Lithium ion batteries are a popular choice for energy storage due to their high ratio of energy capacity to size and their low rate of self-discharge.1 Unfortunately, batteries are difficult to characterize to their high ratio of energy capacity to size and their low rate of discharge.1 A few studies have postulated that d2ε/dQ2, as strain,

\[
\frac{d^2\varepsilon}{dQ^2},
\]

is mathematically proportional to dV/dQ within an electrode stage. We also experimentally quantify peaks in the strain curves for electrode stage transitions at practical charge rates of up to C/2 and confirm that transitions are visible in the practical scenario of discharging at the higher rate of 1C. Moreover, the location of the transition measured by d2ε/dQ2 changes by less than 10% from 0.05 C to 0.5 C, but the transition measured with dV/dQ decreases by more than 15% from 0.05 C to 0.3 C, demonstrating the reliability of strain to measure electrode transitions at moderate charge rates. We also note that d2ε/dQ2 exhibits similar peak shifts as those expected in dV/dQ as the cell ages. Our derivations for the model system of graphite and lithium cobalt oxide can be generalized to other battery systems and used to characterize materials at practical charge rates impossible with only voltage.

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Article:
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During battery use, electrode materials are known to expand and contract in repeatable patterns, and this strain has been previously correlated with battery properties such as state of charge and state of health. In this study, we show that the second derivative of strain, d2ε/dQ2, is mathematically proportional to dV/dQ within an electrode stage. We also experimentally quantify peaks in the strain curves for electrode stage transitions at practical charge rates of up to C/2 and confirm that transitions are visible in the practical scenario of discharging at the higher rate of 1C. Moreover, the location of the transition measured by d2ε/dQ2 changes by less than 10% from 0.05 C to 0.5 C, but the transition measured with dV/dQ decreases by more than 15% from 0.05 C to 0.3 C, demonstrating the reliability of strain to measure electrode transitions at moderate charge rates. We also note that d2ε/dQ2 exhibits similar peak shifts as those expected in dV/dQ as the cell ages. Our derivations for the model system of graphite and lithium cobalt oxide can be generalized to other battery systems and used to characterize materials at practical charge rates impossible with only voltage.

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Experimental

We used commercial pouch cells with 500 mAh nominal capacity (used for calculating C-rates) and nominal dimensions of 25 mm by 35 mm by 6.5 mm. The active materials in the cells are lithium cobalt oxide and graphite, and LiPF6 is the electrolyte in organic solvent. One charge/discharge cycle of a battery consists of a constant current charge step to 4.2 V, a constant voltage charge step until the current decays below a C/20 rate, a rest step for one hour, a constant current discharge step to 2.7 V, then a final rest step of at least an hour. For the high-rate test, we used a commercial pouch cell designed to be charged at 1 C with 2000 mAh nominal capacity and nominal dimensions of 50 mm by 60 mm by 5.8 mm. The active materials in these cells are lithium cobalt oxide and graphite, and LiPF6 is the electrolyte in organic solvent.

The dilatometer setup described in Figure 1 is used to perform all mechanical measurements in this study. The LVDT sensor moves d2ε/dQ2 and dV/dQ are mathematically proportional within an electrode stage. In addition, we demonstrate that strain is a more consistent and reliable tool for determining electrode stage transitions at practical C-rates, quantifying transitions in d2ε/dQ2 and dV/dQ up to C/2 and indicating distinct, albeit more difficult to quantify, transitions in d2ε/dQ2 at higher rates.

Figure 1. A schematic of the dilatometer used in this experiment. The battery is placed under an LVDT sensor to measure expansion and the entire setup is kept at 35°C.

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50 microns per 1 V measured, and the accuracy of the dilatometer is 0.2 microns. The entire setup is inside an oven at 35 °C to avoid temperature effects on both the battery and the setup. All results from the dilatometer are read using Arbin MITS Pro software with a potentiostat.

Analysis of the data is done with MATLAB. All derivatives are simply the quotient \( \frac{\Delta y}{\Delta x} \), and any functional fits were performed using the MATLAB fit function. We recorded data every 0.5 s from the LVDT and every 1 s from the battery. All results are filtered using MATLAB’s implementation of a Savitzky-Golay filter, a filter that essentially replaces every \( n \) data points with a least-squares line where \( n \) increases as the C-rate decreases to account for more data points per cycle.

Part of our analysis required converting from state of charge, or fraction maximum capacity, to \( x \) in Li\textsubscript{x}C\textsubscript{6} in order to compare against literature values. This conversion is a constant factor, specifically the fraction of the graphite capacity utilized in the battery compared to the maximum capacity available in the graphite. To calculate this fraction, we made coin cells of Li vs graphite and LCO vs graphite using 7/16″ diameter LCO and graphite electrodes harvested from the commercial batteries described above. The capacity of the LCO vs graphite coin cells was divided by the capacity of the Li vs graphite coin cells (representing the full lithiation of the graphite electrode) to produce a factor for converting from state of charge to extent of graphite lithiation in these particular batteries. This conversion relies on the assumption that \( x = 0 \) at SOC = 0 (2.7 V in our case). The calculation of this factor is given with the analysis below.

### Results and Discussion

**Slow rates: derivatives of strain compared to dV/dQ.** — In Figure 2, we show the strain from a single charge cycle (Figure 2a) to aid understanding of the expansion process. We then directly compare ds/dQ with dV/dQ (Figure 2b) for a battery charged at C/20. Previous work noted that ds/dQ and dV/dQ display features at similar states of charge, yet no studies have rigorously compared strain and voltage.\(^7,13\) When we visually inspect Figure 2b (displaying ds/dQ), we note that peaks in the dV/dQ curve align nicely with inflection points of ds/dQ (i.e. at the points between plateaus in the ds/dQ data). To quantify these points, we take a second derivative, and \( d^2s/dQ^2 \) is displayed in Figure 2c. A visual inspection of Figure 2c reveals that each peak in the dV/dQ curve has a corresponding peak in \( d^2s/dQ^2 \). Because the peaks in dV/dQ correspond to electrode stage transitions, we attribute the analogous peaks in \( d^2s/dQ^2 \) to electrode stage transitions. Specifically, we know that most of the peaks present in dV/dQ are due to the graphite electrode and hypothesize that the analogous peaks in \( d^2s/dQ^2 \) also represent graphite transitions because the graphite electrode has more stages and exhibits an order of magnitude larger expansion than LCO.\(^12,13\) The last peak in both the strain and voltage curves at around 0.46 Ah is a known exception and belongs to an LCO electrode transition.\(^5\)

While peaks in Figure 2c are visually clear, there are multiple options for quantifying them. A simple method of quantification is to record the state of charge at which the maximum of a transition peak occurs. Another method for quantifying transition peaks is through a standard Gaussian fit. Gaussian fits have the added advantage of providing a peak width and height, a more difficult value to measure by eye due to noise in the data. The center of the Gaussian fit has the same location as the maximum value in a transition peak, so these methods are interchangeable when only looking at the exact point a transition occurs. The peak positions, using either a maximum or the center of a Gaussian fit, are given in Table I along with literature values for graphite transitions.\(^18\) The transition numbering corresponds to the graphite stage following the transitions according to Reference 17 and select transitions are indicated in Figure 2. All values in Table I are for \( x \) in Li\textsubscript{x}C\textsubscript{6} for best comparison to literature and generality. Conversion from state of charge (the units of Figure 2) to \( x \) is done by

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**Figure 2.** Strain (\( \varepsilon \)) from a single charge cycle (a), direct comparison of ds/dQ and dV/dQ (b), and d\(^2\)s/dQ\(^2\) and dV/dQ (c) for a commercial battery cycling at C/20. Select transitions are labeled and the similarity between the d\(^2\)s/dQ\(^2\) and dV/dQ peaks is visually apparent.
multiplying the capacity by the maximum fraction of graphite lithiated in the batteries, using \( x = 0 \) at SOC = 0 (2.7 V). This fraction was determined by making coin cells of graphite vs Li and graphite vs LCO using electrodes from a commercial battery and comparing the capacities (2.90 ± 0.09 mAh and 2.60 ± 0.08 mAh, respectively). The conversion factor is then 0.90 ± 0.04, a reasonable value that makes sense because batteries often have some excess capacity.

In Table I, the peaks in the expansion, voltage, and literature transitions align, supporting our proposed relationship between \( d^2v/dQ^2 \) and \( dv/dQ \). Small discrepancies between literature values and our experimental results are expected, especially in the region below \( x = 0.3 \), where the transitions are much less clearly defined. In this region, there are dilute graphite phases and a potential LCO phase transition, and identifying exact phases in the graphite and LCO is beyond the scope of this paper. In Figure 2, the peak representing transition 2 in the voltage data is more a plateau than a peak. To quantify this transition in Table I, we used the center of the plateau (which was a very slight peak). In the data above, transition 2 (occurring at the lowest state of charge) is not present in the voltage data but is clear in the expansion data. This transition is a known graphite transition, and the fact that it appears in the strain data but not in the voltage is a benefit to characterizing electrodes with strain and could add to previous studies of SEI formation on graphite at low voltages.\(^{10} \)

One trend in the comparison of \( dv/dQ \) and \( d^2v/dQ^2 \) is that the strain peaks consistently occur at slightly higher states of charge than the voltage peaks during battery charging.

The most important peaks used in this paper and in most analyses of batteries are the last two transitions (1 and 2 in Table I and Figure 2). These transitions have the most severe effect on the rate of expansion due to the differences in the graphite-lithium intercalation lattice height for relevant graphite phases.\(^2,22,23 \)

The rest of the peaks in the voltage and strain data are important only because they are visible with both voltage and strain. Notably, there is no clearly defined peak for the transition from stage 3 to stage 2 in the voltage data (transition 2 in Table I). Often, all of the smaller peaks in this region are lumped together as one peak or the trailing edge of this conglomerate of peaks is used to represent this transition since most analyses of graphite phases in batteries only focus on the large regions defined by transitions 2 and 1 and do not worry about the nuances in transitions before 2.\(^3,4 \)

With C/20 charging, we demonstrate the clear analogy between strain (specifically \( d^2v/dQ^2 \)) and voltage (\( dv/dQ \)). Moreover, the peaks present in Figure 2c for \( d^2v/dQ^2 \) are arguably better defined than the peaks in the \( dv/dQ \) curves. In the Theoretical analysis section, we justify this relationship between strain and voltage with a brief theoretical rationale based on fundamental chemistry.

**Faster rates: practical advantages of strain.**—While strain derivatives may contain the same data as voltage derivatives, there is a barrier to using strain instead of voltage because it requires an additional apparatus to collect the required data. However, we propose that strain is a more practical tool than voltage because it retains usable information on electrode stage transitions at higher C-rates. Traditionally, to produce reliable voltage derivatives, batteries must be cycled at slow C-rates. Most reported uses of \( dv/dQ \) use rates of C/10 or below.\(^7,26 \)

These rates are impractical and unrealistic for real world applications. In Figure 3, \( ds/dQ \), \( d^2s/dQ^2 \) and \( dv/dQ \) are displayed at varying charge rates from C/20 to C/2. We demonstrate that strain can be used to determine transitions at higher charge rates than possible with voltage. In particular, transition 1 (as indicated in Table I) is extremely difficult to clearly determine with \( dv/dQ \) but is quantifiable with strain. Although we focus on the effectiveness of strain up to C/2 in this work, strain can produce reliable data at rates higher than C/2, discussed further below.

In Figure 3a, transitions 1 and 2 are distinct steps in the \( ds/dQ \) curve at C/20, but the transitions become slopes as the C-rate increases, giving the curve a bowl-like shape. In Figure 3b, there is a distinct peak in the \( d^2s/dQ^2 \) data at C/20 for transition 1. As charge rate decreases, this peak smooths out to a wide Gaussian, mirroring the increased curvature found in Figure 3b. Despite a wider and shorter Gaussian, the Gaussian is always discernable. In Figure 3c, transition 1 is clearly visible at C/20, but by C/4 it is difficult to quantify, and the peak is nonexistent at C/2. This is likely due to the relatively small difference in voltage before and after the transition. When the transition occurs rapidly, \( dv/dQ \) has a smaller magnitude and is spread out over a longer period of time, making a transition peak difficult to pinpoint. The peaks in the \( dv/dQ \) curve for the transitions at lower states of charge than transition 2 merge with transition 2 into one peak at higher rates. In the strain data (Figure 3b), the peak for transition 2 remains distinct at C/2, and the lower transitions combine from three distinct peaks at C/20 into two peaks at C/2. Referencing Table I, the peaks for transition 3a and 3b are the ones that combine.

Using our setup, we show the transitions in the strain plots at charge rates up to C/2. However, a more realistic scenario would involve higher charge rates. We therefore use a battery designed to be discharged at rates of up to 1 C to demonstrate the applicability of strain to higher rates. In Figure 4, \( dv/dQ \) and \( d^2s/dQ^2 \) are displayed at a discharge of 1 C. The high-rate cell is necessary at 1 C because batteries that are not built to charge at higher rates will exhibit lithium plating and other phenomena at 1 C that would interfere with our expansion measurements. Figure 4a shows the lack of peaks in the \( dv/dQ \) curve at 1 C, and Figure 4b demonstrates how the strain transitions are apparent during discharge and in a practical scenario, although an in-depth study or higher charge rates and discharge curves is beyond the scope of this paper. Specifically, the peaks for the transition from stage 1 to 2 and from stage 2 to 3b are visible in Figure 4b (the equivalent discharge transitions 1 and 2, respectively, from Table I). Overall, the transitions are still clear in the strain data in the practical situation of discharging at 1 C and possibly at even higher rates while the transitions are undetectable in the voltage data.

While Figure 3 visualizes how charge rate affects voltage and strain, in Figure 5, parameters from a Gaussian fit for transition 1 in the \( d^2s/dQ^2 \) are compared to the Gaussian parameters for this transition in the \( dv/dQ \) plot. In Figure 5a, the heights of the Gaussian fits are displayed for strain and voltage. At rates larger than 0.3 C, the peak in \( dv/dQ \) is indistinguishable from the noise and cannot be measured. However, although there is not a recognizable transition in the voltage data, there is a consistent Gaussian transition in the strain data. In Figure 5b, the position of the transition is displayed in the voltage and the strain data. At slower charging rates, the transition occurs at higher states of charge in both voltage and strain. Additionally, the strain transition consistently occurs at higher states of charge than the voltage transition and is much less dependent on charge rate than voltage. The transition peak shifts more than 15% between 0.05 C and 0.3 C in the \( dv/dQ \) data but shifts less than 10% between 0.05 C and 0.5 C in the strain data. Overpotentials in this system could explain why the voltage transition appears at lower states of charge than the strain transition during charging because the overpotential should minimally impact the strain but can significantly affect the voltage. Overall, we conclusively show with Figures 3 and 5 that strain is a more practical tool than voltage for identifying stage transitions at higher rates.

### Table I. Comparison of graphite transition peaks in expansion data, voltage data, and literature.\(^{18} \)

<table>
<thead>
<tr>
<th>Transition</th>
<th>( x ) from Expansion*</th>
<th>( x ) from Voltage*</th>
<th>Graphite x</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.07 ± 0.01</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>0.17 ± 0.01</td>
<td>0.13 ± 0.01</td>
<td>0.12</td>
</tr>
<tr>
<td>3b</td>
<td>0.22 ± 0.01</td>
<td>0.20 ± 0.01</td>
<td>0.21</td>
</tr>
<tr>
<td>2</td>
<td>0.26 ± 0.02</td>
<td>0.24 ± 0.01</td>
<td>0.27</td>
</tr>
<tr>
<td>1</td>
<td>0.56 ± 0.03</td>
<td>0.54 ± 0.03</td>
<td>0.5</td>
</tr>
<tr>
<td>LCO</td>
<td>0.79 ± 0.04</td>
<td>0.76 ± 0.03</td>
<td>–</td>
</tr>
</tbody>
</table>

*All error is 1σ.
Figure 3. Comparison of $d\varepsilon/dQ$ (a), $d^2\varepsilon/dQ^2$ (b), and $dV/dQ$ (c) at charge rates up to C/2. Dashed lines in (b) and (c) indicate transition movement as charge rate changes. Note the vanishing peak as charge rate increases in the voltage data (c) while a distinct curvature remains present in the strain data (b).

Figure 4. Comparison of $dV/dQ$ (a) and $d^2\varepsilon/dQ^2$ (b) in the practical scenario of discharging at 1 C. There are no visible peaks in the voltage data but there are definite peaks at the major transitions in the strain data. The black line in the (b) marks the 0 point, and the transitions are labeled in (b).
Figure 5. Gaussian parameters for transition 1. The height of transition (a) and the position of the transition (b). The heights of the transition are in arbitrary units. Error bars represent 95% confidence on fit parameters. Note that the strain transition remains visible up to C/2 whereas the voltage transition does not. The voltage transition also shifts with charge rate significantly more than the strain transition.

Strain for aging.— As discussed previously, one of the primary uses for dV/dQ is to monitor and study cell aging. Essentially, the distance between peaks in a dV/dQ curve represents how much lithium is transferred during a given stage. As the cell ages, these peaks shift according to how much lithium is lost and how the lithium is lost (i.e. lithium lost to SEI formation results in different peak shifts than those from active material in electrodes being lost). Because strain curves clearly show stage boundaries, similar trends in the strain peaks as those found in voltage curves should be visible. An in-depth study of peak shifts and aging is beyond the scope of this paper, but a quick study to determine the feasibility of using peak shifts as a tool for measuring aging is possible. Cycling continuously at C/2 (possible with strain, but not with voltage), a single battery was cycled 50 times. In Figure 6, d²ε/dQ² is displayed for the first and fiftieth cycles. Cycle number 50 is offset vertically for visibility, and transitions 1 and 2 in the graphite as well as the LCO transition are marked. For cycle one, these transitions occur at 0.306 ± 0.006 Ah, 0.131 ± 0.006 Ah, and 0.463 ± 0.003 Ah, respectively (error represents confidence based on fit and neighboring cycles). For cycle 50, these transitions occur at 0.290 ± 0.002 Ah, 0.119 ± 0.004 Ah, and 0.452 ± 0.004 Ah, respectively. The first transition shifts left by 0.016 ± 0.006 Ah, the second transition shifts left by 0.012 ± 0.07 Ah, and the LCO transition shifts left by 0.011 ± 0.005 Ah. All the transitions shift by the same order of magnitude and are within error of each other.

Additionally, during this 50 cycle test, the battery lost 1.1% of its initial capacity. The shift left in all of the peaks is consistent with previous work, but a separate, longer study is necessary to conclusively propose a mechanism for capacity fade based on expansion peak shifts.4,5 This short aging study is a first step toward a full study investigating how strain data can be used to quantify aging behavior instead of voltage data. An equivalence between strain and voltage is expected since both strain and voltage indicate electrode transitions that are known to change due to various aging mechanisms.

Theoretical analysis.— We have empirically shown that at slow rates, d²ε/dQ² contains analogous peaks as those in dV/dQ that correspond to electrode staging. To explain this empirical observation and better understand why strain and voltage relate to each other and to electrode stages, we build a simple chemical model.

The lithiation and delithiation of electrodes can be modeled with a chemical equation. The delithiation of LCO is a prototypical example of a cathode delithiation.

\[ ν Li_1 CoO_2 \rightarrow ν Li_{1-\frac{1}{2}} CoO_2 + Li \quad [1] \]

For this reaction, the free energy of reaction is given in terms of the energy of formation for the product and reactants:

\[ ΔG_{rxn} = νΔG^f_{Li_1 CoO_2} \left( y - \frac{1}{2} \right) + ΔG^f_{Li} - νΔG^f_{Li_{1-\frac{1}{2}} CoO_2} \left( y \right) \quad [2] \]

Using Li metal as a reference state, \( ΔG^f_{Li} = 0 \), the above equation simplifies to:

\[ ΔG_{rxn} = ΔG^f_{Li_{1-\frac{1}{2}} CoO_2} \left( y - \frac{1}{2} \right) - ΔG^f_{Li_{1-\frac{1}{2}} CoO_2} \left( y \right) \quad [3] \]
If $\Delta n$ moles of Li leave the LCO, where $\Delta n = \frac{1}{3} > 0$, then the instantaneous free energy of reaction is described by:

$$\Delta G^\text{LCO}_{\text{rxn}} = \lim_{\Delta n \to 0} \Delta G_{\text{rxn}} = -\frac{d}{dy} \left[ AG_{Li_xCoO_2}^f \right]$$  \[4\]

An analogous derivation for graphite as a model anode, using the following reaction to represent lithiation yields an expression for the free energy of reaction for graphite lithiation.

$$Li + \eta Li_xC_6 \rightarrow \eta Li_{x+\frac{1}{3}}C_6$$  \[5\]

$$\Delta G_{\text{rxn}}^\text{graphite} = \lim_{\Delta x \to 0} \Delta G_{\text{rxn}} = \lim_{x \to 0} \Delta G_{Li_xC_6} = -\frac{d}{dx} \left[ \Delta G_{Li_xC_6} \right]$$  \[6\]

The full reaction is simply the sum of the two half-reactions,

$$\Delta G_{\text{rxn}}^{\text{full}} = \frac{d}{dx} \left[ \Delta G_{Li_xC_6}^f \right] - \frac{d}{dy} \left[ \Delta G_{Li_xCoO_2}^f \right]$$  \[7\]

Equation 7 matches previous derivations from the literature. While this full cell equation is very general, in the case of a phase transition in the electrode material, the equation can be simplified. Because graphite is known to have multiple phase transitions (many of the stages referred to previously are in fact phase coexistence), it is used as an example. In the graphite electrode, a transition is made from phase $i$, occurring at $x = x_i$, to phase $j$, occurring at $x = x_j$. The lithiation of graphite now represents a phase transition from $x = x_i$ to $x = x_j$. The free energy of reaction then becomes a constant (derived by plugging in the previous bounds into a graphite equation analogous to Eq. 3).

$$\Delta G_{\text{rxn}} = \frac{d}{dx} \left[ \Delta G_{Li_xC_6}^f \right] = \frac{\Delta G_{Li_{x+i}C_6}^f - \Delta G_{Li_{x+j}C_6}^f}{x_j - x_i}$$  \[8\]

The free energy of formations for phase $i$ and phase $j$ are materials properties. Because each lithium atom contains a single charge, the cell voltage can be written as:

$$E_{cell} = -\frac{1}{F} \Delta G_{\text{rxn}} = -\frac{1}{F} \left\{ \frac{d}{dx} \left[ \Delta G_{Li_xC_6}^f \right] - \frac{d}{dy} \left[ \Delta G_{Li_xCoO_2}^f \right] \right\}$$  \[9\]

Should either electrode material be in a phase transition, the respective derivative can be replaced with the constant described in Equation 8 (analogous equation for LCO not shown).

Here we focus on the derivatives of material strain with respect to the extent of lithiation of graphite, $x$. Like the free energy of formation, materials also have lattice constants associated with different phases. Letting $\epsilon_i$ represent the lattice height of the $i$th phase (where $c_0$ is the initial lattice height corresponding to either fully lithiated or delithiated materials), the strain in a material in a single phase is given by:

$$\epsilon_i = \frac{c_i - c_0}{c_0}$$  \[10a\]

$$\frac{d\epsilon_i}{dx} = 0$$  \[10b\]

Should the material be in a phase transition between phases $i$ and $j$, assuming a first order phase transition and short diffusion lengths for lithium, the strain of the material will increase at a constant rate determined by the known lattice heights of the two bounding phases. Letting $\epsilon_{ij}$ represent the strain in going from phase $i$ to phase $j$, the strain is:

$$\epsilon_{ij} = \frac{c_{ij} - c_0}{c_0}$$  \[11a\]

$$\frac{d\epsilon_{ij}}{dx} = \frac{1}{c_0} \frac{d\epsilon_{ij}}{dx} = \frac{1}{c_0} \epsilon_{ij}$$  \[11b\]

Equation 11b can be combined with Equation 8 to yield the following expression for materials during a first order phase transition between phases $i$ and $j$.

$$\frac{\Delta G_{Li_xC_6}^f - \Delta G_{Li_{x+j}C_6}^f}{\epsilon_j - \epsilon_i} = \alpha_{i,j}$$  \[12\]

Where $\alpha_{i,j}$ is a constant for the phase transition $i$ to $j$. Equation 9 can then be simplified in the following manner:

$$E_{cell} = \frac{d}{dx} \left[ \alpha \epsilon_{Li_xC_6} \right] - \frac{d}{dy} \left[ \beta \epsilon_{Li_xCoO_2} \right]$$  \[13a\]

$$\beta$$ in Equation 13a is defined analogously to $\alpha$ (Equation 13b) but for the LCO.

Applying Eq. 13a to transition 1 (or any transition) in the graphite/LCO battery discussed above, 11a simplifies to Eq. 14.

$$E_{cell} \propto \frac{d}{dx} \left[ \epsilon_{Li_xC_6} \right] - \frac{d}{dy} \left[ \Delta G_{Li_xCoO_2}^f \right]$$  \[14\]

During phase coexistence, such as during most of the graphite stages, both voltage and $d\epsilon/dx$ are a combination of pseudo-step functions with different magnitude steps, but steps that occur at the same locations. Thus, a simple model for battery electrodes yields that voltage is proportional to $d\epsilon/dx$ (Equation 14) and $dV/dQ$ is proportional to $d^2\epsilon/dQ^2$ (Equation 15). This supports the empirical relationship we proposed in Figure 2c and supported throughout this study. The reason why strain has larger, better defined peaks than voltage is likely due to the difference in lattice heights being more significant than the difference in free energy of formations. The small differences in free energy of formations results in the $dV/dQ$ peaks becoming impossible to measure at higher charge rates (the step transition is a slow slope indistinguishable from the starting and ending plateaus) whereas the lattice height differences are large enough to produce a quantifiable peak even at faster rates. For example, transition 1 involves a step in equilibrium stage voltage from 120 mV to 85 mV in a graphite vs. Li system and a step in the lattice height from 0.353 nm to 0.37 nm, with an initial lattice height of 0.335 nm. Transition 1 then has a 29% decrease in voltage and a 49% increase in strain, showing that strain has almost twice as much change as voltage at this transition.

In Figure 7, the results of the above derivation, primarily Equations 14 and 15, are shown schematically for two transitions (similar to the graphite system described above). The expansion data is in red on top, with arrows indicating a derivative transformation between curves. The voltage data is in blue on the bottom, and the first derivative transformation is shown with an arrow. The proportionality between voltage and strain is highlighted by dashed vertical lines at peaks in the $dV/dQ$ and $d^2\epsilon/dQ^2$ schematics.

**Conclusions**

The application of mechanical strain to characterize and model batteries has the potential to help researchers predict and understand material evolution during battery operation. Here, we show that $d^2\epsilon/dQ^2$ identifies stage transitions in electrode materials at practical rates of
Figure 7. A schematic of derivatives to clarify derivation of relationship between $d^2\varepsilon/dQ^2$ and $dV/dQ$. The top three schematics are expansion (strain) derivatives (red) and the bottom two graphs are voltage derivatives (blue). Arrows indicate a derivative transformation between curves. The two transitions are schematically similar to a graphite system.

C/2, 1 C, and above, compared to $dV/dQ$ which only indicates reliable transitions at charge rates less than C/4. Additionally we demonstrate the consistency of transition locations in the strain data compared to voltage transitions which move quickly to lower states of charge as C-rate increases. Future studies can further explain some of the recurring differences between strain and voltage, such as why the strain transition peaks tend to follow the voltage ones, or develop models that use strain as a tool to predict and assess cell aging at faster rates. In this study, we use a model battery with graphite and LCO electrodes, but electrode staging applies to other electrodes as well. In theory this analysis can be generalized to other battery systems, but future work is necessary to verify this generalization, particularly with zero-strain materials. Because strain and voltage are intrinsically related and both are materials properties, the use of strain as a tool for characterizing battery materials has the potential to improve fundamental understanding of battery materials as well as aid in battery modeling and predictions.

References