Volume, Pressure and Thickness Evolution of Li-Ion Pouch Cells with Silicon-Composite Negative Electrodes

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In-situ volume, pressure and thickness measurements were performed on Li-ion pouch cells with various silicon-composite negative electrodes to quantify electrode volume expansion, Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2}/SiO-graphite, LiCoO_{2}/Si Alloy-graphite and Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2}/nano Si-C pouch cells were tested in this work. Archimedes-type in-situ volume measurements and in-situ thickness measurements showed cell expansion during charge and contraction during discharge due to electrode lithiation and de-lithiation. An in-situ pressure measurement was used to measure the effect of electrode volume expansion on volumetrically-constrained pouch cells. The volume expansion and contraction profiles measured exhibit a non-linear, asymmetric behavior as a function of cell state of charge for all cell types. To explain this, calculations of the volume expansion contribution of each electrode component were performed. Based on the results of the calculations, conclusions about the mechanisms contributing to the measured expansion profiles can be made.

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Silicon is an attractive negative electrode material for increasing the energy-density of lithium-ion cells due to its significantly higher specific and volumetric capacity than graphite (3579 mAh/g for silicon and 2194 Ah/L for Li_{1.1}Si_{3} vs. 372 mAh/g for graphite and 719 Ah/L for LiCoO_{2}). However, unlike graphite in which lithium intercalates in a structurally benign process, silicon alloys with lithium, significantly altering its structure resulting in a large volume expansion of 280%. Previous studies have shown how this volume expansion can be detrimental to electrodes by causing constituent particles to electrically disconnect from their current collectors, particles to fracture, and damage to the SEI—all of which result in large capacity fade. Confining silicon to nano-sized domains can reduce internal stress on particles to avoid fracture which can mitigate some of these effects. Efforts to reduce electrical disconnection of particles often involve making composites of Si-containing electrode materials with more volumetrically benign materials such as graphite. This effort aims to take advantage of the high capacity of silicon, while diminishing the overall volume expansion of the composite electrode material.

Composite Si-graphite electrodes will experience a volume expansion during silicon lithiation. Additionally, the graphite component—although to a much smaller extent—will experience a volume expansion, as it has been shown to expand by 10% during lithium insertion. Such volume changes have been observed with electrochemical dilatometry techniques for Si-graphite composite electrodes, and SiO electrodes. A full cell, with such a composite negative electrode paired with a positive electrode, will be affected by the volume change of the positive electrode as it charges and discharges. For example, LiCoO_{2} and Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2} positive electrodes have been shown to experience volume changes of a few percent during charge and discharge. Since the volume changes occurring at the negative electrode (made from graphite and a Si-containing material) are much larger, a full cell will experience a net volume expansion while charging. This is an important factor to consider for implementing such cells since commercial applications need to leave room to accommodate for volume expansion.

In this work, the swelling due to electrode volume expansion of Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2}/SiO-graphite, LiCoO_{2}/Silicon Alloy-graphite and Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2}/nano Si:Carbon composite pouch cells was measured with in-situ volume and thickness techniques. The effect of volume expansion on volumetrically-constrained pouch cells, simulating the conditions of hard-canned cylindrical cells, was measured with an in-situ pressure technique. The expansion profiles measured in this work are compared with calculations of predicted volume expansion of each electrode component. These calculations elucidate the measured volume expansion and contraction behavior.

Pouch cell preparation.—Pouch cells of three different electrode chemistries were tested in this work, which will be referred as Type A, B and C cells: (A) Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2} (NCA)/SiO-graphite (Supplier A), with a capacity of 260 mAh balanced for 4.2 V operation; (B) LiCoO_{2} (LCO)/Si Alloy-graphite (Supplier B), with a capacity of 230 mAh balanced for 4.35 V operation; and (C) Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2} (NCA)/nano Si-C (Supplier C) with a capacity of 165 mAh balanced for 4.4 V operation. The values of x and y in the Li(Ni_{1-x-y}Co_{x}Al_{y})O_{2} materials used were in the ranges 0.05 < x < 0.15 and 0.02 < y < 0.10 which are typical for commercial NCA grades. Pouch cells A, B and C were all 402035 size (40 mm long, 20 mm wide × 3.5 mm thick) with a rolled electrode design. However, single stack (i.e one positive and one negative electrode) pouch cells of the chemistry used in Type A cells were used for the thickness measurements. The effect of within-coating porosity on the macroscale expansion of electrodes was not explicitly taken into account. However, the electrodes used in Type A, B and C cells were all heavily calendared (to achieve maximum energy density) and as such, it is believed that particle expansion will cause overall cell expansion, as is observed in this work. In all cases, the Si-containing component of the electrodes showed a potential/Li content curve which matched that of amorphous Si after the first lithiation since the materials were not driven into the Li_{2}Si_{3} phase based on the negative/positive electrode balance. Pouch cells were received from the respective manufacturers sealed without electrolyte. They were opened and placed in a vacuum oven at 100 °C for 14 hours to remove any water contamination and then transferred into an argon-filled glove box for electrolyte filling and sealing.

Electrolyte was prepared in an argon-filled glove box to minimize possible contaminations. Type A cells were filled with 1.2 M LiPF_{6} ethylene carbonate (EC): ethylmethy carbonate (EMC): dimethyl carbonate (DMC) (25:5:70 by volume) with 2% vinylene carbonate (VC, 99.97%). Type B and C cells were filled with 1.2 M LiPF_{6} ethylene carbonate (EC): ethylmethyl carbonate (EMC): fluoroethylene carbonate (FEC) (27:63:10 by volume). All chemicals used here were supplied by BASF.

For formation, all cells were cycled for 24 hours at 1.5 V and then transferred to a Maccor series 4400 charger. Cells were cycled to 4.2 V at C/20 with a 24 h...
OCV storage step performed at 50% state of charge at 40 °C, and then discharged to 3.8 V. Type B and C cells were charged to 4.2 V and back down to 3.8 V at C/20 without the storage step. Cells then were transferred into an argon-filled glove box and opened to remove any gas generated during the formation process and then resealed. It is important to note that experiments not shown verified the formation steps applied to Type B and Type C cells could be applied to Type A cells with absolutely no changes to the data presented in this paper. It is possible that changes in long term lifetime could be affected by the choice of formation protocol, but that is not explored in this paper.

**Half cell preparation.**—2325-type coin cells were prepared as reference cells for dV/dQ analysis. Cells were made for each electrode component of Type A and B cells. The NCA and LCO positive electrodes and SiO-graphite and Si-Alloy/graphite composite negative electrodes were punched directly from disassembled pouch cells of Type A and B. To determine the contribution of each negative electrode component, graphite, Si and SiO half cells were also made. Pure graphite control and pure Si-alloy control electrodes were provided by Supplier B. The SiO reference electrode was made in house using the method described in Ref. 19. A slurry of 80% SiO, 12% Super-S carbon black and 8% NaCMC (by weight) was prepared utilizing water as solvent. This slurry was spread on Cu foil using a 152 μm notch bar, dried overnight at 120 °C, and then pressed at 1000 atm with a roller press.

The working electrodes were precision punched into 1.28 cm diameter disks. Two Celgard 2320 thin film polypropylene microporous films were used as separators. A 150 μm thick lithium metal foil (Chemetall, >99.99%) was punched into 1.4 cm diameter disks as negative electrodes. 1M LiPF₆ EC:DEC (1:2 by volume) was used as electrolyte, fully wetting the electrodes and separators. Coin cells were assembled in an argon-filled glove box. Cells were cycled on an E-One Moli Energy Canada battery testing system.

**In-situ X-ray diffraction.**—In-situ XRD was performed on a NCA vs. lithium half-cell using a Siemens D5000 diffractometer equipped with a Cu target X-ray tube and a diffracted beam monochromator. A slurry with 94% NCA, 4% carbon black (Super S) and 4% polyvinylidene fluoride (PVDF) was purposely made thick with a small amount of N-methyl-2-pyrrolidone (NMP). The slurry was cast using a 660 μm notch bar directly onto a 2 cm diameter beryllium window. The electrodes were dried overnight at 120 °C in a vacuum oven before use. The beryllium window was attached using Roscobond pressure sensitive adhesive to the positive electrode side of the cell case that had a pre-cut 1.5 cm diameter hole. The in-situ cell was then assembled in the same way as the half cells discussed above. The cell was cycled at a rate of C/100 between 3–4.4 V for two cycles using the E-one Moli charger system, while diffraction patterns were collected in the scattering angle (2θ) range of 17–70° with a dwell range at 0.05° intervals with a dwell time of 15 s. Each scan was approximately 2.5 h. This experiment was conducted so the volume changes versus state of lithiation of the NCA electrode used in Type A cells could be determined.

**Volume measurements.**—In-situ volume measurements were made via Archimedes’ principle in the apparatus described in Ref. 20. Pouch cells were suspended in silicon mechanical pump oil from a thin film load cell to measure their mass. The buoyant force acting on the suspended pouch cell changes as the volume of the cell changes, resulting in a change of tension on the load cell and thus a change in mass Δm. Using this and the density of the silicon oil, ρ, the change in volume, ΔV, of the pouch cell can be calculated:

\[ ΔV = -\Delta m/ρ \]

The pouch cells measured in these experiments had an initial volume of ca. 2.5 mL. For in-situ measurements, the pouch cells were connected to a Maccor Series 4000 battery charger. The load cell output was connected to a Keithley 2700 scanning voltameter. These measurements were made in a temperature box at 40 °C—a standard temperature used for experiments in our lab to speed up cell degradation so different cell chemistries can be ranked in a timely manner. However, cell degradation during the in-situ measurements over only a few cycles, as reported in this work, was very minimal. Cells tested here first experienced a formation procedure, as discussed above, before being transferred to this system for charge/discharge cycling from 3–4.2 V.

**Pressure measurements.**—For in-situ pressure measurements, pouch cells were fastened inside rigid aluminum holders, pictured in Figure 1a, such that electrode volume expansion would cause an increase of force exerted on the enclosure. With this holder design, any gas evolved during cycling would be pushed out of the jelly roll into the pouch and not cause a change in measured pressure. The force was measured with subminiature load cells (model LCKD - OMEGA Engineering) with capacities of 100, 250, and 500 lbs (445, 1112 and 2224 N), connected to DP25B-S-A (OMEGA Engineering) strain gauge panel meters. The measured force was converted to Pa using the pouch cell area of ca. 6.0 cm². The load cells were fastened inside the aluminum enclosures, in-between the wall of the enclosure, a force-distributing plate, and the pouch cells, shown in Figure 1b. The position of one wall of the enclosure is adjustable with screws. This allows the enclosure to accommodate cells of different thicknesses as well as allowing the application of a different initial pressure by tightening the screws with a torque-controlled driver. The pressures achieved in this work (about 150–800 kPa) correspond to an elastic response of the system (load cell, pouch cell and force distributing plate) of 10 to 20 μm. For in-situ measurements, the pouch cells were connected to an E-One Moli Energy Canada battery testing system. The analog 0–10 V output of the strain gauge panel meter was connected to a Moli slave channel, allowing for simultaneous voltage and pressure measurements. These measurements were made in a...
temperature box at 40°C. Cells tested here first experienced a formation procedure, as discussed above, before being transferred to this system for charge/discharge cycling from 3–4.2 V.

**Thickness measurements.**—An in-situ thickness measurement was made for a single stack (i.e., one positive and one negative electrode) pouch cell of the chemistry used in Type A cells in the apparatus shown in Figure 1c. The cell was secured to a flat aluminum stage, and a displacement sensor (Keyence GT2) was used to measure the cell thickness changes during charge and discharge cycling. A spring was applied to the displacement pin to minimize noise from inconsistencies in the pouch. The pressure applied by the spring is very minimal, <30 kPa. Therefore, we believe this does not impact the thickness measurements. This measurement was performed at room temperature. The first half cycle of this test was a formation step, as no prior formation procedure was performed on this cell. One cycle of discharge charge cycling followed between 3–4.2 V.

### Results and Discussion

In-situ volume, pressure and thickness measurements for Type A, B and C cells are shown in the first, second and third columns of Figure 2, respectively. The first row shows in-situ volume measurements, the second row shows in-situ pressure measurements, and the third row shows the thickness measurement made for a Type A cell. These measurements are shown in red, and the corresponding voltage-time profiles during charge/discharge cycling are shown in black. Two cycles are shown for the volume and pressure measurements to demonstrate repeatability. Only data for 1.5 cycles of the thickness measurement for the Type A cell is available—the first charge of which corresponds to a formation step, not representative of volume expansion post-formation. All other data shows the first two cycles after formation. Each cell type shows good agreement between the trends observed in the volume, pressure and thickness measurements. Each of these measurements exhibited an asymmetric profile with plateaus during charge and discharge, the latter occurring at a higher volume, pressure, and thickness than the former. Type A and C cells exhibited a plateau near the top of charge (TOC), whereas Type B cells did not. During charge, the negative electrode is lithiated; alloying with the silicon component resulting in up to 280% volume expansion of the Si component, and intercalating into the graphite component resulting in up to 10% volume expansion. The net result is negative electrode volume expansion, causing the jelly roll of the pouch cell to expand in the direction perpendicular to the current collector. For the respective measurements made in Figure 2, this yields a volume expansion, an increase in pressure and an increase in thickness—and the opposite during discharge. The shape of the measurement profiles show that the volume expansion is not simply linear with the state of charge of the full cell and its asymmetry indicates a hysteresis between charge and discharge. Both components of the negative electrode, as well as the positive electrode, contribute to the overall volume expansion and contraction of the full cell. Each contribution must be treated separately to fully understand the expansion behavior of the full cell. In what follows, such a treatment will be done for the components of a Type A cell.

Figure 3 shows the fractional volume expansion and contraction for each electrode component of a Type A cell: silicon (a), graphite (b) and NCA (c). The data for silicon and graphite in Figures 3a and 3b was retrieved from Refs. 3 and 11 respectively. In Ref. 3, the volume expansion of a sputtered amorphous silicon tower was measured with in-situ AFM using a specially made wet cell vs. lithium metal. The following analysis assumes that the fractional volume vs. state of charge of the a-Si tower shown in Figure 3a is the same as the volume expansion of the SiO electrode component of Type A cells. Previous studies have shown that SiO consists of a nanostructure of a-Si and a-SiO2 in a 1:1 ratio. During first charge/discharge, lithium

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**Figure 2.** In-situ volume (a,d,f), pressure (b,e,g) and thickness (c) measurements of NCA/graphite-SiO, LCO/Si Alloy-graphite and NCA/nano Si-C pouch cells shown in red, with their corresponding voltage vs. time profiles shown in black.
irreversibly reacts with SiO$_2$ to form Li$_4$SiO$_4$ which remains inactive throughout subsequent cycling while the amorphous n-Si is reversibly lithiated and delithiated.$^{10,15,18}$ Therefore, the volume expansion and contraction of SiO during charge/discharge cycling post-formation is caused by a-Si lithiation and de-lithiation.$^{16}$ As such, the data from Ref. 3 is appropriate for our analysis.

In Ref. 11, the lattice constants of graphite were measured as a function of $x$ in Li$_x$C$_6$ using in-situ XRD, from which the average spacing of carbon layers was calculated. Graphite has a hexagonal unit cell; therefore, cell volume per layer, $V_u$, can be calculated as:

$$V_u = \frac{a^2d_{02}\sqrt{3}}{2}$$

Where $a$ is in-plane lattice constant that remains relatively unchanged during lithium intercalation, and $d_{02}$ is the distance between carbon layers, measured in Ref. 11. Since the volume is linear with respect to $d_{02}$, normalizing the data from Ref. 11 gives the fractional volume of Li$_x$C$_6$ versus $x$. The unit cell volume of NCA shown in Figure 3c was calculated based on the in-situ XRD measurement described in the Experimental section. Rietveld refinements were performed on the in-situ XRD data assuming one hexagonal layered phase in the $R\bar{3}m$ space group ($\alpha$-NaFeO$_2$-type structure) to extract the lattice information. It was assumed that Li was on the 3a sites (lithium layer), transition metals were on the 3b sites (transition metal layer), and oxygen was on the 6c sites.

Figure 3 shows that silicon and graphite undergo a 280% and 10% volume expansion during charge. The expansion of silicon is fairly linear with state of charge, whereas the volume expansion of graphite experiences a plateau. This is a result of how lithium intercalates into graphite. Between Li$_{0.25}$C$_6$ and Li$_{0.5}$C$_6$, graphite undergoes a phase transformation from stage 2L $\rightarrow$ 2B. Both of these stages have lithium atoms intercalated into every second interstitial layer between carbon layers. Stage 2L is a partially filled disordered phase that transitions into stage 2B which is a fully filled ordered phase. Since this transition does not involve lithium intercalating into any empty interstitial layers, there is no volume expansion that occurs.$^{11}$ Unlike silicon and graphite that expand during charge and contract during discharge, the opposite is true for NCA—contracting by 4.5% during charge, most of which occurs within the top 20% of the state of charge.

In this work, cells were cycled between 3 and 4.2 V, therefore none of the electrode components accessed their full range of state of charge; no component was ever 100% lithiated or de-lithiated. This cycling range corresponds to the positive electrode cycling between about 3.6 and 4.28 V (20 to 97% state of charge (SOC)), and the negative electrode being cycled between about 0.6 and 0.1 V (3 to 84% SOC). As such, none of the electrode components will experience their full volume expansion or contraction — only that of the regions highlighted in Figure 3 corresponding to the cycling range of each component.

To determine the volume expansion of the composite negative electrode, the contribution of both the graphite and SiO components must be resolved. The states of charge of each of these components within the composite negative electrode will not be the same during cycling. This is because each component is lithiated differently at different voltages. The SOC of each component is the normalized capacity of that component which has been delivered to the total composite electrode capacity. Each component will experience the fractional volume change shown in Figures 3a and 3b at their respective states of charge in the composite negative electrode. Therefore, their states of charge within the composite negative electrode during charge/discharge, as a function of the composite electrode capacity, must be determined. To this end, $dV/dQ$ analysis was used to fit each contribution, the results of which are shown in Figure 4. Half cells of the composite negative electrode, the graphite component, and the SiO component were cycled vs. lithium metal as reference data for this analysis. The graphite and SiO component reference data, shown in red and blue respectively, was combined to fit the measured composite electrode data in Figure 4. The result is good fit, shown in solid magenta, to the measured data, shown in dotted purple. This shows the capacity contribution of each component to the composite negative electrode. From this, the state of charge of each component as a function of the composite negative electrode capacity ($Q_{neg}$) can be calculated:

$$\text{Component SOC} = \frac{\text{Component}(Q_{neg})}{\text{Max Component}(Q_{neg})}$$

I.e. the state of charge of a component as a function of the composite electrode capacity ($Q_{neg}$) is equal to the ratio of the capacity of the component and the max capacity of the component as a function of the capacity of the composite electrode. One must realize that component capacity $\neq$ composite electrode capacity; component SOC $\neq$ composite electrode SOC; and component SOC $\neq$ composite electrode capacity.

This calculation is done for both components during charge and discharge in Figures 5c and 5d, respectively. The charge and discharge $dQ/dV$ vs. V for each component is plotted in the panels above (Figures 5a and 5b) to help elucidate the state of charge vs. capacity behavior. The area under the $dQ/dV$ curves of Figures 5a and 5b corresponds to the amount of capacity delivered up to that voltage. The $dQ/dV$ vs. V curve of graphite shows little charge/discharge hysteresis, which is reflected in the SOC of the graphite component vs. the composite
Figure 4. Voltage vs. capacity results of $dV/dQ$ fits for charge (a) and discharge (b) of a graphite-SiO composite negative electrode. The measured voltage vs. capacity of the composite electrode is shown in purple dotted line. The fit graphite and SiO components, shown in red and blue, add to make the calculated composite negative electrode shown in solid magenta.

Figure 5. The $dQ/dV$ vs. $V$ (a,b), component state of charge vs. composite electrode capacity (c,d) and fractional volume expansion (e,f) of the SiO (blue) and graphite (red) components of the composite negative electrode, shown during charge (left column) and discharge (right column).
electrode capacity plots shown in Figures 5c and 5d. Silicon shows a large hysteresis in dQ/dV vs. V, and as such the SiO component SOC vs. composite electrode capacity profile is significantly different during charge and discharge. The dQ/dV vs. V curves of graphite and silicon overlap during charge meaning that both components are lithiated simultaneously. Due to the hysteresis of silicon, there is much less overlap of the dQ/dV vs. V curves during discharge—almost all of the capacity of graphite is delivered before silicon begins to de-lithiate. This is reflected in the component SOC vs. composite electrode capacity plot in Figure 5d that shows that graphite is de-lithiated to 10% SOC before any significant capacity from silicon has been delivered.

The fractional volume vs. state of charge data for each component presented in Figures 3a and 3b and the state of charge vs. composite electrode capacity data presented in Figures 5c and 5d can now be combined to plot fractional volume vs. composite negative electrode capacity for each component, as done in Figures 5e and 5f. This shows how the volume of each component varies during charge and discharge within the composite negative electrode. The volume expansion profile of graphite is dominated by the fractional volume vs. SOC behavior shown in Figure 3b since the SOC of graphite vs. composite electrode capacity is fairly linear during charge and discharge, shown in Figures 5c and 5d. Conversely, the volume expansion profile of SiO is dominated by the SOC of SiO vs. composite electrode capacity behavior shown in Figures 5c and 5d, since the fractional volume vs. SOC of SiO is fairly linear.

In Figures 3c, 5c, and 5f, the fractional volume expansion of the positive electrode and each component of the negative electrode as a function of capacity is shown. Using the initial masses of each component derived from dV/dQ fitting, the initial volumes of each component can be calculated with their respective densities. In SiO, a-Si is the active component which is being reversibly lithiated and de-lithiated during charge/discharge cycling post-formation. Therefore, it is the a-Si mass and density that is used to determine the initial volume of the silicon component. Multiplying the initial volumes by the fractional volume changes of each component results in the volume of each component during charge and discharge. This is shown in Figure 6a. The change in volume of the positive electrode is shown in red. Each component of the negative electrode, graphite and SiO, are shown in light and dark teal, respectively. Their sum contribution, resulting in the composite negative electrode volume expansion, is shown in blue. This is added to the change in positive volume to calculate the full cell change in volume shown in lime green. To compare this calculation with experimental results, the measured volume, pressure and thickness data for Type A cells are overlaid in Figure 6b.

The calculations made in Figure 6a show good qualitative agreement with the experimental results shown in Figure 6b. Specifically, three key features: i) a plateau during charge; ii) an asymmetric plateau near the top of charge; and iii) a rapid volume contraction seen in both calculated and experimental profiles are highlighted in both figures. From the calculations made here, an understanding of these features and the overall asymmetric measured volume expansion profile can be obtained. Feature i) is a plateau in volume expansion due to the stage 2Li → 2 phase transition of graphite as previously discussed. Throughout this transition, graphite does not expand in volume, slowing the overall volume expansion of the cell. Feature ii) is a result of two mechanisms: (a) The first two thirds of the plateau is caused by rapid NCA contraction and expansion at the end of charge and the beginning of discharge, respectively, that effectively cancels out the opposing expansion and contraction of the negative electrode over this region; (b) The final third of the plateau in feature ii) is caused by the graphite 2Li → 2 phase transformation, over which graphite does not contract. This contributes to the volume plateau instead of showing up as a distinct feature like i) due to SiO charge/discharge hysteresis; throughout this transformation during discharge, SiO has yet to begin de-lithiating, therefore it is still at its largest volume, causing this graphite feature to appear higher and distinct from the volume plateau during discharge. Feature iii) is caused by the de-lithiation of the Si in SiO, resulting in a rapid overall volume contraction.

The detailed analysis of Type A cells presented above can also elucidate the volume expansion behavior of Type B and C cells. The volume and pressure profiles of Type C cells shown in Figures 3f and 3g are very similar to that of Type A cells. Each of the 3 features highlighted in the calculated volume profile in Figure 6 can be seen in Type C cells. Therefore, the same mechanisms discussed above for Type A cells to apply to Type C cells. Although the Type B cell

Figure 6. (a) Shows the calculated change of volume for each electrode component during charge and discharge. (b) Shows the measured volume, pressure and thickness data for Type A cells to compare to the calculated volume expansion profile. A plateau on charge, an asymmetric plateau near the top of charge, and a rapid fall seen in both (a) and (b) are highlighted as features i), ii) and iii) respectively.
measurements shown in Figures 3d and 3e exhibit features i) and iii), clearly, there is an apparent difference in that feature ii), the plateau near the top of charge, is not observed. This is because LCO is used as the positive electrode instead of NCA as in Type A and C cells. Whereas NCA exhibits a volume contraction during full cell charge in the voltage range tested, LCO expands in this voltage range, seen in the data adapted from Ref. 16 shown in Figure 7. Although this is a small ~1% expansion, it was the contraction of NCA, specifically the rapid contraction near the TOC that effectively canceled out the expansion of the negative electrode components, resulting in an overall volume plateau. Considering the small expansion of LCO to be negligible, the calculations of Figure 6a for the composite negative electrode shown in blue would be comparable to cell Type B measurements where, to a first approximation, only the negative electrode components contribute to the volume expansion of the cell. This shows a good qualitative agreement with the measured volume and pressure profiles for Type B cells shown in Figures 2d and 2e. This analysis is in good agreement with the electrochemical dilatometry profile of a LiCoO2/nano Si-graphite cell and a Si-graphite half-cell observed in Figure 4 of Ref. 7 and Figure 8 of Ref. 13, respectively. The feature ii) plateau is not observed in Ref. 7 due to the use of LCO as the positive electrode, just as in cell Type B, nor is it seen in Ref. 13 which has no positive electrode. The feature iii) separation between graphite and silicon contraction on discharge is clearly seen in Refs. 7 and 13, as well as a subtle change in slope during charge characteristic of feature i).

The analysis presented above did not consider expansion of the electrodes parallel to the current collector. This is believed to have a negligible effect due to the strength of the copper foil as well as the aspect ratio of the electrodes (thin and wide). Examples in literature showing large expansions perpendicular to the current collector and no expansion parallel to the current collector can be found. For example, in the work by Beaulieu et al., the authors use atomic force microscopy and optical microscopy to measure the expansion of Si-alloy films when lithiated and de-lithiated. Razor blade grid lines were imposed on the electrode to try to observe any expansion in the direction parallel to the current collector. The authors found no expansion in this direction during first lithiation, despite an expected doubling in volume corresponding with that lithiation.

This work has focused on elucidating the volume expansion of full Li-ion cells over one cycle. However, longer-term results have been collected, shown in Figure 8. In-situ pressure measurements were performed on Type B LCO/Si Alloy-graphite and Type C NCA/Si-C cells for 1000 hours. These cells were cycled at 40°C at C/6 between 3 and 4.2 V. The pressure vs. time data is shown in the bottom panel of Figure 8a, with the corresponding voltage profiles of each cell type in the top panel. This shows that both cell types experience irreversible pressure growth, but this effect is more severe in cell Type B. As has been shown earlier in this work, the pressure change observed when cycling cells is caused by electrode volume expansion and contraction. Therefore, the irreversible pressure growth shown here can be attributed to irreversible volume growth within the cell. Understanding this volume growth will be the subject of a future investigation, however we propose that there could be several mechanisms causing this behavior such as irreversible volume changes of the electrodes, particle fracture, as well as SEI growth.

Figure 8b shows the normalized capacity vs. cycle number of the long term in-situ pressure data. Type C cells experience a ca. 7.5% loss while Type B cells experience a ca. 14% loss through 90 cycles. The capacity loss seems to be correlated to the irreversible pressure growth; the Type B cell, which experienced a larger capacity loss, also experienced a larger irreversible pressure growth than the Type C cell. This motivates the use of the in-situ pressure measurements introduced in this work as an in-operando non-destructive technique for characterizing the viability of Li-ion cell chemistries. This technique will be explored further in future work.

Conclusions

In this work, the effects of electrode volume expansion and contraction on pouch cells with silicon-composite negative electrodes were measured. This electrode expansion and contraction caused the
volume and thickness of the pouch cell to increase during charge and decrease during discharge in a non-uniform manner. A technique for in-situ pressure measurements of a constrained pouch cell was introduced. This allowed the effects of volume expansion in a Li-ion cell of a non-compliant format, such as the rigid can of a cylindrical cell, to be measured. The results were a pressure increase during charge and decrease during discharge, the profile of which agreed with those measured by in-situ volume and thickness measurements.

To understand the asymmetric nature of the measured volume expansion profiles, the expansion of each electrode component for Type A NCA/SiO-graphite cells was calculated. To resolve the contributions of the SiO and graphite components of the composite negative electrodes, their respective states of charge vs. composite negative electrode capacity was calculated. It was found that the SiO component has a large charge/discharge hysteresis, resulting in the volume expansion profile of the Si in SiO to be different between charge and discharge, causing the asymmetric volume expansion profile of the pouch cell. Additionally, the calculations elucidated the other irregular features observed in the expansion profiles: i) graphite 2L → 2 staging which causes a plateau during charge; ii) NCA contraction and expansion which opposes the negative electrode expansion and contraction near the top of charge resulting in a volume plateau; iii) SiO de-lithiation which causes a rapid volume contraction. These conclusions for the expansion behavior of Type A cells can be applied to understand the volume behavior of other chemistries with silicon-composite negative electrodes. By showing the results for three very different cell types with Si-containing negative electrodes, which can be explained by the same model, we demonstrate clearly that the specific cell details are unimportant. Cells that contain SiO, Si-alloy or carbon-coated nano Si will behave as shown in this work. The swelling of Li-ion cells with such electrodes that experience a large volume expansion is an important consideration in commercial applications.

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