Electrochemical stiffness in lithium-ion batteries

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Graphite-Lithium Intercalation Compounds (G-LICs)

Lithium intercalation into graphite occurs through the formation of several distinct phases, called graphite-lithium intercalation compounds (G-LICs).1,2 A total of six G-LICs with increasing lithium content form: dilute stage I (LiCx, x>24), stage IV (LiC24), stage III (LiC18), dilute stage II (LiC18), stage II (LiC12), and stage I (LiC6). The roman numerals in the nomenclature of the intercalation compounds refer to the number of graphitic layers associated with each layer of intercalated lithium. In fully-intercalated layers, there is one lithium atom associated with six carbon atoms while in dilute stages (marked by a capital “D”), there is less than one lithium atom per six carbon atoms.

The preference for forming staged compounds instead of randomly organized compounds is due to a combination of attractive intraplanar interactions among the intercalated atoms and repulsive interplanar interactions between layers of intercalant.3 The widely accepted model describing the mechanism of transitioning between intercalation compounds is the Daumas-Héroid intercalant-island model.4 The model proposes that microscopic islands of intercalant form, leading to in-plane local domains of staged behavior. Neighboring domains are similarly staged, but within
different graphite galleries. Transitions between different stages of intercalation compounds occur by sliding of intercalant islands within a gallery, along with the insertion of more intercalant (to increase the total intercalant concentration associated with the new stage).

During cyclic voltammetry, transitions between G-LICs are manifested as peaks in the current response; during galvanostatic cycling, transitions are manifested as voltage plateaus or equivalently as peaks in the derivative of capacity with respect to voltage. By using x-ray diffraction, Dahn et al. associated specific phase transitions with features of the graphite electrochemistry.\textsuperscript{1,2} By comparing features in the electrochemistry data in this work with the results from Dahn et al., the voltages corresponding to transitions between G-LICs in this work are identified. These values are tabulated in Table S1 and are represented graphically by colored regions in figures throughout this work.

**Table S1.** Voltage values associated with specific phase transitions between graphite-lithium intercalation compounds (G-LICs) during the cathodic / lithiation portion of the cycle.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Galvanostatic Cycling\textsuperscript{#} (C/80, C/800)</th>
<th>Cyclic Voltammetry\textsuperscript{†} (25 µV s\textsuperscript{-1})</th>
<th>Galvanostatic Cycling\textsuperscript{†} (C/5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI (\rightarrow) IV</td>
<td>0.20</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>III (\rightarrow) DII</td>
<td>0.13</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DII (\rightarrow) II</td>
<td>0.11</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>II (\rightarrow) I</td>
<td>0.06</td>
<td>0.02</td>
<td>0.06</td>
</tr>
</tbody>
</table>

\textsuperscript{#}Dahn et al.;\textsuperscript{1,2} \textsuperscript{†}This work.

No features were able to be identified for the III \(\rightarrow\) DII transition in this work.
Anodic Sweep during Cyclic Voltammetry

The cathodic sweep of the third cycle CV of a graphite composite electrode at a scan rate of 25 µV s⁻¹ (Fig. 2) is discussed in the main text. Here, the corresponding anodic sweep is discussed. The features observed during the anodic sweep between 0.01 V and 0.30 V correspond to phase transitions between graphite-lithium intercalation compounds (G-LICs) as lithium is removed from the graphite electrode. The small anodic current present in the higher voltage region (ca. 0.3 V – 0.9 V) is indicative of side-reactions that occur at the exposed silicon substrate edge of the cantilever (see section “Electrochemical Cycling” in the SI).

During the anodic sweep, the compressive stress developed during the cathodic sweep is first relieved, reaches a local minimum at ca. 0.2 V, and then slowly decays to the original value at the start of the cycle. The overshoot of the stress relaxation at 0.2 V is hypothesized to result from non-uniform delithiation of the graphite film across the film thickness as its magnitude is scan rate dependent (Fig. 5c in the main text). Expansive strain continues to develop until ca. 0.05 V during the anodic sweep while the current remains negative and the graphite is still being lithiated. At higher potentials, contraction is observed as delithiation of the graphite anode occurs. The rate of contraction decreases substantially at ca. 0.24 V, following the de-intercalation of the main intercalation compounds. Because the overshoot at ca. 0.2 V dominates the stress response of the electrode during the anodic sweep, we focus our discussion in the main text on the cathodic portion of the cyclic voltammetry.
Capacity-Dependent Mechanical Response

During cyclic voltammetry, the instantaneous rate of lithiation is potential-dependent and therefore changes throughout one cycle. Since the stress and strain responses were found to be rate-dependent, we cycled electrodes galvanostatically (at constant lithiation / delithiation rate). The fifth cycle of galvanostatic cycling of the graphite anode at C/5 rate is shown in Fig. S1a, with the corresponding stress response of a constrained electrode (Fig. S1b), and strain response of an unconstrained electrode (Fig. S1c). The independent stress and strain values are coordinated at each capacity value and plotted in Fig. S1d. The capacity-dependent stiffness, $k_Q$, calculated as the slope of the stress vs. strain curve (Eqn. 1 in the main text), is reported in Fig. S1e.

In the initial stages of lithiation, up to ca. 40 mA h g$^{-1}$ (corresponding to voltages above ca. 0.2 V), the capacity is attributed primarily to lithiation of disordered carbon black and early lithiation of graphite. Similar to the high-voltage region (ca. 0.3 – 1.0 V) probed during cyclic voltammetry, these early lithiation events result in an immediate stress development with minimal corresponding strain development. The lagging strain gives rise to an initially stiff response followed by a reduction in stiffness at the beginning of the cycle (Fig. S1e). This behavior is again traced to stress generated during the initiation of lithiation followed by electrode expansion as a significant number of lithium ions are intercalated. As the capacity is further increased, distinct voltage plateaus corresponding to the transitions between different stages of intercalation compounds are observed$^{1,2,5}$. The rate of stress and strain accumulation varies, leading to oscillations in the capacity-dependent stiffness, with peaks at ca. 150 mA h g$^{-1}$ and at ca. 250 mA h g$^{-1}$.

Though the oscillations of the capacity-dependent stiffness observed during galvanostatic cycling are similar to the oscillations of the potential-dependent stiffness observed during cyclic voltammetry, the peaks of the oscillations occur within different phase transitions. No modulation
is observed during galvanostatic cycling in the capacity-dependent stiffness prior to the dilute stage I to stage IV transition or within the stage IV to stage III to dilute stage II transition region. We believe that the faster rate of lithiation used during galvanostatic cycling (compared to the effective lithiation rate during cyclic voltammetry at 25 uV s\(^{-1}\) in the corresponding regions) did not allow sufficient time for the these stages to fully develop. Hence the transitions between these stages were blurred, and no stiffness oscillations were observed. On the other hand, a peak is observed within the stage II to stage I transition during galvanostatic cycling, while a corresponding peak is not observed during cyclic voltammetry. We believe that here, the faster effective lithiation rate during cyclic voltammetry in this region did not allow for full development of the stage II or stage I compounds. In both galvanostatic cycling and cyclic voltammetry, a peak in the electrochemically-induced stiffness is observed during the dilute stage II to stage II transition, where the effective rates of lithiation are similar between the two tests.

These results indicate that stiffness variations caused by transitions between different graphite-lithium intercalation compounds can be masked when the cycling rate is too fast and multiple phases of intercalation compounds co-exist. To control the time allowed for different phase transitions, cyclic voltammetry is a more suitable tool for probing the effects of low-lithium content intercalation compounds, and galvanostatic cycling is more appropriate for probing the effects of high-lithium content compounds.
Figure S1. Capacity-dependent electrode response during galvanostatic (GS) cycling. (a) Fifth cycle of GS cycling at C/5 rate (from strain experiment) with corresponding (b) stress and (c) strain measurements of a graphite anode. (d) The stress and strain responses, coordinated at each capacity value. The dashed lines represent contours of constant capacity in increments of 20 mA h g\(^{-1}\). (e) Capacity-dependent stiffness variations of the electrode during the lithiation portion of the cycle. The y-axis is normalized with respect to the stiffness value at the beginning of the cycle. Absolute values of the stiffness are presented in section “Absolute Values of Electrochemical Stiffness” in the SI. In (a,e), the colored regions correspond to phase transitions between graphite-lithium intercalation compounds (G-LICs): ① = formation of dilute stage I, ② = dilute stage I to stage IV, ③ = stage IV to stage III to dilute stage II, ④ = dilute stage II to stage II, and ⑤ = stage II to stage I.
Absolute Magnitude of Electrode Stiffness

Fig. S2a presents two independent data sets for the normalized potential-dependent stiffness of graphite electrodes during cyclic voltammetry (CV), and Fig. S2b presents two independent data sets for the normalized capacity-dependent stiffness during galvanostatic cycling (GS). Though the absolute magnitude of the stiffness varied between different tests (Table S2), the potential-dependent and capacity-dependent trends of the electrochemical stiffnesses were repeatable.

![Diagram of potential-dependent stiffness](a) ![Diagram of capacity-dependent stiffness](b)

Figure S2. Comparison of electrochemical stiffness variations of multiple experiments. (a) Two independent data sets of the normalized potential-dependent stiffness of graphite electrodes during the third cycle of cyclic voltammetry at 25 µV s⁻¹. (b) Two independent data sets of the capacity-dependent stiffness of graphite electrodes during the fifth cycle of galvanostatic cycling at C/5 rate.

Table S2. Electrochemical stiffness values at the beginning of the third cycle of CV and fifth cycle of GS cycling.

<table>
<thead>
<tr>
<th></th>
<th>Potential-Dependent Stiffness, k_E</th>
<th>Capacity-Dependent Stiffness, k_Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Set 1 (Fig. 3b)</td>
<td>9.4 GPa</td>
<td>1.8 GPa</td>
</tr>
<tr>
<td>Data Set 2</td>
<td>2.6 GPa</td>
<td>2.6 GPa</td>
</tr>
</tbody>
</table>
Electrode Fabrication and Electrochemical Cycling

Graphite composite electrodes for both strain and stress measurements were fabricated in house. First, carboxymethyl cellulose (CMC, average $M_W \sim 700,000$, DOS 0.8-0.95, Sigma-Aldrich) was dissolved in water, in either a 1:100 wt. ratio of CMC to water (for electrodes for strain measurements) or in a 2:100 wt. ratio (for electrodes for stress measurements). Next, graphite ($< 20 \, \mu m$, Sigma Aldrich) and carbon black (CB, 100 % compressed, 99.9+ % pure, Alfa Aesar) were added to the CMC solution, and the suspension was mixed using a homogenizer (Model 15007ST, Omni) at approximately 7,500 RPM for 1 hour. The resulting electrode slurry was immediately spread onto a substrate using a doctor blade to control the slurry thickness, and the water was allowed to evaporate under ambient conditions. The final electrode composition was 80 wt.% graphite, 10 wt.% carbon black, and 10 wt.% CMC.

Electrodes for stress measurements were fabricated on the unpolished side of a silicon wafer (University Wafers, (100) orientation, 250 um thick), which had previously been cleaned with acetone. The silicon wafer had a 200 nm thick thermally-grown oxide layer that electrically isolated the wafer. The graphite layer was approximately 10 µm thick (Fig. S3b), and the wafer was cut into $5 \times 25$ mm rectangular pieces. Typical graphite loading was approximately 2 mg. Cutting the wafer into cantilever beams exposed unpassivated silicon at the edges of the cantilever. Side reactions occurring at the exposed silicon during cycling were evident during the anodic sweep of CV (Fig. S5a) and the delithiation portion of GS cycling (Fig. S6a). These side reactions were not present when the graphite electrode was cycled on a glass substrate, as shown in Fig. S4. We therefore limited our analysis to the cathodic sweep of CV and the lithiation portion of galvanostatic cycling only, where no side reactions from the silicon substrate were observed.

Electrodes for strain measurements were fabricated on a copper foil substrate (10 µm thick, 99.99 %, MTI), which had previously been cleaned with acetone and ethanol. After the electrode
was dry, it was carefully peeled off of the copper substrate, creating a free-standing electrode 90-100 µm thick (Fig. S3d). The electrode was cut into 3 × 7 mm rectangular pieces. Typical graphite loading was 1.2 – 2.0 mg.

Composite graphite working electrodes were cycled against a lithium metal counter electrode (0.75 mm thick, 99.9 %, Alfa Aesar) in a carbonate-based electrolyte (1M LiClO₄ (battery grade, dry, 99.99 %, Sigma Aldrich) in a 1:3 vol. ratio mixture of ethylene carbonate (EC, anhydrous, 99 %, Sigma Aldrich) and dimethyl carbonate (DMC, anhydrous, > 99 %, Sigma Aldrich)). The custom battery cells (Fig. S3a,c) were assembled and sealed in an argon atmosphere prior to measurements.

Cyclic voltammetry (CV) was performed at scan rates of 10 µV s⁻¹ (1.00 – 0.01 V vs Li⁺/0), 25 µV s⁻¹ (1.00 – 0.01 V vs Li⁺/0), and 100 µV s⁻¹ (1.50 – 0.01 V vs Li⁺/0) for three cycles. As each cycle at the scan rate of 25 µV s⁻¹ took 22.2 hours to complete, bleaching of the fluorescent particles utilized during the strain measurements prevented longer cycling. Galvanostatic measurements (GS) were performed at C/5 rate, between 2 V and 0.01 V vs Li⁺/0, for five cycles. The C-rate normalizes the current used to cycle a battery based on the mass, \( m \) (g), and the theoretical specific capacity, \( Q_{\text{theor}} \) (A h g⁻¹), of the active material in the working electrode. For a C-rate of C/X, the working electrode should fully lithiate in X hours with a current, \( I \) (A), defined by \( I = Q_{\text{theor}}m/X \).

For the strain experiment, an 11 min constant voltage hold was performed at the end of each constant current step during galvanostatic cycling. The purpose of the constant voltage hold was to enable image capture of the fully lithiated electrode and the fully delithiated electrode for strain analysis. The corresponding stress experiment omitted the constant voltage hold. Electrochemistry utilized an Arbin potentiostat / galvanostat for the strain measurements, and a CHI 760D instrument for stress measurements.
Figure S3. Custom battery cells for \textit{in situ} stress and strain measurements. (a) Front view of custom battery cell and (b) scanning electron micrograph of the graphite composite electrode on a silicon wafer substrate used in the stress experiment. (c) Front view of custom battery cell and (d) scanning electron micrograph of the free-standing composite graphite electrode used in the strain experiment.
Figure S4. Effect of substrate material on electrochemical measurements. Current response during cyclic voltammetry at 100 μV s⁻¹ of a graphite composite electrode on (a) a silicon substrate or (b) a glass substrate, cycled in the custom battery cell used for the stress measurements.
Synchronization of Stress and Strain Data: Cyclic Voltammetry

A comparison between the current response in the stress experiment and the current response in the strain experiment during cyclic voltammetry at 25 µV s⁻¹ is presented in Fig. S5. A larger voltage hysteresis between the cathodic and anodic sweeps in conjunction with less distinct peaks in the current response from the strain experiment are possibly indicative of greater heterogeneity and/or geometric differences in the electrode used for the strain experiment compared to that used for the stress experiment. To account for differences in the electrochemical responses, the solution resistance of both cells was estimated using electrochemical impedance spectroscopy (EIS). A copper foil working electrode was used in place of the graphite composite electrode to isolate the solution resistance from electrical resistance of the graphite electrode. EIS was performed on a Biologic potentiostat between 675 kHz and 0.5 Hz frequencies. The solution resistance, taken as the real part of the measured impedance when the imaginary part of the impedance was zero, was determined to be 26 Ohm for the stress experiment cell and 57 Ohm for the strain experiment cell. The corrected voltage, $E$, was then calculated according to $E = E_{org} - I\Omega$, where $I$ is the measured current during CV, $\Omega$ is the solution resistance measured in EIS, and $E_{org}$ is the original, uncorrected voltage. The stress and strain data from the two independent experiments were then correlated using the corrected voltage.
Figure S5. Comparison of electrochemical behavior during cyclic voltammetry (CV). Current response of a graphite composite electrode cycled in the custom battery cell used for (a) the stress experiments or (b) the strain experiments, during the third cycle of CV at 25 µV s⁻¹.
**Synchronization of Stress and Strain Data: Galvanostatic Cycling**

A comparison of the voltage response in the stress experiment and the voltage response in the strain experiment during galvanostatic cycling at C/5 rate is presented in Fig. S6. The electrochemical response during lithiation is remarkably similar between the two independent experiments, as exemplified by the distinct voltage plateaus. The high voltage observed during delithiation (ca. 0.6-0.8 V vs Li⁺⁻) in the stress experiment is similar to the anodic current developed during CV at ca. 0.3 – 0.9 V (Fig. S5a), and is attributed to side reactions occurring at the exposed silicon wafer edge. An accurate measure of the mass of the electrode in the stress experiment could not be obtained; therefore, to synchronize the two experiments, we assumed the electrodes in each experiment achieved the same specific capacity at the end of the lithiation portion of the cycle, and scaled the capacity from the stress experiment accordingly. Stress and strain experiments were then correlated through the corresponding capacity values.
Figure S6. Comparison of electrochemical behavior during galvanostatic (GS) cycling.

Voltage response of a graphite composite electrode cycled in custom battery cells used for (a) the stress experiment or (b) the strain experiment, during the fifth cycle of GS cycling at C/5 rate.
References


