particles had been converted to the gold colored, fully lithiated  $\text{LiC}_6$  (Figure 3d). It is worth noting that

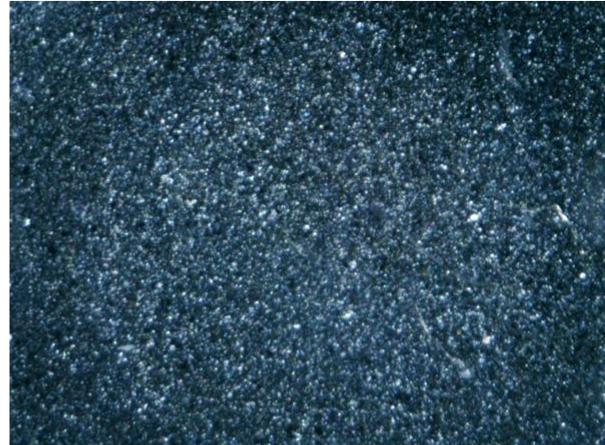
we are limited to observing the top surface of the electrode, and therefore do not know

the state of the inside of particles, nor the bulk of the coating below the surface.

a) Graphite (0.769 V vs  $\text{Li}^{0/+}$ )



b)  $\text{LiC}_{18}$  (0.078 V vs  $\text{Li}^{0/+}$ )



c)  $\text{LiC}_{12}$  (0.011 V vs  $\text{Li}^{0/+}$ )



d)  $\text{LiC}_6$  (0.010 V vs  $\text{Li}^{0/+}$ )



**Figure 3.** Micrographs of the graphite electrode during the various stages of lithiation. All micrographs have the same scale and show the same area of the electrode.

The lithiation of the graphite particles was homogeneously distributed throughout the monitored area, as is evident in the video [5], as well as in **Figure 3c**, in which blue, red, and golden particles are evenly distributed. That is to say, the lithiation did not start preferentially from one direction, such as from the edge of the electrode, which is the case for optical cells in side-by-side configuration. This indicates homogenous and planar diffusion of lithium

ions towards the WE, as in a real LIB, owing to the optimized cell geometry. There is however a trade-off between homogenous current density and low internal cell resistance. With the current design, the relatively large resistance contributes to the polarization between the charge and discharge curves (**Figure 2**). Note that this shifts the plateaus of the lithiation to lower potentials.

Figure 4 shows the portion of blue, red, and gold color in each micrograph recorded throughout the charge/discharge experiment. The transition from the blue  $\text{LiC}_{18}$ , through the red  $\text{LiC}_{12}$ , and to the golden  $\text{LiC}_6$ , is clearly visible. These color transitions coincide with the respective potential plateaus. The reverse processes occur during the de-lithiation. The onset of the occurrence of the blue species is partially obscured by the blue lighting, making the initial grey sample appear blue as well. (cf. Figure 3a and b) It is interesting to note that the red and golden species start to form at roughly the same time, rather than forming in discrete and consecutive steps. All these observations agree with what can be seen qualitatively in the micrographs (Figure 3) and the video [5].

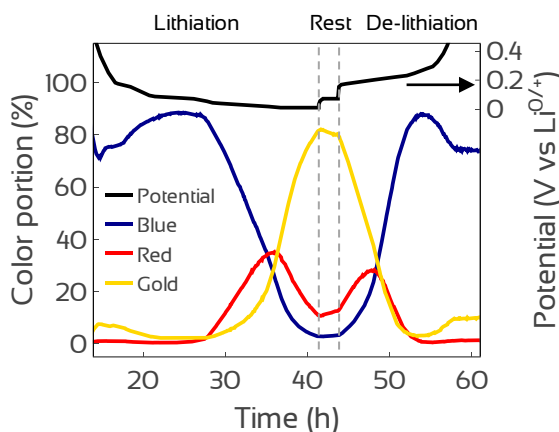


Figure 4. Color change measured *in situ* during the electrochemical lithiation and de-lithiation of the graphite electrode. The potential (WE vs RE) is shown in black on the right y-axis. The portions of different colors in each frame (corresponding to the different lithiation species) are shown in the respective color on the left y-axis. The vertical dashed lines indicate the transitions from lithiation to rest to de-lithiation.

## Summary

The reversible lithiation of graphite is extremely important to the function of a lithium-ion battery, and can be studied by optical microscopy since the visible color changes depending on the amount of intercalated lithium in the graphite structure. In this application note, a top-down type cell for optical *in situ* monitoring was used for this purpose. The color changes corresponding to the  $\text{LiC}_{18}$ ,  $\text{LiC}_{12}$ , and  $\text{LiC}_6$  species could be observed in the micrographs between the respective potential plateaus in the charge/discharge curves. Examining the color composition of each recorded frame allowed for a more quantitative analysis of the progress of the lithiation reaction. This cell could also be used to monitor *e.g.* lithium-plating *in situ*, and using a higher-magnification microscope would enable studying the lithiation of individual graphite particles.

## Literature

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