**Understanding and optimizing formation cycling on carbon black**

Peter M. Attiaz, William C. Chueh

Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, USA

z Corresponding author: [peter.m.attia@gmail.com](mailto:peter.m.attia@gmail.com)

**Abstract**

Lithium-ion battery formation directly affects battery cost, energy density, and lifetime. The design of optimized formation protocols could improve with a better understanding of the first cycle of solid-electrolyte interphase (SEI) growth on the negative electrode. In this work, we systematically study SEI growth during the first lithiation of carbon black negative electrodes. We show that the major reduction reaction at 0.5­–1.0V is unique to the first cycle. We then perform a simple electrochemical experiment to demonstrate that the SEI products of this reaction do not passivate the electrode; only the products created at lower potentials affect the coulombic efficiency of the subsequent cycle. Thus, cycling quickly through the voltage regime of this reaction can reduce formation time and first-cycle losses with no impact on lifetime. Finally, we show that the capacity consumed by this reaction is minimized at low temperatures and high salt concentrations. This work uncovers the fundamental mechanisms underlying the initial stages of SEI growth on carbon negative electrodes and reveals pathways for optimizing battery formation processes.

Improving the energy density, lifetime, and cost of lithium-ion batteries is critical to enable the electrification of transportation and grid storage. In commercial batteries, all three of these factors are influenced by the formation cycle, a key step in battery production.1–4 One of the primary objectives of formation is to create a well-passivating solid-electrolyte interphase (SEI) layer on the graphitic negative electrode, an ubiquitous negative electrode in lithium-ion batteries). However, high irreversible capacity loss during battery formation increases the “dead weight” cathode capacity required to compensate, which decreases the energy density and increases the raw materials cost. Additionally, poor passivation effectiveness of the formation cycle decreases the lifetime. Finally, the long time required for formation increases the manufacturing cost, as the manufacturing time and formation cycling capital expense are among the most expensive costs of battery manufacturing.2 As a result, designing rapid yet effective formation protocols is an active area of research.5–8 A more fundamental understanding of formation cycle reactions will aid in these optimization efforts.

The first lithiation of graphite, and its associated side reactions, has been extensively studied. In fact, the challenges of lithium intercalation into graphite from propylene carbonate (PC) electrolytes delayed the commercial introduction of lithium-ion batteries by 20 years.[] These PC electrolytes were found to be perpetually reduced during the first lithiation, co-intercalating into and exfoliating the graphite. This reduction consumed large amounts of lithium inventory and generated propylene gas. In contrast, the use of ethylene carbonate (EC) electrolytes enabled reversible lithium intercalation and thus the commercialization of lithium-ion batteries. However, EC electrolytes also exfoliate graphite and generally reduce at potentials between 0.6 and 1.0 V. This coupled exfoliation and reduction occurs when solvent co-intercalates at the “non-basal-plane” graphite surfaces, i.e., edge planes and defect sites. 9–11 Furthermore, the reduction of EC was linked to its presence in the lithium-ion solvation sheath.[]

Additional studies have revealed that the irreversible capacity loss of this reaction increases with graphite crystallinity[], increases with oxygen-removing graphite surface treatment[], and decreases with the use of electrolyte additives such as vinylene carbonate (VC) and fluoroethylene carbonate (FEC).[]

Finally, the reported products of EC reduction are ethylene gas[] and a solid-phase carbonate, either LEDC (12,13) or LEMC (14).

While the complex mechanistic details and the ordering of the desolvation, co-intercalation, exfoliation, and reduction steps are currently under study via both theory [] and experiment[], controlling this process is clearly important for optimizing lithium-ion battery formation. Throughout this paper, we refer to these combined steps as the “EC reduction” reaction, though we note that EC may also reduce at lower carbon potentials as well.

However, translating these fundamental insights into design principles for optimized formation protocols is not clear. Markle et al. and Goers et al. found that high currents during the first lithiation suppressed graphite exfoliation. However, the use of high currents at low graphite potentials was found to create poorly passivating SEI (??). From the applied side, previous work on multistep formation protocols has indicated the importance of spending time at high cell potential (i.e. low graphite potentials) to form a well-passivating SEI and improve lifetime.[] For instance, An et al. achieved promising results with a fast formation protocol that charged quickly at low cell potentials and cycled slowly at high cell potentials. These results are consistent with the large body of work demonstrating the passivating ability of SEI formed at low graphite potentials. However, these applied results are somewhat difficult to generalize into more fundamental design principles for formation. Systematic studies of the dependence of the EC reduction reaction on process parameters like current and temperature could reveal both fundamental and applied insights into formation.

In this paper, we electrochemically characterize the EC reduction reaction on carbon black. We first compare the first lithiation of carbon black to graphite. We then systematically examine first-cycle SEI growth under different cycling currents.

Finally, we characterize the behavior of the EC reduction reaction as a function of temperature and salt concentration, finding that low temperatures and high salt concentrations suppress the irreversible capacity loss of the EC reduction reaction. This work illustrates pathways for improving formation cycling in lithium-ion batteries with carbonaceous negative electrodes.

**Experimental**

***Cell fabrication.*—** Carbon black slurries were created with TIMCAL Super P and polyvinylidene difluoride (PVDF) binder (Alfa Aesar) in a 90:10 wt.% ratio with NMP solvent (Sigma-Aldrich). Slurries were mixed with a planetary mixer (THINKY AR-100), cast at a nominal thickness of 100 μm on electrodeposited copper foil (Hohsen), and dried overnight in a vacuum oven at 55°C. The final electrode thickness ranged from 45–55 µm, as measured with a micrometer.

Electrode disks (13 mm diameter, 1.33 cm2 geometric area) were then punched for coin cell assembly and weighed on an analytical microbalance (Mettler-Toledo XPR2). The active carbon black mass per disk is approximately 1 mg. The cells were assembled in an argon glove box (VAC, <1 ppm O2 and <0.5 ppm H2O) using stainless steel 2032 coin cell cases (Hoshen) with 50 μL of 1.0 M LiPF6 in EC:DEC (1:1) by weight (BASF/Gotion Selectilyte LP40), one 25 μm separator (Celgard) and a lithium foil (Alfa Aesar) counter electrode. The geometric volume of the carbon black electrodes is ~7 µL (1.33 cm2 × 50 µm).

The graphite electrode presented in Figure 1 was extracted from a dry A123 20 Ah lithium iron phosphate (LFP)/graphite pouch cell; the particles from one side of the double-sided electrode were removed using a cotton swab soaked in isopropyl alcohol, and then the coin cell was constructed as described in the preceding paragraph. In experiments where we vary the salt concentration, solutions of varying molality were created using LiPF6 (≥99.99%, Sigma Aldrich), ethylene carbonate, EC (99%, anhydrous, Sigma Aldrich), and diethyl carbonate, DEC (≥99%, Sigma Aldrich).

***Electrochemical characterization.*—** Cells were generally cycled inside a temperature chamber (AMEREX IC-150R) at a constant nominal temperature of 30.0°C (±0.5°C) with a Bio-logic BCS-805. In experiments where we increase the temperature beyond 30°C, the cells were cycled in silicone oil baths heated by hot plates, and the temperature was monitored via thermocouples. Unless otherwise specified, all cells were charged and discharged at a constant current between 1.2 and 0.01 V, with no potentiostatic hold at either cutoff potential. All cells rest for 24 hours before cycling to ensure complete electrolyte wetting.

All C rates were calculated with a nominal carbon black specific capacity of 200 mAh g−1 (1C = 200 mA/gCB); these rates are referred to as nominal C rates. In this work, we use the term lithiation to refer to discharging (decrease in cell potential; electron flow to working electrode), and delithiation to refer to charging (increase in cell potential; electron flow from working electrode). All voltages are expressed relative to the Li metal counter electrode.

**Results**

***Comparison of first-cycle reactions of carbon black and graphite***.**—** While graphite is the most commonly used negative electrode material in commercial lithium-ion batteries, carbon nanomaterials such as carbon black grow significantly more SEI per cycle, which enables more quantitative measurements of SEI growth. Previous work has also investigated SEI growth on carbon black, often in the context of its widespread use as a conductive electrode additive15–23; our previous work on “post-first-cycle” SEI growth22 details the differences between these two materials. Importantly, carbon blacks “differ only in the magnitude of their variation from graphite rather than representing different crystallographic structures” (Donnet et al.24). Thus, carbon black serves as a good model system for fundamental investigations of SEI growth.

Figure 1 presents voltage vs. capacity and for graphite and carbon black half-cells cycling at C/10. Differential capacity (*dQ/dV*) vs. voltage is presented in the insets. The most immediate observation is the size of the first-cycle EC-reduction peak in both materials; the magnitude of the peak is much larger in carbon black than in graphite. [BET SA]. The size of this peak in carbon black motivates our use of carbon black in this paper; the exaggerated capacity loss enables a clear visualization of effects.

We also note . No peaks on delithiation and no peaks on subsequent cycles – must be distinguished from subsequent cycle SEI

The peak voltage increases from ~0.6 V in graphite to ~0.9 V in carbon black. The local current density is much larger in graphite than in carbon black, which likely accounts for much of this difference. Smith et al.19 Additionally, the ~5% larger interplanar spacing of carbon black relative to graphite22,24,25 may also contribute to the reduced overpotential.

These results demonstrate that the EC-reducing reaction is truly confined to the first lithiation; this reaction is only seen in subsequent cycles only under exceptionally high rates (Figure S1).

With these differences in mind, the remainder of our experiments are performed exclusively on carbon black.

***Dependence on C rate***.**—** Figure 2 displays the results of two experiments with variable first-cycle currents, termed “constant current” and “multistep current”. In Figure 2a, cells were lithiated at currents ranging from C/100 to 10C (“constant current” experiment). Note that these current range by four orders of magnitude. The size and location of the first-cycle reaction plateau clearly depends on the current magnitude. In contrast, the cells in Figure 2b were lithiated at currents ranging from C/100 to 10C, but only until 0.5 V; below 0.5 V, the cells lithiated at C/10 down to the lower cutoff voltage (“multistep current” experiment). We use the nomenclature X(0.5 V)-C/10 to denote these formation protocols, where X represents the lithiation current until 0.5 V and to be followed by lithiation at C/10. The cells cycled at rates above C/10 naturally exhibit a decrease in overpotential at the transition point.

Figure 2c and 2d display the first-lithiation capacities above and below 0.5 V, respectively. We find that the above-0.5 V capacities of the two experiments (Figure 2c) are in general closely aligned, with the exception of the high current values (likely because the capacities are sensitive to the large overpotentials that occur at high rates). For both experiments, the above-0.5 V capacity decreases with increasing current; due to the size of the irreversible first-cycle reaction in this potential regime, we can assume most of this capacity is irreversible. In contrast, the below-0.5 V capacities of the two experiments (Figure 2d) diverge, as these capacities decrease for the constant current experiment but are relatively level for the multistep experiment.

Figure 2e displays the total time of the first lithiation for both experiments. For the constant current experiment, the lithiation time naturally decreases with increasing C rate. The measured time of the first lithiation is not equivalent to the expected time given the C rate, due to either the large current of the first cycle reaction or the large overpotential when cycled at high rate. In contrast, the lithiation time levels off at ~10 hours for the multistep current experiment, since the formation time below 0.5 V is fixed at C/10.

Figure 2f presents the key result of this paper: the second-cycle Coulombic efficiency for both experiments. We use this metric as a sensitive proxy for lifetime, as a poorly passivating formation process would immediately result in capacity loss. All cycling after the first lithiation occurred at a rate of C/10. For the constant current experiment, the Coulombic efficiency decreases with increasing rate: reducing the initial formation time clearly compromises the future performance. In contrast, the second-cycle Coulombic efficiency for the multistep experiment is essentially independent of the initial current, that is, the current during the first-cycle reaction regime. The general trends in Figure 2d closely match those of Figure 2f; in other words, the correlation between capacity below 0.5 V and second-cycle Coulombic efficiency is strong (r=XX). This result is consistent with the large body of work demonstrating the beneficial passivation ability of SEI products formed at low potential.[] However, to the best of our knowledge, this work is the first to illustrate how the EC reduction products at high potential provide *no* passivation of the electrode. The poor passivation ability of the deposited reaction product could be attributed either to high porosity or high intrinsic material conductivity. A recent study of LEMC reports fairly high ionic conductivities (>1 × 10−6 S cm−1).

This result has clear implications for battery formation: despite consuming massive amounts of capacity, the passivation ability of the SEI from the first-cycle reaction is negligible. Only the SEI-forming reactions that occur at low potential passivate the electrode. Thus, an optimal formation strategy is to rapidly lithiate the electrode through the high-potential regime and then slowly lithiate through the low-potential regime, i.e. 10C(0.5 V)-C/100. This approach reduces the total time and irreversible capacity loss of the first cycle, which directly reduces cost and improves energy density, with no discernible impact on lifetime.

***Quantification of electrochemical parameters.*—** Figure 3a displays *dQ*/*dV* curves for the first lithiation of the constant current experiment (with the exception of the 10C experiment). The decrease in both peak potential and irreversible capacity loss at higher rates is evident. Of course, the decrease in peak potential with rate is due to the increased overpotential. We suspect that the decrease in irreversible capacity loss with rate occurs because the competition between the lithiation and EC-reduction reaction favors lithiation at high rates, due to the relatively poor kinetics of the EC-reduction reaction. This trend is only present in the galvanostatic case, where the total current (to be shared between both EC reduction and lithiation) is constrained. In linear sweep voltammetry, where the current is unconstrained, the EC reduction current increases with increasing sweep rate (Figure S2).

We note that the peak potential of the EC-reduction reaction varies from X to Y. The literature often cites 0.8 V as a canonical reaction potential; however, the peak potential is sensitive to rate and not representative of an equilibrium value.

To quantify the kinetics of this reaction, we fit current vs. peak potential to the Butler-Volmer equation in Figure 3b. Overall, the fit is good, indicating that this process is primarily reaction-limited (at least for this current range). This result is consistent with Goers et al., who also found a Butler-Volmer relationship to hold for the onset potential.

A Butler-Volmer relationship indicates a process limited by surface reaction kinetics. Thus, the strong fit obtained even at very slow currents provides further evidence that the SEI formed by the EC-reducing reaction is not passivating; if it were, we would expect transport limitations through the SEI to reduce the fitting quality at low currents (i.e. when significant amounts of EC reduction products are formed).

From the Butler-Volmer fit, we can also obtain the electrochemical parameters *E*0, *α*, and *i*0, where *E*0 represents the equilibrium potential, *α* represents the charge-transfer coefficient, and *i*0 represents the exchange current density. These values are displayed in the annotation on Figure 3b.

Fit assumes that the number of electrons transferred, *z*, is 1; our previous DEMS work found that 2 moles

***Dependence on temperature and electrolyte salt concentration.*—** Finally, we investigate the dependence of the EC-reduction reaction on temperature and salt concentration (Figure 4). These dependences are interesting from both fundamental and applied perspectives.

Temperature is a common parameter with which formation can be controlled4,5,8. We study the first lithiation at temperatures ranging from 30°C to 80°C (Figure 4a). The position and magnitude of the EC-reduction reaction is highly sensitive to temperature, with peak potentials ranging from X V to Y V. At high temperature, the reaction overpotential is dramatically reduced, and the reaction consumes much more irreversible capacity. Similar to the low-rate behavior, we believe that the reduced overpotential at high temperatures (from improved reaction kinetics) enables the EC-reduction reaction to more effectively compete with lithiation for a higher share of the current than it does at lower temperatures, leading to larger irreversible capacity loss. [Temperature: Activation energy of

Overall, our results indicate that using low temperatures when performing the EC-reduction reaction during formation is optimal, although high temperatures may be optimal for the low-potential SEI reactions. However, other factors during formation, like wetting, may be best performed at high temperature, so these steps should be split if possible.

We also explore the dependence of the EC-reduction reaction on LiPF6 salt concentration (Figure 4b). These homemade electrolytes have consistent solvent ratios (1:1 EC:DEC by weight) but different concentrations of LiPF6 salt.

Concentrated electrolytes have been of recent interest due to their interesting properties, although of course the effect of this parameter cannot be limited to just formation.

The higher salt concentrations likely cause the EC to

solvated Li complexes more stable/resistant

Lower peak potential and peak broadening

See et al.21 varied the relative concentration of solvents in an EC/DMC solvent and found that the first-cycle plateau vanishes with a 100% DMC solvent, which is consistent with our result.

Overall, however, salt concentration is a much less sensitive knob of irreversible capacity loss than temperature.

**Discussion**

These results paint a simplified picture of the first-cycle EC reduction reaction that can explain both the results shown here as well as those of previous literature. Previous literature established that ethylene carbonate in the lithium-ion solvation shell can cointercalate into and exfoliate the graphite non-basal-plane surfaces, and subsequently become reduced by the electrode.26,27 Because the cyclic carbonate reduction products provide no passivation ability, this reaction can continue indefinitely, as is often observed in PC electrolytes with low salt concentration.28,29

However, during galvanostatic cycling, lithium ions and ethylene carbonate compete for current. If EC reduction is promoted relative to lithiation, the electrode potential changes slowly, and large amounts of irreversible capacity loss occurs due to EC reduction. In contrast, if lithium ions obtain most of the current, the electrode lithiates. Subsequently, the lithiated electrode promotes the reduction of electrolyte to create more passivating SEI products, as well as lithiation over solvent co-intercalation (i.e. electrons will increasingly prefer the ionic species over the polar species). Eventually, the electrode will begin to form the low-potential reduction products that do offer passivation ability, which block EC reduction on subsequent cycles. We proposed a similar model of current competition between lithiation and SEI growth in our previous work on “post-first-cycle” SEI growth22; while the irreversible capacity loss decreased with increasing C rate, the *rate* of irreversible capacity loss increased with increasing C rate. In both cases, the exchange current density of SEI growth is slower than that of lithiation.

The implication of this model is that the exclusively deleterious effects of the EC reduction reaction can be suppressed by conditions that favor lithiation over cyclic carbonate reduction. While we have not quantified the *i*0 (and its SOC dependence) of carbon black lithiation, we can infer that its value exceeds that of EC reduction from the relatively fast kinetics of carbon black lithiation.22 We have clearly demonstrated that the kinetics of the EC reduction reaction are exceedingly slow; thus, we assume *i*0 of intercalation exceeds *i*0 of EC reduction.

Thus, an optimal formation protocol can be obtained via a combination of high currents, low temperatures, and the use of electrolytes with slow reduction kinetics. In fact, Peled30 reported a correlation between the aqueous *k*0 of an electrolyte and its peak dQ/dV reduction potential on graphite. What influences the electrolyte reduction kinetics is beyond the scope of this work, but we speculate that cyclic carbonate solvents that tightly bind lithium in its solvation shell do better????. This hypothesis is consistent with the poor performance of PC and the strong performance of VC and FEC.

We note that this mechanism is specific to the case of galvanostatic control. In controlled-potential settings like sweep voltammetry, lithiation and EC reduction do not compete for current, so high sweep rates concurrently promote both processes (linear sweep voltammetry results are presented in Figure S2). Galvanostatic control is uniquely suited for minimizing the irreversible capacity loss of the EC reduction reaction.

This model would predict that high currents, low temperatures, and high salt concentrations can suppress the first-cycle irreversibility, even for solvents that are assumed to have exceedingly large irreversible first-cycle capacity fade. Indeed, propylene carbonate has been reported to have a minimal first-cycle irreversibility at high salt concentrations28,29 and high currents31. Additionally, the beneficial role of common electrolyte additives like vinylene carbonate (VC) and fluoroethyelene carbonate (FEC) appears to be their suppression of irreversible capacity loss, not the properties of their reduction products (at least for the first-cycle reduction reaction; their reduction products at lower potentials may be beneficial). Thus, EC-free electrolytes[] could be enabled by a combination of high currents, low temperatures, and additives during formation.

**Conclusions**

In this work, we present systematic studies of the EC reduction reaction during the first lithiation of carbon black. We first compare the first few cycles of graphite and carbon black; the first-cycle reaction is truly confined to the first lithiation, making it a distinct reaction from subsequent-cycle SEI growth. We then perform a simple electrochemical experiment to demonstrate that while the first-cycle reaction leads to major irreversible capacity loss and consumes time, its products provide no additional passivation benefit (as measured by second-cycle Coulombic efficiency). We also quantify the electrochemical parameters of this reaction. Finally, we demonstrate how the irreversible capacity loss of the first cycle reaction decreases with low temperature and high salt concentration; low temperature appears to be an especially large knob.

These results provide a promising pathway towards optimizing formation cycling in commercial lithium-ion batteries—that is, reducing the time, first-cycle losses, and subsequent-cycle losses. An optimized formation process balances time, irreversible capacity loss, and passivation ability, and this paper illustrates and quantifies the tradeoffs between these parameters in a model system. While our model system differs substantially from a commercial cell, we expect that the principles outlined in this work should generalize to any cell with a graphite negative electrode and ethylene carbonate cosolvent. Developing relationships between these properties for commercially relevant negative electrodes and electrolytes holds promise for improving the energy density, lifetime, and cost of lithium-ion batteries.

Further optimization of the low-potential step can likely lead to additional improvements.

Wetting

**Acknowledgements**

This work is sponsored by the Ford-Stanford Alliance. P.M.A. is supported by the Thomas V. Jones Stanford Graduate Fellowship and the National Science Foundation Graduate Research Fellowship under grant No. DGE-114747. We thank \_\_ for insightful discussions.

**References**

1. V. A. Agubra and J. W. Fergus, *J. Power Sources*, **268**, 153–162 (2014).

2. D. L. Wood, J. Li, and C. Daniel, *J. Power Sources*, **275**, 234–242 (2015).

3. S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, and D. L. Wood, *Carbon*, **105**, 52–76 (2016).

4. D. L. Wood, J. Li, and S. J. An, *Joule*, **3**, 2884–2888 (2019).

5. S. J. An, J. Li, Z. Du, C. Daniel, and D. L. Wood, *J. Power Sources*, **342**, 846–852 (2017).

6. V. Müller, R. Kaiser, S. Poller, D. Sauerteig, R. Schwarz, M. Wenger, V. R. H. Lorentz, and M. März, *J. Energy Storage*, **14**, 56–61 (2017).

7. V. Müller, R. Kaiser, S. Poller, and D. Sauerteig, *J. Energy Storage*, **15**, 256–265 (2018).

8. C. Mao, S. J. An, H. M. Meyer, J. Li, M. Wood, R. E. Ruther, and D. L. Wood, *J. Power Sources*, **402**, 107–115 (2018).

9. J. P. Olivier and M. Winter, *J. Power Sources*, **97–98**, 151–155 (2001).

10. T. Placke, V. Siozios, R. Schmitz, S. F. Lux, P. Bieker, C. Colle, H.-W. Meyer, S. Passerini, and M. Winter, *J. Power Sources*, **200**, 83–91 (2012).

11. T. Placke, V. Siozios, S. Rothermel, P. Meister, C. Colle, and M. Winter, *Z. Für Phys. Chem.*, **229**, 1451–1469 (2015).

12. G. V. Zhuang, K. Xu, H. Yang, T. R. Jow, and P. N. Ross, *J. Phys. Chem. B*, **109**, 17567–17573 (2005).

13. M. Nie, D. Chalasani, D. P. Abraham, Y. Chen, A. Bose, and B. L. Lucht, *J. Phys. Chem. C*, **117**, 1257–1267 (2013).

14. L. Wang, A. Menakath, F. Han, Y. Wang, P. Y. Zavalij, K. J. Gaskell, O. Borodin, D. Iuga, S. P. Brown, C. Wang, K. Xu, and B. W. Eichhorn, *Nat. Chem.*, 1–8 (2019).

15. A. K. Sleigh and U. von Sacken, *Solid State Ion.*, **57**, 99–102 (1992).

16. K. Takei, N. Terada, K. Kumai, T. Iwahori, T. Uwai, and T. Miura, *J. Power Sources*, **55**, 191–195 (1995).

17. R. Yazami and M. Deschamps, *J. Power Sources*, **54**, 411–415 (1995).

18. L. Fransson, T. Eriksson, K. Edström, T. Gustafsson, and J. O. Thomas, *J. Power Sources*, **101**, 1–9 (2001).

19. A. J. Smith, J. C. Burns, X. Zhao, D. Xiong, and J. R. Dahn, *J. Electrochem. Soc.*, **158**, A447–A452 (2011).

20. A. L. Michan, M. Leskes, and C. P. Grey, *Chem. Mater.*, **28**, 385–398 (2016).

21. K. A. See, M. A. Lumley, G. D. Stucky, C. P. Grey, and R. Seshadri, *J. Electrochem. Soc.*, **164**, A327–A333 (2017).

22. P. M. Attia, S. Das, S. J. Harris, M. Z. Bazant, and W. C. Chueh, *J. Electrochem. Soc.*, **166**, E97–E106 (2019).

23. S. Das, P. M. Attia, W. C. Chueh, and M. Z. Bazant, *J. Electrochem. Soc.*, **166**, E107–E118 (2019).

24. J.-B. Donnet, R. C. Bansal, and M.-J. Wang, Eds., *Carbon black: Science and Technology*, 2nd ed., Dekker, New York, (1993).

25. K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, Wiley, New York, (1988).

26. J. O. Besenhard, M. Winter, J. Yang, and W. Biberacher, *J. Power Sources*, **54**, 228–231 (1995).

27. M. R. Wagner, J. H. Albering, K.-C. Moeller, J. O. Besenhard, and M. Winter, *Electrochem. Commun.*, **7**, 947–952 (2005).

28. S.-K. Jeong, M. Inaba, Y. Iriyama, T. Abe, and Z. Ogumi, *Electrochem. Solid-State Lett.*, **6**, A13–A15 (2003).

29. M. Nie, D. P. Abraham, D. M. Seo, Y. Chen, A. Bose, and B. L. Lucht, *J. Phys. Chem. C*, **117**, 25381–25389 (2013).

30. E. Peled, D. Golodnitsky, C. Menachem, and D. Bar‐Tow, *J. Electrochem. Soc.*, **145**, 3482–3486 (1998).

31. H.-Y. Song and S.-K. Jeong, *J. Anal. Methods Chem.*, **2018**, 1–5 (2018).

**Figures**

**Figure 1.** Comparison of the first five cycles for **(a)** graphite and **(b)** carbon black half cells cycling at C/10. Differential capacity (*dQ*/*dV*) is displayed in the insets. The first

**Figure 2.** Controlling the first cycle .

**Figure 3.** Comparison of the first few cycles for **(a)** graphite and **(b)** carbon black half cells cycling at C/10.

**Figure 4.** Linear sweep voltammetry (LSV) of the first lithiation of carbon black as a function of sweep rate. In LSV, the size of the EC reduction peak increases with sweep rate; in contrast, the size of the EC reduction peak decreases with C rate in galvanostatic experiments (Figure 2a).

**Figure 4.** Additional dependencies of the EC-reduction reaction. Voltage vs. capacity is displayed for five values of **(a)** temperature and **(b)** salt concentration. All cells cycle at a nominal rate of C/10. Differential capacity (*dQ*/*dV*) is displayed in the insets. Both overpotential and irreversible capacity loss decrease with decreasing temperature and increasing salt concentration.

**Figure 6.** Schematic illustrating the competition between EC reduction and lithiation at a carbon edge plane.

(a) During the first lithiation, lithium ions solvated by EC co-intercalate into the edge plane. Under galvanostatic conditions, the reduction current is shared between lithiation and EC reduction. Lithiation is promoted over EC reduction with high currents, low temperatures, and low i0 (controlled by the properties of the electrode and electrolyte).

(b) On subsequent lithiations, the SEI formed at low graphite potential blocks solvent co-intercalation.