Abstract
Nanosized silicon materials are being developed for use in the anodes of high-energy lithium-ion batteries. However, the high surface areas of these materials increase the rate of parasitic reactions in the electrode, which consume cyclable Li\(^+\) and degrade battery performance. Prelithiation offers a realistic strategy to compensate for this reactivity, by injecting additional charge into the cell to counterbalance the Li\(^+\) loss. Interestingly, the benefits offered by prelithiation extend beyond its more obvious purpose. Here, by using a reference electrode in NMC532/Si–Gr cells, we show how prelithiation alters the cycling potentials experienced by the Si-containing anode and how that translates into gains in cycle life. The rate of consumption of the prelithiated charge is lower than that expected from the behavior of non-prelithiated cells. Curiously, the Si particles become partially unresponsive during the C/3 cycling apparently because of kinetic constraints. Electrochemical studies on harvested electrodes in half-cells show that capacities are intact after the long-term cycling and that most of the lithium reservoir is still present in the anode. We conclude that the high capacity retention displayed by the prelithiated cells mainly results from a higher participation of graphite particles during the extended electrochemical cycling.

1. Introduction
Li-ion batteries (LIBs) are among the most disruptive technologies of the past century. The leap in energy densities provided by these devices have enabled ever more complex portable gadgets and have led to the successful commercialization of high performance electric vehicles (EVs) [1]. Further increases in energy density are essential to reduce the costs of large battery packs and crucial for the widespread adoption of EVs [2]. From a materials perspective, silicon has attracted considerable attention because it is capable of storing roughly 10 times more charge than graphite, which is the major anode constituent of commercial cells. Therefore, electrodes containing silicon in various amounts and forms have been the subject of extensive investigations in the past decade [3–11].

The caveat is that Li,Si alloys have much lower densities than the parent metalloid and thus lithiation of silicon can produce volume changes that approach 300% on a particle level. Upon repeated cycling, this extensive ‘breathing’ of silicon can cause severe degradation in the electrode and battery performance. One solution is to use silicon in the form of nanoparticles or other nanostructures, which can better accommodate these dimensional changes [5, 10, 12]. Although this approach has succeeded in maintaining electrode integrity over repeated cycling, the silicon particle ‘downsizing’ increases the surface area, amplifying the extent of parasitic reactions in the electrode [11]. These undesirable processes lower coulombic efficiencies, particularly during the initial cycles when large amounts of charge are consumed to form the solid electrolyte interphase (SEI).

An approach to compensate for this initial inefficiency is to inject additional charge into the cell prior to fabrication. This practice is known as prelithiation, as it essentially consists in providing additional Li\(^+\) to the anode [6–8, 10, 13]. Low levels of prelithiation are used to compensate for the Li\(^+\) lost during SEI formation, resulting in higher initial capacities in full-cells (where the Si-electrode is coupled with materials that have a limited inventory of Li\(^+\) ions). Higher levels of prelithiation can be used to create a Li\(^+\) reservoir in the anode that...
is gradually released into the cell to reduce the magnitude and rate of capacity loss. Note that this second scenario requires higher anode/cathode capacity ratios, which can partially offset the energy gains brought about by silicon [7].

In this study, we use a reference electrode cell to investigate the effects of relatively high prelithiation levels on the behavior of silicon–graphite (Si–Gr) electrodes. We demonstrate that the relative contribution of Gr to charge storage increases after prelithiation, resulting in stable cycling with little consumption of the Li^+ reservoir. In fact, most of the prelithiated charge in our cells is apparently inactive, as the lithiated silicon develops high kinetic barriers during the test. We also provide markers that would indicate similar behavior in full-cells, as most cycled cells do not contain a reference electrode.

2. Methods

Experiments were conducted using positive electrodes (cathodes) based on Li_{0.13}(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2 (NMC532), and negative electrodes (anodes) containing a blend of silicon (Si) and graphite (Gr). The NMC532 electrode contained a mix of 90 wt% oxide (Todia), 5 wt% C45 conductive carbon (Timcal) and 5 wt% PVDF binder (Solef 5130, Solvay), coated on an aluminum current collector. The Si–Gr negative electrode contained a mix of 73 wt% Gr (Hitachi MAGE), 15 wt% Si (50–70 nm, Nanostructured & Amorphous Materials, Inc), 2 wt% C45 and 10 wt% of LiPAA binder, coated on a copper current collector [3, 4]. The total coating loading of the cathode was 9.17 mg cm^{-2}, resulting in a thickness of 34 μm at 33.5% porosity; for the anode, a loading of 2.94 mg cm^{-2} and 42.4% porosity yielded a 25 μm thick coating. The relative areal capacity ratio of the anode and the cathode (N/P ratio) for the baseline (non-prelithiated) cell was ~1.75.

Electrochemical testing of full-cells was carried out using a reference electrode cell assembly, which is described elsewhere [9, 14]. In this cell 20.3 cm^2 electrodes are separated by two Celgard 2325 sheets, and a piece of metallic lithium rolled over a 25 μm thick Sn wire is used as a reference electrode (RE). This RE was positioned laterally (next to the electrode stack); in this configuration, the relative variation of electrode potentials can be tracked, with the values being more accurate at slow rates (≤C/10) [14]. Testing of half-cells (cells with Li counter electrode) were conducted in 2032-type stainless steel coin–cells (1.6 cm^2 area electrodes). All cells were assembled in an Ar-atmosphere glovebox. The electrolyte contained 1.2 M LiPF_6 in a solution of 3:7 w/w ethylene carbonate (EC) and ethyl methyl carbonate (EMC) and 10 wt% of FEC as a film-forming additive [3, 9]. The electrolyte content of all cells was ~20 μl per cm^2 of the electrode.

Prelithiation of the negative (Si–Gr) electrode was performed by charging a full-cell to a capacity of 1 mAh cm^{-2} (45% of the total anode capacity) and then replacing the delithiated cathode with a pristine NMC532 electrode. This level of prelithiation (45%) is close to the maximum that can be safely accommodated by our anode before over lithiation becomes likely. Most full-cells (without and with prelithiation) were cycled galvanostatically between 3.1 and 4.1 V. Some cells were cycled to a lower cutoff voltage of 3.0 V and these are indicated in the text. Our basic cycling protocol consists of three initial cycles at C/20 rate; in this configuration, the relative variation of electrode potentials can be tracked, with the values being more accurate at slow rates (≤C/10) [14]. Testing of half-cells (cells with Li counter electrode) were conducted in 2032-type stainless steel coin–cells (1.6 cm^2 area electrodes). All cells were assembled in an Ar-atmosphere glovebox. The electrolyte contained 1.2 M LiPF_6 in a solution of 3:7 w/w ethylene carbonate (EC) and ethyl methyl carbonate (EMC) and 10 wt% of FEC as a film-forming additive [3, 9]. The electrolyte content of all cells was ~20 μl per cm^2 of the electrode.

3. Results and discussion

3.1. Electrode potentials and the effect of prelithiation

Consider the cycling profiles of a NMC532//Si–Gr full-cell displayed in figure 1(a). After reaching the cutoff voltage of 4.1 V during the first charge the cell is discharged to 3.0 V, presenting a capacity loss of 0.45 mAh cm^{-2}. Due to this capacity fade, the discharge curve does not reach the point where charging was initiated (~0 mAh cm^{-2}). The additional charge loss from future cycles will further shift the curves to the right. This movement is shown in figure 1(a), which provides a compact representation of performance loss and changes to the shape of cycling profiles. After an extended number of cycles and severe capacity fade, obvious changes can be seen in the voltage profiles (figure 1(b)). Although charge profiles still extend over the same voltage window (3.0–4.1 V), they store less charge in the process, resulting in steeper slopes. If electrode potentials are measured versus a reference electrode (figures 1(c), (d)), we observe that the capacity fade causes both cathode and anode to experience progressively higher potentials during charge and discharge. High voltages can be detrimental to the positive electrode [15], and so capacity fade slowly steers the cathode towards
more damaging conditions. Conversely, in the absence of Li$^+$ loss, cutoff potentials at both electrodes remain constant and the profiles do not change during cycling.

When a reference electrode is not available, the shifts experienced by electrode profiles can be envisioned using data acquired from half-cells [9, 16]. For a perfectly efficient full-cell (no loss of Li$^+$ ions), the profiles from the cathode and the anode are stationary, and the charge cutoff of 4.1 V is achieved at constant electrode potentials (figure 2(a)). A cycle with net capacity loss will shift the profiles with respect to each other; in figure 2(b), this loss is shown as a translation of the anode profile to the right with respect to the cathode. This movement leads to higher electrode potentials at the charge cutoff, just as described in figure 1. In contrast, an eventual net capacity gain produces a relative shift of the anode profile to the left, producing lower electrode potentials at the cutoff (figure 2(c)).

Figure 2 is useful to illustrate the effects of prelithiation on the electrodes. In the absence of prelithiation, the capacity lost during the formation cycles produces a case similar to figure 2(b). When prelithiation is only used to compensate for Li$^+$ losses associated with SEI formation, the cell could be close to the case illustrated in figure 2(a). On the other hand, if prelithiation occurs to the extent of creating a reservoir of Li$^+$ at the anode, the electrode potentials are as described by figure 2(c). The charge stored in the reservoir equals the relative shift between the profiles (width of shaded area).

This simple description can provide interesting insights about how prelithiation alters the electrode behavior. Consider the case represented by figure 2(c). The Li$^+$ stored in the reservoir only becomes accessible to the cell if the anode can be delithiated to higher potentials. When that happens, however, the cathode is discharged (lithiated) to proportionally higher potentials; that is, it can no longer be re lithiated to the same extent as in the previous cycle. This exercise explains why prelithiation can improve capacity retention but cannot completely eliminate capacity fade: Li$^+$ release from the reservoir always comes at the expense of the
cathode’s ability to accept charge. To access the reservoir, the cell needs to operate at net capacity loss, cycle-by-cycle.

This relationship between reservoir accessibility and electrode potential creates interesting features. The first one is that, in principle, anode potentials measured with a reference electrode can be used to estimate the residual capacity present in the reservoir; note that this is only accurate if changes to the delithiation profiles are small during cycling. A second feature is that the rate of Li\(^+\) release from the reservoir back into the cell should depend on the particular shapes of the cathode and anode profiles and on the size of the reservoir itself. Reservoir accessibility in figure 2(c) is limited by how much the anode profile can be ‘shifted to the right’ before the difference between the electrode potentials meet the 3.0 V discharge cutoff. With this example in mind, a smaller reservoir would approximate the steeper ends of the cathode and anode profiles, resulting in a scenario in which minute capacity increments (slippage) produce large voltage changes. That is, a limited amount of charge can be injected into the cell before it meets the discharge cutoff. The consequence is that reservoir accessibility depends on materials (shape of profiles, rate of capacity fade etc) and fabrication (N/P ratio, extent of prelithiation) parameters, which will cause variations in the stability offered by prelithiation on a cycle-by-cycle basis.

A final feature of the accessibility/potential relationship is that prelithiation confines the anode to a smaller potential window. Turning once more to figure 2(c), if full-cells are designed to initially reach a fixed lower cutoff potential at the anode, then a prelithiated version of this cell would have the anode being lithiated from a lower starting potential, resulting in a smaller initial window. Limiting the potential range experienced by silicon particles can assist in extending cycle life of the cell [17].

3.2. Cycle life of the baseline (no prelithiation) and prelithiated cells

As stated earlier, prelithiation was performed by charging the full-cell to 1 mAh cm\(^{-2}\), which is 45% of the anode (Si–Gr electrode) capacity. The cell was then opened and the NMC532 cathode was replaced with a fresh one. This process compensates for SEI formation and creates a Li\(^+\) reservoir of \(\sim 0.64\) mAh cm\(^{-2}\) at the anode. During the first charge of this re-built cell, a coulombic efficiency of 88.5% is achieved, compared to 77.1% exhibited by the baseline cell. The first cycle of a prelithiated cell will generally have the efficiency limited by the cathode, justifying the relatively low value [7]; after the initial charge, the positive electrode is unable to accept a fraction of the extracted Li\(^+\) at reasonable rates due to kinetic limitations [15]. This extra lithium will then join the reservoir at the anode, amounting to a total of \(\sim 0.81\) mAh cm\(^{-2}\).

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Figure 2. Shifts in electrode potentials in a NMC532//Si–Gr full-cell: in the absence of capacity fade, electrode potentials remain stationary (a), while net capacity loss or gain causes the anode to shift to the right (b) or to the left (c), respectively, relative to the cathode. As in figure 1, capacity loss leads to higher electrode potentials at the same full-cell voltage cutoff of 4.1 V.
Figure 3 shows the cycle life of the baseline and prelithiated cells. As already clear at first glance, prelithiation increases both cell capacity (by supplying electrons to construct the SEI) and capacity retention (apparently by releasing Li\(^+\) stored in the reservoir). While the baseline cell loses 46% of its capacity in 100 cycles, the prelithiated cell only loses \( \sim 20\% \) in five times as many cycles (figure 3(b)). The fade regimes are also qualitatively different between the two cells. Capacity fade occurs quasi-linearly for the baseline cell, whereas the prelithiated cells exhibit a bimodal decay, with an accelerated fade in the initial \( \sim 40 \) cycles followed by a slower performance loss in the remainder of the test. The transition between these two modes in the latter cell also coincides with an increase in coulombic efficiency of the C/3 cycles, which starts at 0.995 and saturates at \( >0.998 \) at cycle 40 (figure 3(c)).

The differences between the rates of decay of both cells can be better understood by inspecting the cycling profiles of the Si–Gr anodes, recorded using the reference electrode. Profiles of selected C/3 cycles are shown in figure 4. In the absence of major changes in the anode impedance and/or morphology, profiles of successive cycles should maintain the same general ‘shape’, i.e., the amount of overpotential should remain constant at a given state-of-charge (SOC). This is the case for the baseline cell, in which the lithiation profiles lie on top of each other and are only shortened by capacity fade (figure 4(a)). The general form of the delithiation profiles is also maintained. However, this is clearly not the case for the prelithiated cell, which experiences significant changes in the profiles during the initial 40 cycles (figure 4(b)). During lithiation, there is a slight increase in polarization at higher SOCs, while the delithiation profiles develop a much steeper termination; these transformations saturate shortly after cycle 40, with the characteristics of the profiles persisting for hundreds of cycles thereafter. These trends are not present in the profiles of the cathode (omitted for brevity), which just present the expected potential shifts caused by slippage.

A recent report by Wetjen et al proposed that silicon nanoparticles can undergo sizable morphological transformations during the initial \( \sim 60 \) cycles, with the silicon being converted to a nanoporous framework \([17]\). The evolving surface area of the resulting structures would then prompt electrolyte reduction, resulting in an initial period of accelerated capacity fade. In half-cell tests, this initial performance loss is mostly due to permanent isolation of Si domains; in full-cells, the side-reactions would also directly contribute to capacity fade. The irreversible structural changes are self-limited and, eventually, performance degradation would fall...
into a slower regime [17]. This conceptual model can rationalize our experimental observations after prelithiation: morphological evolution of the silicon particles can produce both the changes in the anode profiles (figure 4(b)) and the zones with distinct rates of Li$^+$ loss (figure 3(a)). Note, however, that none of this applies to the baseline cell, suggesting that structural changes in the Si particles are mitigated when cycled above a certain SOC. The anode is always above 112 mV versus Li/Li$^+$ in the baseline cell, but can go below 10 mV versus Li/Li$^+$ after prelithiation; lowering the utilization of Si helps maintain the integrity of particles in the baseline cell.

An additional consequence of the changes in anode profiles shown in figure 4(b) is that we can no longer use the measured potentials to quantify the residual amount of Li$^+$ in the reservoir. Nevertheless, a comparison between the baseline and prelithiated samples provides valuable insights. After 100 cycles, the capacity fade exhibited by the baseline corresponds to a loss of 0.64 mAh cm$^{-2}$; that would correspond to 79% of the initial 0.81 mAh cm$^{-2}$ reservoir. If the prelithiated cell is assumed to fade at a similar rate as the baseline, then the reservoir would certainly exhaust before 200 cycles are completed. This is clearly not what happens. Reservoir consumption often manifests as a sudden increase in the rate of capacity loss [7], while the prelithiated cell in figure 3 continues to perform unperturbed by such sudden changes. A logical explanation is that, somehow, prelithiation also changes the intrinsic rate of fade of an electrode pair. That is, once the cell is prelithiated, capacity could be maintained stable at a much lower consumption rate of the Li$^+$ from the reservoir than initially anticipated. This is conceptually similar to observations reported by Chevrier et al [7] in which a prelithiated cell presented higher coulombic efficiency than the baseline even after the exhaustion of the reservoir. These behaviors are rationalized below.

### 3.3. Modulated graphite utilization

The anode profiles of the prelithiated cell (figure 4(b)) bear remarkable resemblance to the profile of a silicon-free, graphite electrode: the three characteristic plateaus of Gr [14] contributes to most of the delithiation (discharge) capacity. This becomes even more obvious after inspecting the hysteresis in the profiles shown in figure 5. In a Gr-half-cell, both the forward (lithiation) and reverse (delithiation) reactions occur with little kinetic hindrance, resulting in minimal hysteresis (figure 5(a)). In a Si–Gr half-cell, however, the presence of silicon imposes significant hysteresis on the system (figure 5(b)) [18, 19]. While silicon can be continuously lithiated from ~0.5 V versus Li/Li$^+$ down to very low potentials, it only begins to delithiate above ~0.25 V versus Li/Li$^+$ [18, 20]. This is even more significant if the crystalline Li$_{15}$Si$_4$ phase is formed, in which case a hysteresis of ~0.4 V can exist [18]. This hysteretic behavior (that is characteristic of Si-containing systems) is not observed in our prelithiated cell for most of the test (figure 5(c)). In fact, the electrode begins the test responding as one would expect for a Si–Gr system, but the curves eventually assume a strong Gr character. Inspection of
Figure 4 suggests that this happens soon after the C/3 cycles begin. This behavior indicates that, for some reason, silicon appears to be inactivated when the graphite accepts charge. A direct consequence of this behavior is that most of the reversible capacity exhibited by the prelithiated cell is being stored in the graphite, with little utilization of silicon. An estimate of the relative contributions between these two components is shown in figure 6(a), in which we assume that all discharge capacity above 270 mV versus Li/Li^+ comes from delithiation of Li_xSi. In figure 4(a), after some number of cycles, graphite participation in the activity of the anode increases quickly, stabilizing at 80% after ~40 cycles. Note that this range coincides with the initial transition in capacity fade and coulombic efficiency, exhibited in figure 3. After 40 cycles, the prelithiated cell has a very high Gr character, and so it will also tend to lose capacity in a way closer to how Gr would. As a
consequence, in addition to supplying the cells with a Li$^+$ reservoir, prelithiation also provides intrinsic stability to the cell.

Although the behavior we report here is quite unique (and somewhat extreme), we believe it is applicable to all Si–Gr systems. Prelithiation will always force the anode to operate at lower potentials. Even if the lower cutoff of the baseline is the same as the prelithiated cell, the upper cutoff potential will be different, because of the existence of the Li$^+$ reservoir. That means that, on day one, the prelithiated cell will always have greater Gr character: the larger the reservoir, the greater the Gr character. Because the baseline cell will lose capacity faster, slippage will reduce the Gr character over time. A final point is that, assuming that capacity fade in Si–Gr is related to Si$^{[17]}$, any permanent losses of Si while the reservoir exists will result in a cell with less Si upon its exhaustion. In one way or the other, prelithiation can produce cells with higher Gr character. We believe that this rationalization enabled by our studies using a reference electrode can be useful to other researchers in the field.

Note that this additional benefit of prelithiation can potentially be extended to Si-rich, Gr-free cells. Prelithiation limits the upper cutoff potential of the anode, which has been reported to be beneficial for cell health$^{[17]}$.

A question that remains is why Si becomes almost completely unresponsive in our prelithiated cell during the C/3 cycles. This observation will be discussed in the following sections.

3.4. Analysis of harvested electrodes

Silicon nanoparticles can experience significant damage during cycling, making particle inactivation caused by cracking a common mechanism of capacity loss$^{[19, 21]}$. One can hypothesize that the dominant Gr character of the prelithiated cell in figure 6(a) is caused by rapid degradation of silicon particles. Analysis of electrodes harvested from the prelithiated cell, however, does not support this idea. Figure 6(b) shows that silicon particles in the prelithiated cell are just as responsive after 500 cycles as they were when the cell was first built; capacities are similar to those exhibited by a pristine electrode. Si particles are still present, but some mechanism is rendering them unresponsive to electrochemistry. This mechanism does not affect the bulk impedance of the anode, as other experiments (not shown here) with our 3-electrode cell found no impedance rise at the negative electrode.

The tests with harvested electrodes hint at what is causing this inactivation of silicon. Prior to further testing, half-cells containing the harvested electrodes were delithiated to 1.5 V at C/20 rate, to quantify any residual capacity trapped in the anode. Figure 7(a) exhibits one such profile, showing that there is still 0.63 mAh cm$^{-2}$ remaining at the electrode, stored in the Si particles. This capacity is 78% of the initial reservoir present in the anode, demonstrating that it is mostly intact, and that the high stability of our prelithiated cell arises mostly from its high Gr character.
3.5. Kinetic Impediment

An interesting element of figure 7(a) is the occurrence of an initial spike in the delithiation profile, followed by a constant decrease in potential before delithiation proceeds. Following cycles do not show this behavior. This spike is similar to what is commonly observed during Li stripping from metallic lithium [22, 23], for example, and is generally ascribed to kinetic barriers being overcome. Another feature of figure 7(a) is the unusually large amount of capacity existing above 0.6 V versus Li/Li⁺ (compare with figure 6(b), for example). These observations suggest that, during testing, lithium dealloying from silicon becomes kinetically hindered, imposing a large overpotential. The potentials required to extract lithium from Si (0.6–0.7 V versus Li/Li⁺), as per figure 7(a) are actually never met by the anode during discharge in the prelithiated full-cell (figure 7(b)), resulting in the persistence of an inactive LiₓSi phase. Under such conditions, the Gr particles are the preferred destination for incoming Li⁺ during lithiation, resulting in the graphite-like behavior discussed above. All these factors result in the rather unique scenario in which we have a nearly intact reservoir that persists for kinetic reasons.

Under the right conditions, nevertheless, silicon dealloying can also occur in the prelithiated full-cell. This is shown with a similar prelithiated cell (cell 2 in figure 8(a)), tested under a slightly modified protocol; in cell 2, cycles 201, 301 and 401 are preceded by a 12 h potentiostatic hold at 3.0 V (the discharge cutoff of this cell is 100 mV lower than in cell 1 at all cycles, resulting in a slightly higher capacity throughout the test). The C/20 cycles immediately after this deep discharge present much larger capacities than other cycles at this same rate. This excess capacity also comes with a larger hysteresis (figure 8(b)), producing profiles consistent with a higher Si utilization. After a few cycles, however, the profiles resume showing a Gr-like behavior. In the absence of a deep discharge (around cycle 100, for example), no sudden variations in capacity and hysteresis are observed.

3.6. Markers in the full-cell data

The observations above were only made possible through the use of a reference electrode. Since this resource is not always available to battery scientists, we discuss ways to infer similar behavior from the inspection of full-cell data.

One of the interesting findings reported here is that prelithiation in Si–Gr cells increases the relative participation of graphite in the cell. Although our system presents a rather extreme version of this behavior, it can be expected to happen to some extent in samples with large Li⁺ reservoirs. Analysis of our data suggests that...
Hysteresis is a good marker for the activity of silicon, as illustrated in figure 9(a). In general, since prelithiation lowers the initial discharge cutoff potential of the anode, one could expect to observe less hysteresis at the low- to mid- capacity regions of figure 9(a) as participation of Gr increases. Differential capacity \( (dQ/dV) \) plots can also be useful, as the peaks associated with Gr staging tend to be prominent [9]; in our experience, it is easier to account for these peaks when \( dQ/dV \) is plotted versus capacity, rather than in the usual form versus voltage.

Perhaps the most surprising topic presented in this work is the ‘freezing’ of Si particles. Due to kinetic barriers, unusually high anode potentials are required before silicon can be fully delithiated. A slight bowing of the delithiation profile of cycle 490 in figure 4(b) gives an indication of this delayed reactivity, which is even more visible at slower rates. In full-cells, this creates a plateau in the discharge profile (figure 9(b)), which is very distinct from the usual behavior of these cells with NMC-based cathodes.

4. Conclusions

At high levels of prelithiation, the excess charge injected into the cell forms a reservoir of \( \text{Li}^{+} \), which can slowly be released to compensate for the capacity lost during normal operation of the cell. In Si–Gr systems, the reservoir usually takes the form of Li-deficient Li$_x$Si phases, since they form at high anode potentials (versus Li/Li$^{+}$), and are the first lithiated phases that are created as electrons flow to the negative electrode. Due to the preexistence of these phases, the anode of a prelithiated full-cell begins lithiating already at a lower potential than in the baseline cell. Similarly, it also delithiates to a lower potential. For Si–Gr electrodes, these changes in the potential window will limit the amount of charge that can be recovered from silicon, while the activity of Gr is either invariant or increased, depending on the original capacity balancing of the cell. All in all, prelithiated anodes will have a larger fraction of the incoming Li$^{+}$ stored in Gr rather than Si, if compared to an identical, non-prelithiated cell. In other words, the cell will behave as if it had a higher Gr content, which should per se contribute to increase the cycling stability, regardless of the presence of the extra charge available in the reservoir. We believe that this higher Gr participation contributes to the performance improvements commonly observed in prelithiated cells. In principle, this enhanced Gr activity could also persist after the exhaustion of the reservoir. Assuming that some of the Si particles are permanently damaged early during testing, by the time the reservoir is consumed an electrode with higher ‘effective Gr content’ is left. This could explain recent observations reported...
in the literature, in which prelithiated cells cycle with higher coulombic efficiency than the baseline even after the reservoir is consumed [7].

Although the rationale above can be expected to be fairly general, our prelithiated Si–Gr cells actually exhibited an even more extreme version of this behavior. Through the inspection of the hysteresis of anode profiles, we demonstrated that the Si particles became nearly unresponsive during most of the test, at times contributing to only ∼20% of the capacity of the cell. Additional experiments showed that this occurred due to high kinetic barriers, and that the Si–Gr anodes remained otherwise intact after the test. In fact, most of the reservoir was still present in the negative electrode after 500 cycles, showing that the relatively high stability we observed in the cell (20% fade after ∼500 cycles) essentially derived from the large relative contributions of Gr to the anode capacity. The mechanism for this kinetic deactivation of Si particles is not well understood at this time, but we believe these observations can be useful to other groups investigating Si-based systems.

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References

[1] Winter M, Barnett B and Xu K 2018 Chem. Rev. 118 11433–56
[2] Myung S-T, Maglia F, Park K-J, Yoon C-S, Lamp P, Kim S-I and Sun Y-K 2017 ACS Energy Lett. 2 196–223
[3] Kalaga K, Rodrigues M-T F, Trask S E, Shkrob I A and Abraham D P 2018 Electrochem. Acta 280 221–8
[4] Rodrigues M-T F, Trask S E, Shkrob I A and Abraham D P 2018 J. Power Sources 395 289–94
[5] Ababtain K, Babu G, Lin X, Rodrigues M-T F, Gullapalli H, Ajayan P M, Grinstaff M W and Arava L M R 2016 ACS Appl. Mater. Interfaces 8 15242–9
[6] Betz I, Nowak L, Winters M, Placke T and Schumch R 2019 J. Electrochem. Soc. 166 A3531–8
[7] Chevrier V I, Liu L, Wohl R, Chandrasoma A, Vega J A, Eberman K W, Stegmaier P and Figgemeier E 2018 J. Electrochem. Soc. 165 A1129–36
[8] Forney M W, Gaunter M J, Staub J W, Ridgley R D and Landi B J 2013 Nano Lett. 13 4158–63
[9] Klett M, Gilbert J A, Trask S E, Polzin B J, Jansen A N, Dees D W and Abraham D P 2016 J. Electrochem. Soc. 163 A873–87
[10] Liu N, Hu L, McDowell M T, Jackson A and Cui Y 2011 ACS Nano 5 6487–93
[11] Wetjen M, Pritzl D, Jung R, Solchenbach S, Ghadimi R and Gasteiger H A 2017 J. Electrochem. Soc. 164 A2840–52
[12] Vlad A, Reddy A L M, Ajayan A, Singh N, Gohy J-F, Melante S and Ajayan P M 2012 Proc. Natl. Acad. Sci. 109 15168–73
[13] Zhang L, Dose W M, Yu A D, Johnson C S and Lu W 2018 J. Power Sources 400 549–55
[14] Rodrigues M-T F, Kalaga K, Trask S E, Dees D W, Shkrob I A and Abraham D P 2019 J. Electrochem. Soc. 166 A996–1003
[15] Rodrigues M-T F, Kalaga K, Trask S E, Shkrob I A and Abraham D P 2018 J. Electrochem. Soc. 165 A1697–705
[16] Smith A J, Dahn H M, Burns J C and Dahn J R 2012 J. Electrochem. Soc. 159 A705–10
[17] Wetjen M, Solchenbach S, Pritzl D, Hou J, Tilèvi L and Gasteiger H A 2018 J. Electrochem. Soc. 165 A1503–14
[18] Klett M, Gilbert J A, Puppek K Z, Trask S E and Abraham D P 2017 J. Electrochem. Soc. 164 A6095–102
[19] Obrovac M N and Chevrier V I 2014 Chem. Rev. 114 11444–502
[20] Yao K P C, Okainsinski J S, Kalaga K, Almer J D and Abraham D P 2019 Adv. Energy Mater. 9 1803380
[21] McDowell M T, Lee S W, Nix W D and Cui Y 2013 Adv. Mater. 25 4966–85
[22] Bieker G, Winter M and Bieker P 2015 Phys. Chem. Chem. Phys. 17 8670–9
[23] Liang Z et al 2016 Proc. Natl. Acad. Sci. 113 2862–7