

# Multi-phase formation induced by kinetic limitations in graphite-based lithium-ion cells: Analyzing the effects on dilation and voltage response



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## ABSTRACT

In this research work, dilation and voltage effects related with the formation and dissolution of overshooting phases in graphite electrodes are investigated and a modeling approach is proposed. These multi-phase effects are induced by kinetic limitations under high-rate conditions. Therefore, high-rate charge loads are applied to a graphite|NMC pouch cell at different temperatures, current rates and SOC ranges. Particularly at low temperatures, the dilation relaxation after the current phase is significantly influenced by multi-phase effects. For the first time, the dilation effects are also compared to the simultaneous voltage effects, which provide additional information about multi-phase-formation. By analyzing the time derivative of voltage during the relaxation phase subsequent to high-rate charge phases, individual multi-phase-features resulting from stage-2-relaxation, stage-1-relaxation and lithium plating are distinguished from each other. Finally, an electrochemical transmission line model for predicting and simulating multi-phase-effects is introduced. The model allows to simulate voltage responses both under heavy charge loads and during subsequent relaxation phases. Furthermore, it provides a representation of inhomogeneous graphite lithiation and allows to predict the onset of lithium plating. The approach is particularly promising with regard to fast charging applications, where the charge current needs to be limited to avoid lithium plating.

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## 1. Introduction

In our previous work [1], we have investigated the dilation response during and after high-rate current pulses applied to a 16 Ah graphite-based lithium-ion pouch cell. According to a 10-step-GITT (galvanostatic intermittent titration technique) scheme, the pulses have been designed to cover the whole SOC range in steps of 10% of the nominal cell capacity  $C_N$  at a current rate of  $I = 1.5 C$ . This means, the charge amount of each single pulse was  $Q = C_N/10$ . Pulses were followed by a 1-h relaxation phase.

As a result, we could observe both positive (cell expands) and negative (cell shrinks) dilation phenomena in the relaxation phase subsequent to the pulses.

At intermediate temperatures ( $T \approx 22.5 \pm 10^\circ \text{C}$ ), positive relaxation occurred after pulses ending at a state of charge (SOC) up to 0.3, whereas negative relaxation was found at higher SOC's (compare Fig. 5 in Ref. [1]).

Moreover we observed a second type of negative dilation relaxation which only occurred after high current pulses at very low temperatures. In agreement with Bitzer and Gruhle [2], we could ascribe this low temperature relaxation phenomenon to the chemical intercalation of lithium ions which have been deposited as a metallicly deposited during the preceding high-rate pulse. Obviously the formation of a metallic lithium layer on top of the graphite anode [3–5] results in additional, positive dilation during the plating event. Consequently, the subsequent dilation relaxation during chemical re-intercalation of metallic lithium can only

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**Table 1**

Relevant graphite staging compounds and corresponding characteristics:  $x$  denotes the lithiation in  $\text{Li}_x\text{C}_6$  [8],  $d$  is the layer spacing as published in the referenced publications. The stage numbers follow the nomenclature used in Ref. [7],  $L$  is for dilute, “liquid-like” intercalation stages and  $2H$  is the hexagonal graphite phase.

Stage	2H	1L	4L	3L	2L	2	1
$x$	0	<0.04	~1/6	~2/9	~1/3	1/2	1
$d/\text{\AA}$ [8]	3.36	N/A	3.44	3.47	N/A	3.52	3.70
$d/\text{\AA}$ [9,10]	3.35	N/A	N/A	3.47	3.53	3.51	3.71

be negative (contraction). It is well known that besides reversible lithium plating, there is also some share of irreversible lithium plating [6], which may result in irreversible dilation [2] but does not contribute to dilation relaxation.

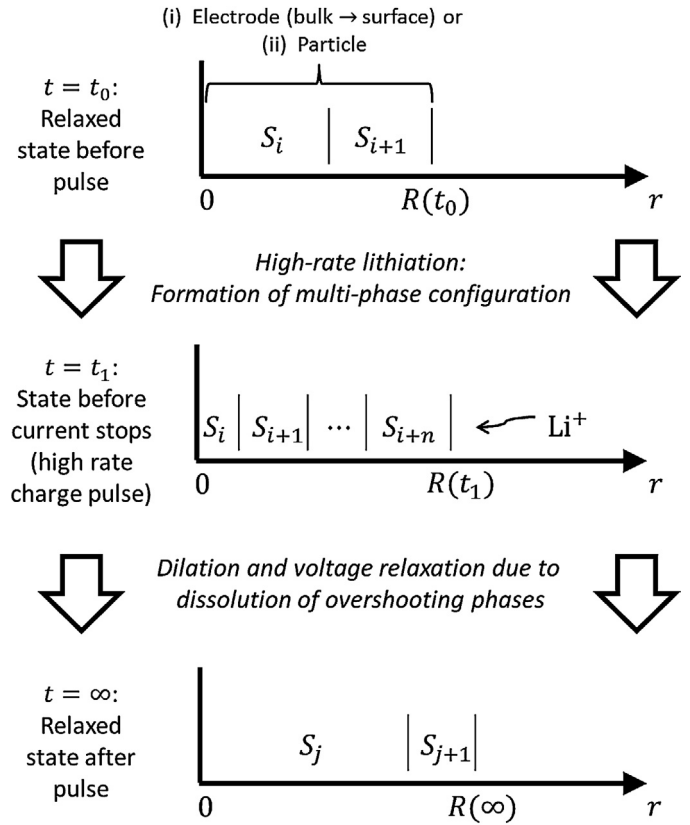
Concerning the positive and negative relaxation phenomena at higher temperatures, the mechanistic explanation is more complex. As demonstrated in Ref. [1] we have come to the conclusion that these relaxation effects are caused by the temporary formation and subsequent dissolution of a layered structure of multiple graphite intercalation stages under high-rate conditions. Such kind of multi-phase formation in the graphite electrode has originally been reported by Heß and Novák [7].

It is well known that the lithiation of graphite anodes is not a continuous process [11–13]. Instead, there are some energetically preferred lithiation states known as graphite intercalation compounds or *stages*. In Table 1, the intercalation compounds are listed according to the nomenclature recently used by Heß and Novák. The corresponding degrees of lithiation as well as the layer spacings are drawn from the referenced literature [8–10].

Regarding a high-rate charge phase with a subsequent relaxation phase, we expect that the multi-phase formation and dissolution occurs in the way depicted in Fig. 1. Before the charge phase, at time  $t_0$ , there is an equilibrium state that fits the overall degree of lithiation of the graphite anode. According to Gibbs' Phase rule, there are no more than two coexisting phases  $S_i \leftrightarrow S_{i+1}$ . For instance, for an overall degree of lithiation  $1/6 < x < 2/9$  at  $t = t_0$ , the initial equilibrium  $S_i \leftrightarrow S_{i+1}$  would be equivalent to  $4L \leftrightarrow 3L$  (compare Table 1). As soon as the high-rate lithiation is initiated, additional graphite staging compounds with higher degrees of lithiation are formed beginning from the surface, i.e. at  $r = R$ . Therein, the  $r$ -axis can be interpreted as a path-length of ionic diffusion both through the thickness of the electrode and through single particles of the electrode. Gradients of the electrochemical potential in  $r$ -direction are induced by kinetic limitations of ionic diffusion. They act as the driving force of multi-phase formation in the graphitic anode. Before the charge current is cut off at time  $t_1$ , a number  $n$  of coexisting phases forms a layered structure shaped according to the kinetic properties of ion diffusion on the electrode level and inside the graphite particles [7].

After the charge phase, a thermodynamic equilibrium is re-established. This implies the dissolution of overshooting phases and results in the equilibrium equivalent to the overall degree of lithiation after the charge phase. For instance, for a final degree of lithiation  $x$  between  $2/9$  and  $1/2$ , the resulting equilibrium  $S_j \leftrightarrow S_{j+1}$  would be equivalent to  $3L \leftrightarrow 2$  (see footnote<sup>1</sup>). As shown in Ref. [1] and later in this article, the time constants of multi-phase relaxation are significantly dependent on temperature. This is easily explained by the necessary changes in graphite configuration, equivalent to a charge transfer and therefore empirically governed by a temperature dependent Arrhenius equation. Moreover, the diffusion effects responsible for transporting ions from one phase boundary to the next during relaxation are strongly temperature dependent [14].

<sup>1</sup> In agreement with a previous suggestion by Hahn et al. [15], the formation of a dilute stage 2 compound (2L) is neglected here. Refer to [1] for more information.



**Fig. 1.** Model of multi-phase formation and relaxation in graphite for high-rate charge phases. For multi-phase formation on the electrode level (i), the  $r$ -axis can be interpreted as the electrode thickness from bulk to surface. For multi-phase formation on the particle level (ii),  $r$  is the particle radius.

We have shown in our previous work that the dissolution of overshooting phases after the pulses is accompanied by dilation relaxation phenomena in the range of up to a few tenths of a percent of total cell thickness. This can be detected by means of dilatometry. In Fig. 1, the corresponding expansion or contraction of the anode structure is represented by  $R(\infty) \neq R(t_1)$ . We have also provided an explanation for this by calculating average graphite layer spacings before and after the relaxation process [1]. In this analysis, it has turned out that the interplay of phase shares, individual layer spacings and degrees of lithiation (compare Table 1) of the phases involved can give rise to the effects of dilation relaxation observed in our measurements.

Unfortunately, measurements of external dilation do not allow conclusions about the shape of the individual layers formed inside the anode during multi-phase formation. However, it seems likely to us that anode characteristics like porosity or particle size have great impact on these processes. In their study on multi-phase formation [7], Heß and Novák reported an annuli-like formation and propagation of the individual staging layers on particle level. These results were obtained with thin-film graphite anodes, thereby excluding the influence of kinetic limitations on the electrode level due to ion transport in the liquid phase. On the other hand, it is well known that for typical (commercial) graphitic anodes, gradients of lithiation can also be found in the direction of bulk to surface after high-rate lithiation or delithiation [3,16,17,7]. It can be concluded that the intra-particle annuli-like morphology must be prominent if solid-state diffusion inside the particles is a limiting factor which is true for large particle sizes. Regarding thick electrodes as used in high-energy lithium-ion cells, we expect significant kinetic limitations of ionic diffusion on the electrode level. A lack of ionic diffusivity on that level would

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