Diffusion-Controlled Lithium Trapping in Graphite Composite Electrodes for Lithium-Ion Batteries

Yu-Kai Huang, Jean Pettersson, and Leif Nyholm*

Although graphite-based composite electrodes currently are widely used as negative electrodes in lithium-ion batteries due to their good cycle performances, improvements of their long-time cycling stability are still desirable. Herein, a series of lithium-metal half-cell experiments is performed to demonstrate that the diffusion-controlled lithium-trapping effect constitutes an additional, and so far, largely unrecognized, aging mechanism for graphite-based electrodes. This trapping effect, which stems from incomplete delithiation due to diffusion-controlled redistribution of intercalated lithium in graphite, is shown to account for around 30% of the total accumulated capacity loss during long-time cycling. The trapping effect is caused by the concentration gradients present at the end of the lithiation steps as these gradients result in lithium (i.e., coupled Li⁺ and e⁻) diffusion in the electrodes. As a result, a small fraction of the lithium becomes inaccessible on the timescale of the subsequent delithiation step. The results, however, also show that the inclusion of constant-voltage delithiation steps can increase the delithiation efficiency and decrease the influence of the lithium-trapping effect. This work consequently demonstrates that diffusion-controlled lithium-trapping effects need to be considered when trying to increase the lifetimes of graphite-based electrodes.

1. Introduction

The development of lithium-ion batteries has brought numerous changes and improvements to our daily lives by enabling realizations of many cutting-edge technologies. The need for cleaner energy conversion and the development of electric vehicles have greatly increased the demand for lithium-ion batteries with higher energy and power densities as well as longer lifetimes. The negative electrode (i.e., anode) in the lithium-ion battery is generally considered to play an important role in the degradation of the battery due to the fact that this electrode usually is operated at rather low potentials where irreversible side reactions can take place. One such side reaction involves the formation of the solid–electrolyte interphase (SEI) layer due to the reduction of the components of the electrolyte. This phenomenon is usually considered to be one of the main reasons, together with the cracking of the electrode material due to changes in its volume during cycling, for the aging of lithium-ion batteries as these effects give rise to capacity losses.¹⁻⁶ Recently, it has, however, been shown that capacity losses also can result from elemental Li becoming trapped in alloy-forming electrode materials such as silicon, aluminum, and tin.⁷⁻¹¹ For silicon-negative electrodes, such lithium trapping was, in fact, found to be the main reason for capacity losses seen during the long-time cycling of half cells containing silicon composite and lithium metal electrodes.⁷⁻¹¹ A two-way diffusion trapping model was introduced by Rehnlund et al.,⁷⁻¹¹ indicating the importance of the time domains of the lithiation and delithiation steps on the development of lithium concentration gradients in the electrodes. During the lithiation step, lithium diffuses into the electrode and a concentration gradient is formed with a higher concentration of lithium close to the electrode surface. When the delithiation step starts, the lithium concentration at the electrode surface starts to decrease, which leads to a concentration profile with an intermediate region exhibiting a higher lithium concentration than both the surface and bulk regions within the electrode. As this means that the lithium will be redistributed within the electrode via diffusion also during the delithiation step, a small amount of the lithium which diffused too deep into the electrode cannot be extracted within the time domain of the delithiation step. This small amount of lithium then becomes trapped inside the electrode. The trapping model was further extended and used by Lindgren et al.¹⁶ to explain the capacity losses seen during the cycling of optimized nanosilicon composite electrodes in an optimized electrolyte system. It was found that the lithium trapped in the silicon electrode accounted for 80% of the total accumulated capacity loss and that the molar ratio of lithium to silicon in the cycled silicon electrode was 3.28 after a long-time capacity-limited cycling experiment. It was also
demonstrated that a constant-voltage step, included after the constant-current (CC) delithiation step, could be used to extract some of the trapped lithium from the silicon electrode and hence extend the lifetime of the silicon electrode. By combining different microscopy and spectroscopy techniques, Bordes et al.\cite{9} observed lithium becoming progressively trapped in silicon electrodes and considered this effect one of the reasons for the observed capacity loss. Lithium trapping in silicon electrodes was also discussed by Zhu et al.\cite{10} in an attempt to minimize this effect.

As proposed by Rehnlund et al.\cite{7,11} it is reasonable to assume that the diffusion-controlled lithium-trapping effect should also be seen for other types of electrode materials than lithium alloy-forming materials. As the trapping effect is caused by lithium (elemental Li or Li\textsuperscript{+}) concentration gradients and diffusion, such effects should also be seen during the cycling of intercalation anode materials such as graphite. It should, however, be noted that lithium concentration gradients can be multidirectional and that these gradients may be caused by many factors including inhomogeneous lithiation and delithiation processes. As previously explained,\cite{8} lithium-trapping studies are preferably carried out using half cells containing lithium metal electrodes since the SEI effect and the performances of the positive electrodes (i.e., cathodes) otherwise may complicate the interpretation of the results.

Although the diffusion-controlled lithium-trapping effect has not yet been demonstrated for graphite electrodes, there are published experimental results suggesting the presence of lithium trapping in graphite electrodes, despite the fact that the authors were focusing on other topics.\cite{12–18} Using a combination of secondary-ion mass spectrometry (SIMS) and inductively coupled plasma–mass spectroscopy (ICP–MS), Li et al.\cite{12} found that some lithium was located deep inside a delithiated graphite electrode after cycling full cells for 1500 cycles. The presence of trapped lithium was further supported by the fact that the first phase transition plateau (i.e., LiC\textsubscript{6}, with x of around 0.05–0.1) was absent causing the voltage to drop directly to the second phase transition plateau (i.e., LiC\textsubscript{12}, with x around 0.2–0.5) during the lithiation of the cycled graphite electrode in subsequent half-cell experiments. In an online mass spectrometry study conducted by McShane et al.,\cite{13} a small amount of residual lithium was likewise found in the delithiated graphite electrode after the initial cycles using a half-cell setup. In a study conducted by Reynier et al.,\cite{14} where both in situ and ex situ X-ray diffraction (XRD) were used to track the stage 1 (LiC\textsubscript{6}) and stage 2 (LiC\textsubscript{12}) phases of lithiated graphite in the graphite electrode, residual stage 1 and stage 2 species were found in the graphite electrode even after the electrode was delithiated to 1.5 V in half-cell experiments. As described earlier, the lithium-trapping effect stems from the lithium concentration gradients (and inhomogeneities) present in the electrode, and this was exactly what was observed in the XRD study mentioned above. The residual stage 1 and stage 2 species could hence have been due to trapped lithium. Yao et al.\cite{35} also found residual stage 1 and stage 2 species deeper within the graphite electrode (i.e., close to the copper current collector) when a full cell was first discharged to 3 V and then subjected to a 30 min-long controlled voltage step at 3 V. In a neutron diffraction study performed by Senyshyn et al.,\cite{16} variations in the microstructure of graphite, or inhomogeneous distributions of lithium in graphite, were found for “fatigued” full cells after 200 cycles. The results also indicated that it became more difficult to insert lithium into graphite in the “fatigued” cells during cycling, resulting in a decreasing lithiation capacity. This may imply that some lithium was trapped in the electrode in analogy with previous findings for silicon electrodes.\cite{7,8} Krachkovskiy et al.\cite{17} used magnetic resonance imaging (MRI) and nuclear magnetic resonance spectroscopy (NMR) to study the lithium concentration profiles and phase transitions in a thick graphite electrode in real time using a half cell. A concentration gradient was found to be built up from the graphite electrode surface (i.e., the separator side) toward the current collector side during a 25 h-long lithiation step. This concentration gradient-triggered lithium movement toward the current collector side during subsequent delithiation, in excellent agreement with the two-way lithium diffusion model, used to explain the trapping of lithium in silicon electrodes.\cite{7,8} A similar two-way diffusion phenomenon was also seen in an in situ XRD study conducted by Finegan et al.,\cite{18} where residual lithiated graphite species were found at the end of the delithiation to 2.8 V in full cells. Furthermore, the amount of stage 2 species in the deeper regions (i.e., closer to the current collector) was found to increase during delithiation without a decreasing amount of stage 1 species (i.e., the effect was hence not due to phase transition resulting from delithiation) when the amounts of stage 1 and stage 2 species in the more surface-close regions were decreasing.

Based on the experimental results discussed above, it is reasonable to assume that the lithium-trapping effect also can be seen for conventional graphite composite electrodes. In this case, lithium diffusion should clearly involve coupled diffusion of Li\textsuperscript{+} and e\textsuperscript{−} rather than the diffusion of elemental Li seen for lithium alloy-forming electrode materials. In this work, the term lithium diffusion will, nevertheless, be used to denote the coupled diffusion of Li\textsuperscript{+} and e\textsuperscript{−}, for simplicity. The lithium-trapping effect should be less pronounced for graphite electrodes than for silicon electrodes due to the fact that silicon electrodes have a much higher theoretical capacity and hence can exhibit much larger capacity losses.\cite{16} We are, however, not aware of any previous study attempting to explicitly illustrate and investigate the influence of the diffusion-controlled lithium-trapping effect on the performances of graphite-based composite electrodes for lithium-ion batteries.

In this work, the results of a series of electrochemical half-cell experiments, designed to investigate if a diffusion-controlled lithium-trapping effect can also be seen for conventional graphite-composite electrodes, are discussed. By studying galvanostatic cycling curves (i.e., the lithiation and delithiation chronopotentiograms) during capacity-limited long-term cycling experiments, it is shown that the lithiation process gradually becomes increasingly hindered, whereas the delithiation process remains rather unaffected. The subsequent lithiation process is shown to be less hindered when the preceding delithiation step is conducted using a combination of CC and constant-voltage steps to 1 V. As the latter steps are used to increase the delithiation efficiency, the different behaviors seen in the capacity-limited long-term cycling experiments together with the different amounts of lithium found in the electrodes, using ICP–atomic emission spectroscopy (ICP–AES), demonstrate the presence of the lithium-trapping effect. In further electrochemical experiments,
the diffusion of the inserted lithium is studied under various conditions. The results indicate that the trapping effect stems from the concentration gradients (and inhomogeneities) present at the end of the lithiation step, in analogy with previous findings for silicon composite electrodes.[7,8]

2. Results and Discussion

As indicated earlier, the main aim of the present work is to investigate if diffusion-controlled lithium trapping contributes to capacity losses seen for graphite composite electrodes during long-term cycling. As explained in more detail in the Experimental Section, all experiments were conducted with half cells containing a graphite composite electrode and a lithium disk counter electrode as well as LP40 (i.e., 1 M LiPF₆ in ethylene carbonate (EC): diethyl carbonate (DEC) = 1:1 v/v without any additive) electrolyte. This setup allowed the electrochemical behavior of the composite graphite electrode to be studied individually. The large capacity of the 450 μm-thick lithium counter electrode made the graphite electrode the capacity-limiting electrode and also compensated for the charge associated with the formation of SEI layer. The SEI formation should therefore not affect the capacity of the studied graphite composite electrodes even though the SEI formation process contributed to the total accumulated capacity loss.[7,8] A low cycling rate (i.e., 35 mA g⁻¹ (about 0.094C)) was used in all the experiments to minimize the risk of problems associated with lithium plating on the graphite electrodes. Such problems could otherwise complicate the interpretations of the galvanostatic cycling curves.[19]

The low current density used in this study should also ensure stable cycling of the lithium counter electrodes and hence allow the performances of the graphite electrodes to be studied properly.

The results of some basic electrode characterization experiments, including cyclic voltammetry, galvanostatic charge/discharge, and scanning electron microscopy (SEM), are presented in Figure S1, Supporting Information, for the as-fabricated Timrex SLP30 graphite-based electrodes. The graphite electrodes, containing graphite particles with a size of 10–20 μm, featured characteristic galvanostatic charge/discharge curves with three major plateaus corresponding to LiₓC₆ with x values of around 0.05–0.1, 0.2–0.5, and 0.5–1, respectively. Corresponding reduction and oxidation peaks were likewise seen in the cyclic voltammograms. The obtained results are therefore analogous to those presented in a previous study using the same type of graphite (i.e., SLP30).[20]

2.1. Long-Term Capacity-Limited Cycling Experiments

To be able to detect capacity losses for the graphite composite electrodes, long-term capacity-limited cycling experiments (with a current density of 35 mA g⁻¹) were performed. In these experiments, a lithiation cutoff capacity of 170 mAh g⁻¹ was used as the primary limit with a lithiation cutoff voltage of 0.01 V as the secondary and also safety limit, while a cutoff voltage of 1 V was used as the only delithiation limit. The used lithiation capacity hence corresponds to around 46% of the theoretical capacity of graphite (i.e., 372 mAh g⁻¹). Here it should be mentioned that the full capacities of the graphite electrodes almost never are used in commercial full cells[21] due to the capacity balancing of the electrodes aiming at preventing lithium plating on the graphite electrodes. Theoretically, a lithiation capacity of 170 mAh g⁻¹ should correspond to a position close to the end of the LiC₁₂ phase transition plateau (i.e., the second plateau seen in Figure S1a, Supporting Information) as a completely formed LiC₁₂ phase would correspond to a lithiation capacity of 186 mAh g⁻¹. After the LiC₁₂ plateau, there should be a drop in the potential as the formation of the LiC₆ (i.e., the final) phase starts. The selected lithiation capacity limit should therefore facilitate the detection of changes in the shapes of the chronopotentiograms during long-term galvanostatic cycling. A too low capacity limit would cause the behavior of the graphite electrode to deviate too much from that seen in practical applications, whereas a too high capacity limit would make the interpretations of the chronopotentiograms more difficult. Using a capacity limit of 170 mAh g⁻¹ also further decreases the risk of lithium plating as the most condensed phase (i.e., LiC₆), in theory, should not be formed. This ensures space for the lithium ions to be inserted into the graphite electrode. In addition, the applied capacity limit and the low current density used also mean that the lithium counter electrodes were cycled using a low areal current density with a low areal capacity. This should ensure a stable cycling of the lithium electrodes during the experiments, allowing the obtained electrochemical data to properly reflect the performances of the graphite electrodes.

The long-term cycling performances are illustrated in Figure 1, whereas the corresponding galvanostatic cycling curves are presented in Figure 2. The capacity-limited cycling experiments were conducted using two procedures: 1) capacity-limited CC cycling (i.e., standard galvanostatic cycling) and 2) capacity-limited CC cycling with a constant-voltage step of 1 V following the delithiation to the cutoff voltage of 1 V on every fifth cycle from the 21st cycle (i.e., capacity-limited CCCV cycling). As shown in Figure 1a,b the performance of the graphite half cell remained quite stable during the first 500 cycles with coulombic efficiencies of around 99.7% after the initial cycles. This is not surprising as the stability of graphite has made it the most commonly used negative electrode material in commercial lithium-ion batteries. However, between the 521st and 570th cycles, some variations in the delithiation capacity and coulombic efficiency appeared, as shown in Figure 1a,b. The latter effects also gave rise to a change in the accumulated capacity loss curve in Figure 1c, causing the accumulated capacity loss to increase at a lower rate during the final 102 cycles. These results indicate that the electrochemical behavior of the graphite electrode changed in this part of the cycling experiment. A closer look at the galvanostatic cycling curves in Figure 2a,b shows that while the 126th and 351st curves almost overlapped, a small voltage drop could be seen toward the end of the 351st lithiation. This implies that it was more difficult to insert lithium into the graphite electrode toward the end of the 351st lithiation compared with that of the 126th lithiation. An even larger voltage drop could be seen at the end of the 516th lithiation. When reflecting on the variations seen between the 521st and 570th cycles mentioned earlier, the change in the slope (and curvature) of the 556th lithiation curve toward the end of the lithiation in fact indicated a transfer from the LiC₁₂ to the LiC₆ plateau. The latter became even more
obvious during the 621st lithiation. The first lithiation phase transition plateau seen at 20–30 mAh g\(^{-1}\)) also gradually disappeared during the cycling in agreement with the findings discussed in a previous study.\(^{[12]}\) This means that the performance of the graphite electrode gradually changed during cycling, most likely due to a gradual loss of capacity. The fact that the coulombic efficiency generally was lower than unity means that the delithiation capacity was smaller than the lithiation capacity during the cycling experiment. While this effect typically is ascribed to SEI formation,\(^{[3,12,22,23]}\) it could also indicate a capacity loss due to lithium ions being trapped in the graphite electrode. As previously explained, the lithiation capacity should correspond to the sum of the graphite lithiation capacity and the capacity associated with the formation (or maintenance) of the

---

**Figure 1.** Long-term capacity-limited cycling performances of the graphite|lithium half cells with a–c) the CC cycling protocol and d–f) the constant-current and constant-voltage (CCCV) cycling protocol (see the text). The insets in (a), (b), (d), and (e) show the magnified views of the corresponding plots. In (c), the circle highlights the period with a rather unstable increase in the accumulated capacity loss between the 521\(^{st}\) and 570\(^{th}\) cycle of CC cycling. The lithiation capacity limit was 170 mAh g\(^{-1}\).
SEI layer. The SEI formation will hence contribute to the accumulated capacity loss, that is, the sum of the differences between the lithiation and delithiation capacities for all cycles. However, as the lithium counter electrode should be able to compensate for the charge associated with the SEI formation, the capacity of the graphite electrode should not be affected by the SEI formation as long as the capacity of the lithium electrode remains larger than that of the graphite electrode. It should also be noted that changes in the shapes of the lithiation curves due to an increasing interfacial resistance caused, for example, by a thicker SEI layer also should have affected the shapes of the delithiation curves equally. The fact that the shapes of the delithiation curves remained rather unaffected therefore suggests the presence of another phenomenon than SEI formation. Given that the SEI hypothesis cannot explain the changes seen in the shapes of the lithiation curves, it is reasonable to assume that these changes may have stemmed from diffusion-controlled trapping of lithium ions in the graphite electrode. The latter hypothesis is further supported by the fact that analogous changes in the shapes of the lithiation curves have been found to be caused by lithium becoming trapped in silicon composite electrodes.[8]

Increasing lithium concentrations in graphite electrodes due to the trapping effect could hinder the lithiation process,[7,8] yielding a shorter (or disappearing) first phase-transition plateau as well as the appearance of the LiC_{12}-to-LiC_{6} phase-transition plateau, as shown in Figure 2a,b. The experimental results in Figure 1 and 2 could therefore be early indications of capacity loss due to diffusion-controlled lithium trapping in the graphite electrode. However, considering that graphite electrodes generally exhibit high coulombic efficiencies and relatively low capacities, the amount of lithium trapped in the graphite electrode should clearly be much smaller than that for a silicon electrode.[7,8] A trapping effect may consequently be difficult to detect for a graphite electrode unless the latter is cycled for many cycles. According to previous results,[7,8,11] the influence of the lithium-trapping effect can be decreased by increasing the efficiency of the delithiation step, by, for example, including a complementary constant-voltage delithiation step of 1 V on every fifth cycle. This CCCV strategy was consequently also used together with a graphite electrode. As shown in Figure 1d,e, the performance of the graphite electrode was very stable when the CCCV cycling protocol was used. There was no sudden variation in the delithiation

Figure 2. Galvanostatic cycling curves of various cycle numbers for the graphite|lithium half cells cycled with the capacity limited a) CC cycling protocol and c) CCCV cycling protocol (see the text). The arrows indicate major changes in the lithiation curves. Magnified views of the lithiation curves toward the lithiation capacity limit are presented in (b) and (d) for the CC and CCCV cycling protocol, respectively. The lithiation curve of the 516th cycle has been included in (b) to better illustrate the trend (see the text). The lithiation capacity limit was 170 mAh g\(^{-1}\).
capacity and coulombic efficiency, as seen in the CC cycling case, apart from the “oscillations” caused by the constant-voltage delithiation step itself (see Figure 1d,e). This phenomenon, which incidentally also was observed in the silicon study,[8] should stem from the constant-voltage delithiation step further decreasing the surface lithium concentration in the graphite electrode. This facilitated subsequent lithiation but also caused more lithium to be trapped on the subsequent cycle.[8] As shown in Figure 1f, there was no change in the slope of the plot of the accumulated capacity loss versus cycle number when the CCCV cycling protocol was used. This indicates that while the CCCV cycling improved the cycling performance it did not solve the fundamental problem. This is in excellent agreement with previous findings for the silicon electrodes.[8]

Nevertheless, improvements in terms of the shapes of the cycling curves could readily be seen as the curves in Figure 2c remained almost unchanged throughout the CCCV cycling. A closer look at the lithiation curves in Figure 2d reveals that the voltage drop toward the end of the lithiation step still became larger during cycling. As LiC₁₂ to LiC₀ phase-transition plateau was not clearly observed, the use of the constant-voltage steps did decrease the degradation rate of the cycling performance of the graphite electrode. As the only difference between the CC and CCCV cycling protocols was the constant-voltage delithiation steps used in the latter protocol, this improved performance can clearly not be explained by SEI formation or volume expansion effects. This and the effects of the constant-voltage delithiation steps will be discussed in more detail. This leaves diffusion-controlled lithium-trapping effect as the most likely explanation for the gradual degradation of the cycling performances of the graphite electrodes. Given the almost linear dependence of the accumulated capacity loss on the cycle number, it is also clear that about the same amount of charge was lost on each cycle. This behavior is in good agreement with the previously described increase in the lithium concentration in (delithiated) electrodes that were cycled for a great number of cycles.[7,8]

To further test the lithium-trapping hypothesis, the amounts of lithium remaining in delithiated cycled graphite electrodes were determined by ICP–AES after 673 and 676 cycles using the CC and CCCV protocols, respectively. As summarized in Table S1, Supporting Information, the electrodes were found to contain 107.7 (with the CC protocol) and 99.4 μg (with the CCCV protocol) lithium which correspond to capacities of 111.8 and 102.3 mAh g⁻¹, respectively, based on Faraday’s law. The lower amount of lithium in the CCCV-cycled graphite electrode is in good agreement with the abovementioned effect of the CCCV cycling protocol on lithium trapping. The ICP–AES data hence demonstrate not only that the diffusion-controlled lithium-trapping effect can be seen during the cycling of graphite composite electrodes, but also that the constant-voltage steps in the CCCV cycling protocol resulted in a recovery of some of the trapped lithium. As the total accumulated capacity losses were 365.2 and 376.9 mAh g⁻¹ for the CC and CCCV cycled graphite electrodes, respectively, the capacity losses due to lithium trapped in the electrodes hence accounted for about 31% and 27%, respectively, of the total capacity losses (see Table S2, Supporting Information). The remaining 69% and 73% for the CC- and CCCV-cycled graphite electrodes, respectively, can then be attributed to the charge consumed by the formation and maintenance (due to the dissolution) of the SEI layer upon cycling. This indicates that the contribution from SEI formation and maintenance was larger for the graphite electrodes compared with for the silicon electrodes for which 80% of the accumulated capacity loss could be ascribed to trapped lithium.[8] This can explain why SEI effects usually are considered to be responsible for the capacity losses seen for graphite electrodes. The present results, however, clearly show that the lithium-trapping effect also should be considered as it may explain up to almost one-third of the total accumulated capacity loss.

2.2. Open-Circuit-Rest Experiments

As mentioned in the Introduction, the present lithium-trapping effect can be ascribed to a “two-way diffusion” effect caused by the concentration gradients generated during the lithiation and delithiation steps.[7,8,11] To reveal the presence of lithium concentration gradients generated during the lithiation steps, experiments were designed to include open-circuit periods with increasing durations of up to 256 h between the lithiation and delithiation after preconditioning the electrodes for 32 cycles (see the Experimental Section for details). The delithiation capacity obtained after the open-circuit period was then plotted as a function of the duration of the open-circuit period to test the following two ideas: 1) if a concentration gradient is present at the end of the lithiation step, there should be lithium diffusion (re-equilibration) during the subsequent open-circuit period, which should affect the obtained delithiation capacity, and 2) if there is lithium diffusion, the delithiation capacity should depend on the duration of the open-circuit period in a certain way. A square-root-of-time (i.e., R₀.5) dependence would, for example, be expected in the case of semi-infinite planar diffusion. However, as graphite composite electrodes are porous, a R₀.7 dependence would be more likely based on previous results for silicon composite electrodes.[8] In addition to the lithiation capacity limit of 170 mAh g⁻¹ used in the CC and CCCV cycling experiments, two additional capacity limits, that is, 100 and 275 mAh g⁻¹, were also adopted. As shown in Figure 3 and S2, the R₀.5 linear fittings were found to be better than the R₀.7 ones in all three cases as higher R² values and/or more reasonable y-axis intercepts, reflecting the normal delithiation capacities in the absence of open-circuit rest, were obtained. The results therefore indicate that the decrease in the delithiation capacity with increasing rest duration was caused by, at least, one diffusion-controlled phenomenon.

The diffusion-controlled capacity loss could stem from 1) lithium diffusing further into the electrode due to the concentration gradients present at the end of the lithiation (i.e., the lithium-trapping effect) and/or 2) diffusion of lithium from the graphite electrode toward the SEI layer due to partial dissolution of the SEI layer. In the latter case the reduced (i.e., lithium-ion-containing) graphite electrode would continuously restore the SEI layer by reducing the electrolyte. However, a closer look at the capacity losses and the time scales (see below) indicates that the main part of the open-circuit capacity losses should stem from the lithium-trapping effect.

According to the long-term CC cycling experiment, the total accumulated capacity loss (due to both the lithium trapping
and SEI formation effects) and the total capacity loss due to lithium trapped in the electrode were 365.2 and 111.8 mAh g\(^{-1}\), respectively, after 673 cycles. These yield average capacity losses of about 0.54 and 0.17 mAh g\(^{-1}\) per cycle, respectively. In Figure 3b, a capacity loss of about 3.5 mAh g\(^{-1}\) was found when an open-circuit period of 256 h was applied between lithiation and delithiation. This clearly shows that the introduction of an open-circuit rest period gave rise to an increased capacity loss which can be explained by assuming that the lithium concentration gradients present at the end of the 4.6 h-long lithiation were modified during the subsequent 256 h-long open-circuit period. Given that the total time prior to the delithiation, with and without the rest period, were 260.6 and 4.6 h, respectively, and that the diffusion effect was found to depend on the time raised to the power of 0.7 (i.e., \(t^{0.7}\)), this means that the ratio between the corresponding capacity losses due to the trapping effect should be about 16.9. This is in good agreement with the ratio of the experimental capacity loss versus the average capacity loss due to trapped lithium of around 20.6 (i.e., 3.5 divided by 0.17) as the difference should result from the SEI maintenance. On the other hand, the ratio of the experimental capacity loss versus the average total capacity loss was around 6.5 (i.e., 3.5 divided by 0.54). The results thus also indicate that the accumulated capacity loss due to the SEI formation/maintenance was much smaller during the open-circuit period than during cycling, in good agreement with previous findings.\(^{[24]}\) As the duration of the open-circuit period was increased, lithium should diffuse further into the electrode, rendering a larger fraction of the lithium inaccessible during subsequent delithiation. This hypothesis is further supported by the fact that the plots in Figure 3 were found to be linear for open-circuit rest time up to at least 256 h. Such a behavior is unlikely to be seen for continuous reformation of the SEI layer due to the much shorter diffusion lengths associated with this effect. Based on the capacity losses and the associated time scales, it is therefore reasonable to assume that the extra capacity loss in the presence of open-circuit period mainly was due to lithium trapping, that is, coupled Li\(^+\) and e\(^-\) diffusion from the electrode surface regions toward the bulk of the electrode. This clearly reveals the presence of lithium concentration gradients at the end of lithiation steps.

As shown in Figure 3, there was no obvious trend in the capacity loss rates (i.e., the slopes of the plots) for the different lithiation capacity limits. This may be due to the pretreatment of the electrodes (see the Experimental Section) and the complex interplay between the concentration gradients present at the end of the lithiation and the diffusion of lithium taking place during the experiments. As the same current density of 35 mA g\(^{-1}\) was used for lithiation, the established concentration profiles/gradients should be different with different lithiation capacity limits. In addition, as will be shown later, significant changes in the diffusion-associated resistance could in fact be seen for different lithiation degrees (i.e., states of charge (SOC)).

2.3. Electrochemical Impedance Spectroscopy During an Open-Circuit Period

The lithium diffusion in the graphite electrodes was further studied using electrochemical impedance spectroscopy (EIS) experiments performed during an open-circuit period after lithiation to 170 mAh g\(^{-1}\) (see Experimental Section). As shown in Figure 4a and S3, Supporting Information, the impedances in the high-frequency region (>1000 Hz) remained unchanged over time, indicating that the electrolyte resistance remained constant during the open-circuit period. Major changes in the impedances were, however, seen in the medium- and low-frequency regions as the compressed semicircle became larger during the open-circuit period. This resulted in an increasing impedance \(|Z|\) at 5.385 Hz, indicating an increasing charge transfer resistance (see Figure 4b). The variation in the impedance seen in Figure 4b as well as the change in the open-circuit cell voltage (which could be considered as the open-circuit potential of the graphite electrode) seen in Figure 4c reveal that an equilibration process took place during the open-circuit period. These observations are in very good agreement with previous findings by Barai et al.\(^{[25]}\) and Kindermann et al.\(^{[26]}\). Barai et al. studied the effect of the relaxation time on the EIS measurements and found that the charge transfer resistance increased when longer relaxation time was used prior to the measurement. This effect was attributed to solid-state diffusion of lithium, leading to a rearrangement of lithium in the electrodes.\(^{[25]}\) To explain the observed long-term equilibration effects, Kindermann et al. proposed a model involving solid-state intra- and interparticle lithium diffusion in the graphite electrode.\(^{[26]}\) It was proposed that interparticle lithium was the dominant process and
that the diffusion was caused by concentration (or SOC) gradients in the graphite electrode in both lateral and perpendicular directions. The digital photos shown in Figure S4, Supporting Information, confirm the presence of inhomogeneous lithiation of the graphite electrodes, in very good agreement with previous findings.\cite{14,27,30} As the 170 mAh g\(^{-1}\) lithiation capacity should correspond to a lithiation degree close to the end of the LiC\(_{12}\) phase-transition plateau, LiC\(_{12}\) should be present at the electrode surface after lithiation. As LiC\(_{12}\) is known to have reddish color, the inhomogeneous lithiation thus reflected on the nonuniform distribution of reddish color seen on the graphite electrode right after lithiation (See Figure S4a, Supporting Information). Such a nonuniform color distribution was, however, not seen for the graphite electrode subjected to a subsequent open-circuit period of 226 h after lithiation (See Figure S4b, Supporting Information). This indicates that lithium diffused further into the graphite electrode during the open-circuit period. Such diffusion would also explain the increasing cell voltage with time seen in Figure 4c. The photos in Figure S4, Supporting Information, together with the results in Figure 4 thus demonstrate the presence of solid-state lithium diffusion due to the concentration gradients (and inhomogeneities) present at the end of the lithiation, in good agreement with the results of the open-circuit-rest experiments discussed earlier.

### 2.4. Intermittent Current Interruption Experiments

As the lithium-trapping effect is associated with lithium (i.e., Li\(^+\) and e\(^-\)) diffusing in the electrode, techniques such as the galvanostatic intermittent titration technique (GITT) could provide further insights. The GITT technique is often used to measure the diffusion coefficient of lithium as a function of the SOC during lithiation and delithiation in different electrodes.\cite{31,32} However, GITT is unfortunately not straightforward to be used with electrodes featuring multiple phase-transition plateaus and the results have also been found to be unreliable.\cite{33} The latter is further illustrated in Figure S5, Supporting Information. To circumvent this problem the intermittent current interruption (ICI) method, developed by Lacey and Chien et al.,\cite{34,35} was used in this work. With the ICI method, the internal resistance (R) and diffusion resistance coefficient (k) can be measured continuously throughout the whole SOC range (see the Experimental Section). While the internal resistance corresponds to the total resistance of the cell, the diffusion resistance coefficient reflects the resistance associated with diffusion. In the present case, the variations in the internal resistance and diffusion resistance coefficient should mainly reflect the changes taking place within the graphite composite electrode during the lithiation and delithiation steps. The ICI experiment results, which are presented in Figure 5, will be discussed below.

In the beginning of the lithiation (see Figure 5b), a relatively high \(k_{\text{lithiation}}\) value was obtained, indicating that the lithium diffusion (i.e., the coupled Li\(^+\) and e\(^-\) diffusion) was somewhat hindered in the almost delithiated graphite. When the lithiation degree increased, \(k_{\text{lithiation}}\) then decreased, most likely as a result of the graphite structure “opening up” gradually. A relatively low \(k_{\text{lithiation}}\) value was then seen up to \(x = 0.3\) (i.e., line I) after which the value increased with increasing SOC until \(x = 0.541\) (i.e., line II). This increase seen between line I and II can be explained by the fact that an increasing amount of lithium in the graphite electrode should hinder further lithiation (i.e., the lithium diffusion). Interestingly, in the SOC range between \(x = 0.541\) (i.e., line II) and \(x = 0.651\) (i.e., line III), \(k_{\text{lithiation}}\) first decreased slightly and then remained rather constant. This may be attributed to the gradual formation of the LiC\(_{6}\) phase which “opened up” the structure further as line II in Figure 5a marks the initiation of the LiC\(_{12}\)-to-LiC\(_{6}\) phase-transition plateau. From \(x = 0.651\) to the end of the lithiation, \(k_{\text{lithiation}}\) increased rapidly as the graphite electrode was gradually filled up with lithium.

During delithiation (which started immediately after lithiation), it was found that the first \(k_{\text{delithiation}}\) value (obtained after delithiation time of 5 min) was significantly lower than the final \(k_{\text{lithiation}}\) value. This can be attributed to the removal of lithium from the electrode surface during the first 5 min of CC delithiation greatly facilitating lithium diffusion via the generation of more free space in the electrode. However, the \(k_{\text{delithiation}}\) value then subsequently exhibited a slower decrease down to \(x = 0.651\) compared with the increase in \(k_{\text{lithiation}}\) seen during lithiation from \(x = 0.651\). This may be due to the fact that the LiC\(_{6}\)-to-LiC\(_{12}\) phase transition should give rise to a gradually compressed
structure which is not beneficial to lithium diffusion. When compared with the rather constant $k_{\text{lithiation}}$ values seen during lithiation from $x = 0.541$ to 0.651, the $k_{\text{delithiation}}$ value decreased relatively fast between $x = 0.651$ and $x = 0.541$ despite the fact that the structure should become increasingly compressed. This indicates that the influence of the latter phase transformation was larger during lithiation (than during the delithiation step) in this SOC range as lithiation should be significantly facilitated by a volume expansion effect. During delithiation from $x = 0.541$ to $x = 0.3$, $k_{\text{delithiation}}$ gradually decreased to a value corresponding to the $k_{\text{lithiation}}$ value obtained after the lithiation to $x = 0.3$. From $x = 0.3$ to the end of the delithiation, $k_{\text{delithiation}}$ first remained rather constant only to increase rapidly for $x$ values below about 0.05, in analogy with the findings for $k_{\text{lithiation}}$. This indicates that the conditions for the diffusion of lithium in the graphite electrode were the same during both the lithiation and delithiation steps in this SOC range. Note that the increase in $k_{\text{delithiation}}$ close to $x = 0$ indicates that it was difficult to extract the final $\approx 5\%$ of the inserted lithium.

The variations of the internal resistances during lithiation and delithiation are shown in Figure 5c. In general, the variations seen for the internal resistances were analogous to those seen for the diffusion resistance coefficients discussed earlier. This is not unexpected as the variations in the internal resistances should include the changes in the resistances associated with lithium diffusion in the graphite electrode. The relatively high internal resistance values seen in the beginning of lithiation and in the end of delithiation can hence be attributed to the corresponding high diffusion resistance coefficient values discussed earlier. Upon lithiation, $R_{\text{lithiation}}$ then decreased and subsequently remained practically constant up to $x = 0.76$ after which a rather rapid increase was seen until the end of the lithiation. The significant difference seen between the diffusion resistance coefficients at the end of the lithiation and at the beginning of the delithiation was, however, not observed for the internal resistance. This was most likely due to the fact that the internal resistance was affected also by other factors (i.e., contributions from other resistances that may have different SOC dependencies). The changes in lithium diffusion conditions in the graphite electrode during the lithiation and delithiation steps are therefore more clearly seen in the diffusion resistance coefficients. During delithiation to $x = 0.3$, $R_{\text{delithiation}}$ decreased at a lower rate and remained higher than the corresponding $R_{\text{lithiation}}$ at the same SOC. This reveals the asymmetric behavior of the graphite.
electrode during lithiation and delithiation, especially at medium and high SOCs. From $x = 0.3$ to the end of the delithiation, $R_{\text{delithiation}}$ remained similar to $R_{\text{lithiation}}$ seen during lithiation to $x = 0.3$ and then increased to a relatively high value. The results of the ICI experiments thus indicate that lithium diffusion in the graphite electrode and the total resistance of the graphite electrode depended, not only on the SOC, but also on whether a lithiation or a delithiation step of the graphite electrode was conducted. This asymmetric behavior, demonstrating that the delithiation step is inherently more straightforward than the lithiation step, is in very good agreement with previous findings.[37–41] Here it should also be noted that apart from the high values seen for SOCs below 0.05, both the diffusion resistance coefficients and the total resistance increased with increasing SOC. This means that the diffusion of lithium became more facile when lithium was removed from the electrode, and more hindered when more lithium was inserted into the electrode, in excellent agreement with previous results obtained for, for example, TiO$_2$ electrodes.[42] This clearly indicates that the diffusion coefficient for lithium (i.e., Li$^+$ and e$^-$) in graphite should depend significantly on the SOC. For sufficiently high SOCs (e.g., SOCs > 0.7), different lithium diffusion coefficients should also be found during the lithiation and delithiation steps.

The ICI method was also used to study the concentration gradients present at the end of 170 mAh g$^{-1}$ lithiation, as well as the influence of an open-circuit period on the subsequent delithiation step. The rest-ICI experiment was conducted to compare $R_{\text{delithiation}}$ and $k_{\text{delithiation}}$ values in the presence and absence of the open-circuit period (see Experimental Section), and these results are presented in Figure 6. In Figure 6a, it is clearly seen that $R_{\text{delithiation}}$ values remained higher during delithiation when there was an open-circuit period between the lithiation and delithiation steps. This finding which is in good agreement with the EIS results discussed above indicates that the higher $R_{\text{delithiation}}$ values should result from lithium redistribution via lithium diffusion due to the concentration gradients present at the end of the lithiation step. The open-circuit period, however, only affected $k_{\text{delithiation}}$ close to the end of delithiation where higher $k_{\text{delithiation}}$ values were obtained with the rest period (see Figure 6b). This indicates that the extraction of the final portion of the lithium was further hindered when an open-circuit period was included between the lithiation and delithiation steps. This behavior is in very good agreement with the delithiation capacity losses seen in the open-circuit-rest experiments depicted in Figure 3.

2.5. Influences of Constant-Voltage Delithiation Steps on the Lithium-Trapping Effect

When comparing the results present in Figure 1 and 2, it can be seen that the influence of the diffusion-controlled lithium-trapping effect could be reduced significantly with the CCCV cycling protocol. This improvement can be ascribed to the constant-voltage steps increasing the total duration of delithiation and hence the delithiation efficiency. While the total duration of the delithiation can be readily controlled with constant-voltage steps, the durations of CC delithiation steps depend on the concentration gradients generated in the electrode material. During a CC delithiation step the surface concentration of lithium in the electrode decreases, yielding a decreasing concentration gradient. At some point, the diffusion can no longer support the constant current (causing the delithiation cutoff voltage to be reached) and the delithiation step is terminated. The durations of constant-voltage steps (and thus the total duration of delithiation) can, on the other hand, be controlled by setting the step time or by terminating the steps as soon as the current drops below a preset limit. In the long-term cycling experiments discussed earlier, the constant-voltage steps were terminated when the current dropped below a value corresponding to a current density of 7 mA g$^{-1}$.

To study the effects of constant-voltage delithiation steps in more detail, experiments (denoted rest-CV experiments) were conducted in which a constant-voltage step of 1 V with a duration of 8 h was applied after the conventional CC delithiation step. In these experiments, an open-circuit period (of various durations) was applied between the CC lithiation (to the capacity limit of

![Figure 6](image-url)

Figure 6. Rest-ICI experiment results showing a) the derived internal resistance ($R$) and b) the diffusion resistance coefficient ($k$) as a function of the SOC during the delithiation with and without an open-circuit period of 64 h between the lithiation to 170 mAh g$^{-1}$ and the delithiation. The oval in (b) highlights the dramatic increase in the difference between the $k_{\text{delithiation}}$ values close to the end of the delithiation.
170 mAh g\(^{-1}\)) and the CC delithiation to 1 V which was then followed by the constant-voltage delithiation step (see Experimental Section). As shown in Figure 7a, during the constant-voltage step, the accumulation rate of the delithiation capacity decreased with time so that a major part of the constant-voltage delithiation capacity was obtained during the first 1.5 h. This behavior is not unexpected as the current due to a constant-voltage step (with a sufficiently high voltage) should decrease with the square root of time (i.e., \(i \propto t^{-0.5}\)) according to the Cottrell equation (assuming semi-infinite planar diffusion). As a result, the delithiation capacity (given by the integrated Cottrell equation) should increase with the square root of time (i.e., \(Q \propto t^{0.5}\)). As semi-infinite planar diffusion only would be expected during a relatively short period of time, a closer examination of the data collected during the first 10 min was made. As shown in Figure 7b, the good fitting results indicate that the current obtained during this period of the constant-voltage delithiation step was diffusion controlled. This clearly shows that delithiation efficiency can be increased by increasing the total duration of the delithiation and that the delithiation capacity depends on the rate at which the lithium (i.e., Li\(^{+}\) and e\(^{-}\)) in the electrode diffuses toward the electrode surface, which is in excellent agreement with the diffusion-controlled lithium-trapping effect discussed earlier. The conclusion regarding the function of the constant-voltage delithiation step is also supported by the cyclic voltammogram obtained for a pristine graphite electrode between 0.8 and 1 V shown in Figure S6. It can be clearly seen that this electrode exhibited a capacitor-like behavior and that there was no sign of any electrochemical reaction. This implies that the major electrochemical reaction occurring during the constant-voltage delithiation step involved the assumed diffusion-controlled delithiation of the graphite electrodes. Note also that constant-voltage delithiation capacities of about 1.5 and 1.7 mAh g\(^{-1}\) were obtained with and without an open-circuit rest period of 64 h, respectively. As lithium could diffuse further into the electrode during the open-circuit period, additional lithium was thus rendered inaccessible during subsequent delithiation. When an open-circuit period was applied, a shallower lithium concentration profile was consequently obtained within the electrode resulting in a lower diffusion rate (see the decrease in the value of the constant in the fitting function in Figure 7b). This is also in very good agreement with the higher \(k_{\text{delithiation}}\) values seen at the end of the delithiation step in Figure 6b when an open-circuit period of 64 h was applied between lithiation and delithiation.

Given the lithiation capacity of 170 mAh g\(^{-1}\), the constant-voltage delithiation capacity of about 1.5–1.7 mAh g\(^{-1}\) (see Figure 7a) would correspond to about 1% of the lithiation capacity. While this extra delithiation capacity may seem insignificant, it should be noted that a loss of 1% of the capacity per cycle should result in a significant accumulated capacity loss during extended cycling. With a 1% loss, only about 37% of the initial capacity should remain after 100 cycles (i.e., 0.99\(^{100}\) = 0.37). The significantly improved cycling performances seen in Figure 2c,d compared with Figure 2a,b can consequently be ascribed to the introduction of the constant-voltage delithiation steps on every fifth cycle from the 21\(^{\text{st}}\) cycle. This demonstrates that the capacity loss due to diffusion-controlled lithium trapping can be decreased by increasing the efficiency of the delithiation, as has previously been shown for lithium alloy-forming negative electrode materials such as silicon, aluminum, and tin.\(^{7,8,11}\)

3. Conclusion

The experimental results clearly demonstrate that a diffusion-controlled lithium-trapping effect, analogous to that previously seen for alloy-forming negative electrode materials, can be seen also for graphite composite electrodes. This indicates that this trapping effect could be a general phenomenon for intercalation-based electrode materials.

The diffusion-controlled lithium-trapping effect caused the lithiation of the graphite electrode to become increasingly hindered during long-term capacity-limited CC cycling of a half cell containing graphite and lithium metal electrodes. The increasing

![Figure 7](image-url)
accumulated lithium concentration in the graphite electrode, which can be explained by a small portion of the lithium becoming trapped on each cycle, gave rise to changes in the shapes of the charge curves as well as shifts in the lithiation potentials. This is further supported by the fact that the amount of trapped lithium, determined by the ICP–AES analysis of the cycled (delithiated) electrode, corresponded to about 30% of the total accumulated capacity loss.

The diffusion-controlled trapping effect stems from the lithium concentration gradients generated in the graphite electrodes during the lithiation step. During the subsequent delithiation step, the lithium concentration gradients result in lithium (i.e., coupled Li\(^+\) and e\(^-\)) diffusion not only toward the electrode surface but also further into the electrode. This would be expected whenever complete lithiation of the electrode is not reached during the lithiation step. The two-way diffusion effect causes a small fraction of the lithium to become inaccessible on the time scale of the subsequent delithiation step. This was clearly demonstrated in the experiments in which open-circuit periods were applied between the lithiation and delithiation steps as they resulted in larger capacity losses. The latter capacity losses were also shown to depend on the duration of the open-circuit rest in a manner demonstrating that the effect was due to lithium (i.e., coupled Li\(^+\) and e\(^-\)) diffusion further into the electrode.

As demonstrated herein, the inclusion of a constant-voltage step after CC delithiation on every fifth cycle can decrease the influence of the diffusion-controlled lithium-trapping effect significantly. The fact that current during these constant-voltage delithiation steps was found to be diffusion controlled demonstrates that the preceding CC delithiation step was incomplete as a result of the delithiation being prematurely terminated when the diffusion of lithium to the electrode surface no longer could support the employed CC. Constant-voltage delithiation steps can therefore be applied to increase the lifetime of graphite electrodes in analogy with previous findings for silicon electrodes. This is important as this demonstrates that the influence of the trapping effect can be decreased by increasing the efficiency of the delithiation and that it should be possible to recover the trapped lithium by, for example, applying a sufficiently long constant-voltage delithiation step. The lithium trapped in the graphite electrodes is consequently not irreversibly trapped but merely inaccessible within the time domain of the conventional CC delithiation step. By realizing the presence of such an effect, it should be possible to develop strategies to decrease the total capacity loss and increase the cycling lifetimes of lithium-based batteries.

4. Experimental Section

**Materials:** The graphite powder (Timrex SLP30, Timcal), sodium carboxymethyl cellulose (CMC) (Walocel CRT 2000 PA, Dow), conductive carbon black (C-NERGY Super C65, Imerys), carbon-coated copper foil (11 μm, MTI Corporation), lithium disks (450 μm, 15 mm in diameter, China Energy Lithium Co., Ltd.), and Celgard 2400 mono-layer polypropylene (PP) separator (25 μm, Celgard Co.) were purchased from the indicated companies. The Celgard 2400 separators were cut into disks with a diameter of 17 mm which then were vacuum dried at 170 °C for 2 h and then 120 °C for 12 h in a Büchi glass oven in a glovebox prior to cell assembly. The graphite composite electrodes contained 93% of the SLP30 graphite, 5% of the CMC, and 2% of the conductive carbon black with active material (i.e., SLP30 graphite) mass loadings of around 3.65–3.8 mg or 2.75–2.86 mg cm\(^{-2}\).

**Cell Assembly:** All the experiments were conducted with two-electrode graphite|lithium half cells in the form of CR2025 coin cells. The graphite electrode and the lithium disk were separated by the Celgard separator soaked with 100 μL LP40 electrolyte. The cells were sealed in a glovebox in argon atmosphere with oxygen and water contents lower than 1 ppm. The cells were rested for 12 h before electrochemical experiments.

**Electrochemical Experiments:** The cyclic voltammetry experiments were conducted at scan rates of 0.01, 0.02, 0.05, and 0.1 mV s\(^{-1}\) within voltage windows from 0.01 to 1 V and 0.8 to 1 V using a multichannel potentiostat/galvanostat (MPG, Biologic).

The experiments involving the GITT, ICI method and EIS were conducted using a Biologic VMP-2 multichannel potentiostat/galvanostat.

*Other experiments including the long-term cycling experiments, open-circuit-rest experiments, and rest-CV experiments were conducted using a multichannel potentiostat/galvanostat (BT2043, Arbin).*

The long-term cycling experiments were conducted with a current density of 35 mA g\(^{-1}\) for both lithiation and delithiation. The cells were subjected to a capacity-limited cycling where lithiation was terminated once the lithium capacity of 170 mAh g\(^{-1}\) was reached, with a delithiation cutoff voltage of 1 V. A cutoff voltage of 0.01 V was also adopted as the safety and secondary limit for lithiation. The capacity-limited cycling experiments were conducted both with and without a constant-voltage step at the end of delithiation (i.e., a voltage hold at 1 V until the current density dropped to 7 mA g\(^{-1}\)) on every fifth cycle from the 21st cycle.

The open-circuit-rest experiments were conducted in the capacity-limited manner with three different delithiation capacity limits of 100, 170, and 275 mAh g\(^{-1}\). Prior to these experiments, the cells were cycled for 32 cycles with the corresponding capacity limits. After the 33rd lithiation to the corresponding capacity limits, the cells were rested for 8 h under open-circuit conditions and then continued with the delithiation to the cut-off voltage of 1 V. The cells were then subjected to two cycles of the normal capacity-limited cycling with the corresponding capacity limits. These three cycles (i.e., one cycle with open-circuit rest and two normal cycles) were considered as “one round.” The duration of the open-circuit period was doubled for every round until it reached 256 h (i.e., six rounds in total with open-circuit rest of 8, 16, 32, 64, 128, and 256 h, respectively). A current density of 35 mA g\(^{-1}\) was used for both lithiation and delithiation.

After 38 cycles of capacity-limited cycling and the 39th lithiation to the capacity limit of 170 mAh g\(^{-1}\), the EIS experiments were conducted with a frequency range from 10 kHz to 100 mHz and an amplitude of 5 mV. The impedance measurements were conducted every 10 min for the first 24 measurements and then every 30 min for the next 248 measurements. Between each two measurements and before the first one, the cell was rested under open-circuit conditions, which led to total rest time of 128 h and total experiment time of around 133 h.

The GITT experiments were conducted with galvanostatic (35 mA g\(^{-1}\)) lithiation and delithiation with periodic pauses (i.e., a 1 h pause every 5 min) until the cutoff voltages of 10 mV and 1 V, respectively, were reached. The diffusion coefficients of lithium in the graphite electrode, \(D_{li}\), at various SOCs were calculated as:

\[
D_{li} = \frac{V_{cut}}{f \cdot \Delta t}
\]

where \(V_{cut}\) is the cutoff voltage, \(f\) is the frequency of the GITT experiment, and \(\Delta t\) is the time duration of each step.
The capacity limit of 170 mAh g⁻¹ was used for the delithiation step. The rest-ICI experiment was performed with a lithiation period of 5 min. Long-term cycling experiments were determined using ICP-MS analysis of the amounts of lithium present in the delithiated graphite electrodes after the repetitions. The lithiation and delithiation were studied using SEM (Leo 1530, Zeiss). The graphite electrodes were washed with dimethyl carbonate (DMC) several times to remove residual electrolyte. After the graphite electrodes were dry, they were carefully placed in glass vials. The glass vials were then sealed in pouch bags in the glovebox prior to transfer to the ICP-AES lab. The electrodes were then put into 40 mL Kjeldahl flasks containing 1.5 mL sulfuric acid, and the flasks were then heated up. When the sulfuric acid boiled, drop-wise additions of nitric acid (0.5 mL in total) were made with extreme care. The solutions were then kept boiling for about 2 h. The colorless solutions that were obtained after cooling down were then diluted and fed into the ICP-AES instrument (Spectro Ciros Vision, Germany) for measurements against acid matched standards at the wavelength of 670.780 nm.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

Financial support from the Swedish Research Council (VR-2019-04276), The Ångström Advanced Battery Center, and StandUp is gratefully acknowledged.

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

diffusion, graphite electrodes, lithium trapping, lithium-ion batteries, lithium–metal half cells

Received: March 31, 2022
Revised: May 12, 2022
Published online: June 3, 2022
