

Article

Mitigating Silicon Anode Mechanical Damage with Electrode Architecture

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Abstract

Large volume expansions due to lithiation create problems for silicon anode mechanical stability, as volume changes apply large stresses to the electrode composite and copper current collector. The resulting mechanical damage includes current collector wrinkling or active material delamination, or both, which lead to capacity fade and current hotspots. Strategic design of the electrode microstructural properties, including controlling electrode porosity and adhesion, has the potential to help alleviate these issues. Two strategies to control microstructure are the choice of current collector and electrode drying conditions after casting; however, these strategies are not found to be sufficient to fully solve the damage caused by high stress. As a third approach, this paper investigates a different slurry formulation that uses less silicon content (75 wt%, compared to the usual 92 wt% active material) to limit anode mechanical damage. Reducing the silicon content of the anode eliminates delamination from high-strength current collectors, improving electrochemical cycle lifetimes significantly. However, lower silicon content leads to potential losses in energy density, which we address using a multilayer architecture comprising the 75 wt% Si layer as an interface between the current collector and the 92 wt% active material layer; this interfacial layer prevents delamination while maximizing energy density. Despite improvement, minor wrinkles remain evident even with the multilayer architecture, indicating the need to combine this work with additional mitigations in the future.

Keywords: batteries; silicon anode; stress; mechanical properties; wrinkling; delamination; electrode engineering; electrode architecture; electrode processing conditions; multilayer electrodes



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1. Introduction

Electric vehicles captured 25% of the market share of cars sold worldwide in 2025, and that share is projected to increase in the future [1]. However, extensive adoption of battery-powered electric vehicles is still curbed by their higher cost and limited range compared to internal combustion engine vehicles. To address this, next-generation lithium-ion batteries must have high energy densities and high cycle lifetimes. The incumbent lithium-ion anode, graphite, cycles well, but its energy density is too low to meet electric vehicle targets (greater than 350 Wh/kg) [2–4]. Silicon anodes are a promising solution, as silicon has a much higher theoretical specific energy density (3500 mAh/g for the $\text{Si}_4\text{Li}_{15}$

phase) than graphite (372 mAh/g). Furthermore, Si anodes are attractive for emerging electrified manned and unmanned aerial vehicle applications, where high energy density and specific energy are required.

However, silicon is not yet ready to replace graphite as the ubiquitous lithium-ion anode chemistry. A consequence of silicon's higher energy density is the larger volume expansion of the material due to lithiation (over 300% compared to only 10% for graphite) [5]. This significant volume expansion creates large stresses, which can cause mechanical damage to the electrode matrix. Silicon also does not passivate easily, due to its high surface reactivity, and any passivation that is formed is continually broken apart due to the material's volume changes during a charge–discharge cycle [6–8]. Thus, lithium inventory in the battery is consumed as the solid-electrolyte-interphase (SEI) repeatedly forms and breaks during cycles, leading to fast capacity fade of the battery.

Ultra-small (<10 nm) silicon nanoparticles (Si NPs) have been made into stable slurries due to hydrophilic coatings that promote good nanoparticle dispersion in solution [9,10]. These high-silicon content electrodes have excellent cycle life, reaching 1000 cycles before the battery relative capacity drops to 80% [9–11]. This favorable cyclability is due to the ultra-small Si NP size, which limits (but does not eliminate) the damage to the electrode matrix typically caused by volume expansion [12]. Additionally, these NPs form extremely low-porosity (<10–15%) electrodes, which reduce exposed surface area and protect the majority of the NP surfaces from contacting electrolyte [12].

While these electrodes have demonstrated 1000 cycles in low-loading (~ 1 mAh/cm²) anodes in prior work, as is common for demonstrations in the literature, anode loadings greater than 3 mAh/cm² are required to meet the 350 Wh/kg energy density target [13]. These high-loading anodes face significant challenges. Even ultra-small NPs expand, and with limited porosity to accommodate such expansion in high-loading anodes, large stresses are transmitted to the copper current collector through the polymer binder, which is sturdy enough to withstand silicon's expansion but also strongly adheres to both the silicon and copper. This expansion can result in mechanical damage that includes cracking of the electrode matrix, delamination of active material from the copper, and wrinkling of the electrode caused by unequal expansion in a bilayer composite. These stresses are exacerbated in pouch cells; therefore, if this damage is visible in coin cells, larger-format cells are anticipated to experience even worse damage [14]. Wrinkles could cause delamination and discrepancies in lithium transport distances across the electrode, leading to localized current hotspots that could cause faster degradation or even lithium plating [14–17].

To combat these problems, it is necessary to control electrode structure by creating a morphology that is more accommodating of dynamic volume changes and can withstand high stresses. One way to do this is through controlling the electrode drying condition, by controlling the rate of solvent evaporation from the slurry. Prior literature has shown that tuned drying can be used to tune electrode porosity, adhesion to the current collector, and electrode component migration (e.g., conductive carbon), all of which influence the propensity for electrode cracking [18–22]. Another solution is to use current collectors with higher tensile strength that can withstand high stresses [15,23,24]. This paper investigates these strategies using the ultra-small silicon nanoparticle electrode formulation demonstrated previously [10,12]; while drying conditions are shown to enable minor changes in electrode current collector stress—as evidenced by changes in current collector damage patterns—and stronger current collectors can limit wrinkling, these low-porosity, high-loading anodes still generate enough stress that wrinkling or delamination occurs. Therefore, a different slurry formulation is investigated using reduced silicon content (75 wt% compared to the typical 92 wt% active material) to lower the overall stress in the electrode composite. This lower silicon content anode improves wrinkling and eliminates delamination

issues, drastically improving the cyclability of the anode. However, to maximize energy density, silicon anodes should have more than 75 wt% active material. Therefore, we also demonstrate a multilayer electrode architecture that uses the 75 wt% silicon layer as an interface between the current collector and higher active material content 92% silicon layer, achieving an electrode with an effective total active material content of 86%. While this electrode architecture eliminates delamination, minor wrinkling is still observed with the multilayer structure, so there is a need for continued future work in this area to combine this mitigation with others.

2. Methods

2.1. Nanoparticle and Slurry Fabrication

Silicon nanoparticles averaging 5.9 nm in diameter were made using a plasma-enhanced chemical vapor deposition (PECVD) process, in a custom nonthermal RF-enhanced plasma reactor [9,25]. Nanoparticles were surface-coated with allyloxy (poly)ethylene oxide (PEO), with an $n = 2$ ligand length, and purified using toluene and hexane, as described in previous reports [10,12]. The particles were suspended in *N*-Methyl pyrrolidone (NMP), with 20 wt % Si@PEO in NMP, at 50 °C and mixed overnight. To the Si@PEO and NMP solution, single-walled carbon nanotubes (SWCNTs) were added (Tuball™ Batt NMP, 97% NMP, 2% polyvinylidene fluoride (PVDF), and 1 wt% SWCNT), and the slurry was stirred overnight at 50 °C. Then the polyimide binder (P84, dissolved in NMP) was added, and the slurry was stirred for another four hours at room temperature.

Right before casting, the slurry was mixed using a Mazerustar KK-250S planetary mixer, at a rotation rate of 430 rpm and revolution rate of 1450 rpm for 4.5 min. Two current collectors were used: CF-T8G-UN-18 (18 µm nominal thickness, 7–8 µm additional roughness on the casting side, Hohsen, purchased from United Mineral Corporation, Lyndhurst, NJ, USA) and HTA®-750 (10 µm nominal thickness, Schlenk, Ashland, MA, USA). Different drying conditions were tested; electrodes with an initial drying temperature under 100 °C were additionally dried at 100 °C in vacuum after the electrode was visibly dry, to ensure complete evaporation of the NMP. The first layer of the multilayer electrode was visibly dried (but not annealed) before the second layer was cast. Single-layer electrodes were cast with a 200 (for 92 wt% Si electrodes), 300 (for 75 wt% Si electrodes cast onto the roughened copper), or 400 µm (for 75 wt% Si electrodes cast onto HTA copper) wet gap thickness, aiming for around 2 mg/cm² mass loading. The first layer of the multilayer electrodes had a 100 µm wet gap, followed by a second layer with a 200 µm wet gap. The authors note that each electrode manufacturing condition was cast as only one replicate, so electrode-to-electrode batch repeatability was not tested in this work.

Electrodes were then annealed at 420 °C for 4 h under nitrogen. At this temperature, it is assumed that all the PEO is burned off based on our previously reported thermogravimetric data [10], but the PVDF and P84 remain. The final wt% ratio, after annealing, for the high-silicon content slurry was 92:1:2:5 Si NP/SWCNT/PVDF/P84 *w/w/w/w*, and for the low-silicon content slurry was 75:5:10:10 Si NP/SWCNT/PVDF/P84 *w/w/w/w*. Note that the ratio of SWCNT:P84 was 1:5 in the 92 wt% Si slurry and 1:2 in the 75 wt% Si slurry. Changing the ratio of Si to inactive components necessitates more inactive components; however, the ratio of SWCNT:P84 was set lower in the 75 wt% Si slurry due to challenges in preparing a slurry keeping these a consistent ratio. Iteration and ratio modification were needed to enable a slurry of an appropriate viscosity for casting. Furthermore, the P84 for the 92% Si was a 10% polyimide solution in NMP, and for the 75% Si slurry was a 5% solution, as the Tuball nanotubes added significant viscosity to the slurry, and more NMP was needed for better casting.

2.2. Coin Cell Fabrication and Electrochemical Testing

Cells were made in a 2032 coin cell configuration, with a 19 mm diameter Celgard 2500 separator and 40 μL of electrolyte (1.2 M lithium hexafluorophosphate LiPF_6 in EC:EMC 3:7 *w/w* with 3 wt% fluoroethylene carbonate added). Coin cells were cycled with a Maccor (Tulsa, OK, USA) 4300 tower in a temperature-controlled oven at 30 $^{\circ}\text{C}$. Half cells were made with a 15 mm diameter Si anode against a 9/16" diameter lithium metal reference (0.75 mm thick, 99.9% metals basis, Alfa Aesar Product 10769, Ward Hill, MA, USA). Full cells were made with a 15 mm diameter Si anode and a 14 mm diameter NMC 811 cathode (4.00 mAh/cm^2 areal capacity) fabricated by the Cell Analysis, Modeling, and Prototyping (CAMP) facility at Argonne National Laboratory (Lemont, IL, USA).

The electrochemical prelithiation protocol in half cells was two C/20 cycles, followed by a C/10 cycle, between 50 and 700 mV, with a 1C rate set based on a 1600 $\text{mAh}/\text{g}_{\text{Si}}$ assumption for that voltage window. Full cells were cycled between 3 and 4.2 V, in which the anode range would match approximately a 50–650 mV potential window, based on three-electrode measurements (see Figure S1). Cycle performance was measured in full cells, with a delithiation rate of C/3 and a lithiation rate of C/10 (and a constant voltage (CV) step to C/20 on lithiation only), chosen because rate limitations during charging might limit performance. Reference performance tests (RPTs) were performed every 100 cycles, starting with the first cycle, where one RPT consisted of three cycles with C/10 lithiation and a CV step to C/20, followed by a C/10 delithiation. Mass loadings of these electrodes varied from 1.8 to 2.4 mg/cm^2 , with most electrodes exhibiting approximately 2 mg/cm^2 . The variation within a given electrode cast was similar to the variation across electrodes. Areal capacities were approx. 3 mAh/cm^2 , so assuming the 4.00 mAh/cm^2 NMC cathode can supply around 3.6 mAh/cm^2 capacity at C/3, the typical N/P ratio of the full cells started at around 0.8. The cathode was oversized initially to account for first-cycle losses. At least three coin cells were tested for each electrode condition, and error bars are indicated by shaded regions in figures throughout.

2.3. Microstructural Characterization

X-ray microscopy experiments were conducted at the University of Colorado, Boulder, using a Zeiss (White Plains, NY, USA) 520 Versa X-ray microscope. Electrode samples were prepared into half-cells against lithium metal (Tomiya, Katsushika, Tokyo, Japan) in a stainless steel 2032 coin cell configuration (United Mineral & Chemical Corp., Lyndhurst, NJ, USA) with a Celgard (Charlotte, NC, USA) 2325 separator. A total of 60 mL of Gen 2 (70:30 by mass ethylene carbonate:ethyl methyl carbonate (Tomiya, Tomiya) and 1.2 M LiPF_6 (Tomiya) with 3 wt% fluoroethylene carbonate (Tomiya) were used as the electrolyte. Cells were rested at open circuit potential for 12 h and then cycled through various conditions using a current density corresponding to C/10 on a Neware (Shenzhen, China) battery cycler.

Coin cells were centered on a cylindrical mounting fixture and loaded into the microscope. An accelerating voltage of 140 kV and 10 W of power against a tungsten target and exposure time of 1 s were used for all images. Cross-sections of complete coin cells were collected using a 0.4 $\times$ objective and binning of 2. The X-ray source and detector were placed 22.5 mm ahead and 39.3 mm behind the sample respectively, yielding a pixel size of 24.2 μm . Images of the current collector were generated using a 4 $\times$ objective. The source and detector were positioned approximately 16.8 mm ahead and 13.9 mm behind the sample's center respectively. These parameters yielded a pixel size of 3.82 μm using a bin size of 2.

Cross-sections of a C150V coin cell (notation is explained further in the results section and refers to an electrode cast on conventional copper foil and dried at 150 $^{\circ}\text{C}$ under vacuum) were prepared using a Thermo Fisher Scientific (Waltham, MA, USA) Helios 5 Laser

Hydra at the National Laboratory of the Rockies, a system containing a Scanning Electron Microscope (SEM), multiple ion species Plasma Focused Ion Beam (PFIB), and an coincident in situ femtosecond pulsed laser (fs-Laser) using methodologies developed previously for Li-metal anode coin cells [26,27]. The use of cryogenic fs-Laser PFIB workflows enables cross-sectioning and analysis of cells without disassembly, preserving interfaces and internal architecture. The coin cell was mounted in a custom 29° pre-tilt holder designed to fit a 2032 coin cell to be mounted on a Thermo Fisher Scientific cryogenic stage for fs-Laser and PFIB workflows. The cell and holder were mounted to a pre-cooled cryogenic stage at a temperature range of −170 °C to −196 °C to preserve the electrolyte and sensitive layers in solid state. A 2 × 1.5 × 1.7 mm cross-section was prepared using the in situ fs-Laser at 1030 nm and 30 kHz with a pulse energy of 18 µJ in bulk milling and subsequently imaged with the SEM at 5 kV and 0.1 nA.

Pristine electrode cross-sections before being fabricated into coin cells were also prepared using the Helios 5 Laser Hydra PFIB-SEM at the National Laboratory of the Rockies. Mechanically sectioned electrode pieces were mounted onto 45-degree pre-tilted holders to enable normal incidence fs-Laser processing and PFIB workflows at room temperature. First, 1 mm wide cross-sections were prepared through the thickness of the electrodes with the in situ fs-Laser at 515 nm in 2 min of patterning time. Cross-sections were made at least 400 µm from the mechanically sectioned edge to ensure sections were free of mechanical damage. In order to obtain higher resolution morphological, structural, and compositional information in the electrodes, Xe⁺ PFIB was used to polish the fs-Laser cut cross-sections and remove laser-induced surface texturing. A rocking polish approach was used to minimize curtaining artifacts, where the sample was rotated back and forth by 8 degrees at a glancing angle to the PFIB operating at 30 kV and 100 nA. SEM imaging of the PFIB polished region was conducted to reveal microstructural and interfacial details. Energy Dispersive X-Ray Spectroscopy (EDS) was done on the PFIB polished regions using an EDAX Octane Elite EDS system (Gatan Ametek EDAX, Pleasanton, CA, USA). Automated SEM montages were collected across the 1 mm wide fs-Laser cross-sections to evaluate thickness and bulk morphology, where some were collected in Secondary Electron (SE) mode for higher throughput imaging and others in Backscatter Electron (BSE) mode if SE-contrast was not suitable for segmentation. Image segmentation was performed for Si electrode layers in the SEM montage images, which were used to analyze the thickness profiles using a custom Python script.

3. Results and Discussion

High stresses due to silicon volume expansion cause significant mechanical damage to the anode during cycling. These damages include macroscale wrinkling of the anode due to uneven expansion between the silicon and copper current collector, and microscale cracking of the electrode composite, as shown in Figure 1. Microscale computed tomography (micro-CT) of a coin half-cell (setup shown in Figure 1a) reveals the copper current collector deforms even under the 0.1–0.2 MPa of pressure placed on the electrodes by the springs and spacers in the coin cell [28]. Radiographs were taken after the first full lithiation (at 50 mV versus lithium metal) after the cell was assembled, then at various points during the first delithiation (after 2 and 4 mAh of delithiation capacity, and at full delithiation to 750 mV, or approximately 5.5 mAh). Radiographs of the copper current collector at these different points are shown in Figure 1b. No wrinkling is observed during the *first lithiation*, as the anode appears flat. However, during the *first delithiation*, wrinkles become visible, with wrinkle amplitude increasing with further delithiation, as seen from the images at 4 mAh delithiation capacity and 750 mV. This suggests that in the first lithiation, the silicon layer expands enough to plastically deform the copper foil, and then during delithiation the silicon layer contracts while the copper remains stretched, causing wrinkles; this is

typical for layered composites (i.e., Si porous electrode on Cu sheet) that have uneven expansion [29–32]. This finding is consistent with predictions from computational modeling of SiO_x electrodes fabricated with polyimide binder that suggest forces are high enough to plastically deform the Cu during lithiation, with contraction of the SiO_x particles causing formation of wrinkles upon delithiation [13]. These wrinkles create differences in lithium transport lengths across the electrode, which could lead to current hotspots and lithium plating [14,15]. Image segmentation that isolates the copper current collector shows that the wrinkle pattern matches the visible pattern in the anode after cell disassembly, indicating that the wrinkles seen in post-mortem images are a good representation of the wrinkles inside the cell and do not arise only in the disassembly processes (Figure S2).

At the microscale, damage to the electrode due to stresses and copper current collector wrinkling are even more apparent, as seen in Figure 1c in a cross-sectional SEM image prepared with a cryogenic fs-Laser PFIB system where the fs-Laser was used to mill through a cycled coin half-cell's top outer casing. The half-cell had been cycled for 68 cycles, starting with a rate performance test, followed by C/3 asymmetric cycling for 50 cycles (see Supplemental Figure S3 for half-cell results). Figure 1c shows significant wrinkling of the anode, which creates gaps between the silicon surface and the separator (which appears bright in the SEM images due to charging effects in the polymer). These gaps indicate that wrinkling affects the ion transport distances across the anode, which would affect the diffusion lengths of lithium and lead to current hotspots or even localized lithium plating in the regions that were closer to the separator. Anode cracking, particularly at high spots in the wrinkles where the anode is closer to the separator, is visible from the inset SEM image in Figure 1d. We note that this cracking may lead to continuous degradation during cycling; however, because cracking occurs in early cycles, impacts of cracking on electrochemical performance likely begin manifesting early in the data rather than as a sudden failure mode later in cycling. Additionally, stress concentrations at folds of the anode may contribute to accelerated mechanical damage during cycling because these regions likely experience greater lithiation due to shorter Li^+ transport distances. Therefore, not only does wrinkling lead to uneven currents, which could cause lithium plating, but it also causes inhomogeneous utilization and degradation of the active material, further affecting the cell's electrochemical performance.

Therefore, a solution to this mechanical damage must be found to enable high-loading anodes with long cycle lifetimes. Drying conditions after slurry casting have been shown in the literature to change how quickly the solvent evaporates, which could help limit volume changes by controlling slurry component migration, porosity, and adhesion [18–22]. Fast drying conditions at high temperature risk silicon particle oxidation; while the particles are coated with PEO for good dispersion in the slurry, chances of oxidation remain if the coating is imperfect. Therefore, previous results have used a high-temperature (150 °C) drying step combined with vacuum conditions to limit oxidation and quickly dry the electrode [9–12]. However, this aggressive drying condition might be the reason why these anodes collapse and form a dense structure, so gentler drying conditions at lower temperatures (70 °C) were tested, with and without vacuum conditions. Additionally, the copper current collector strength and surface roughness also affect silicon adhesion and resulting electrode structure. Copper alloys, which increase current collector tensile strength from 280–300 MPa (for copper, Hohsen's CF-T8G-UN-18) to 750 MPa (for Schlenk's HTA[®]-750), could limit electrode wrinkling, but also change the surface roughness of the material, as copper foil used in this paper has one rough side, and the HTA[®]-750 has two smooth sides. Roughness could help adhesion by increasing surface area and increasing resistance to shear forces; additionally, surface roughness features also wick solvent via capillary forces, which changes the solids loading of the slurry while drying and likely affects component migration (see Figure S4).

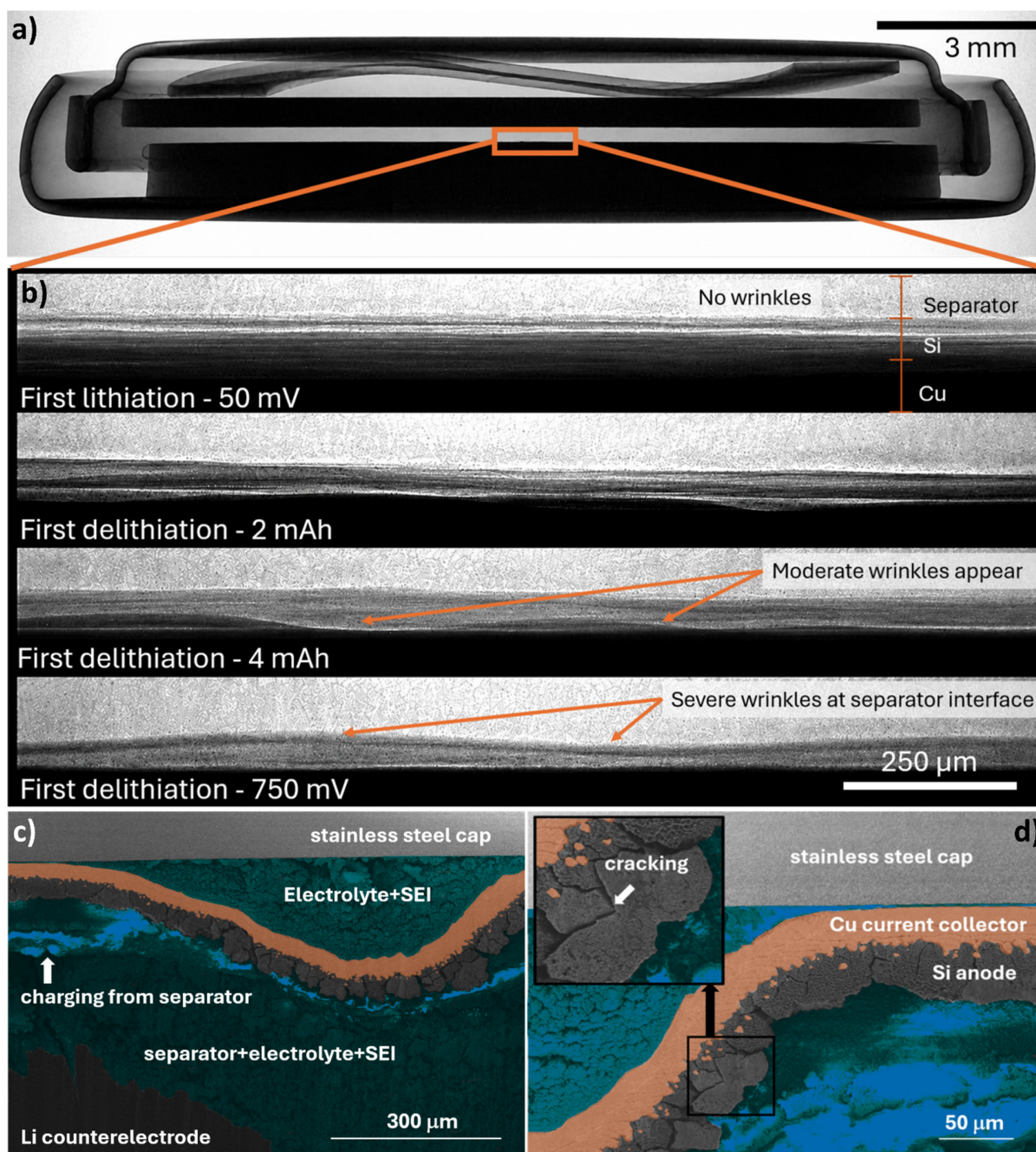


Figure 1. Mechanical damage due to silicon volume expansion during cycling. (a) Micro-CT image of coin cell. (b) CT images of the copper current collector during first lithiation and delithiation. (c) SE-SEM image of cryogenic fs-Laser PFIB cross-sectioned coin cell highlighting gaps between anode and separator due to wrinkles. False color indicates copper (in orange) and electrolyte (in blue). Bright blue regions indicate charging from separator locations. (d) SE-SEM image showing Si active material damage from stress concentrations. Inset shows cracking of the anode.

The effect of drying condition and current collector on the high-silicon-content (92 wt% active material) electrode microstructure is shown in Figure 2. Electrodes are labeled with the drying temperature (in °C) and condition (A for ambient, V for vacuum), and whether the foil was the HTA[®]-750 (H) or CF-T8G-UN-18 (C). Figure 2a,b present SEM images of laser-cut cross-sections for both electrodes dried at 70 °C under ambient conditions (C70A and H70A). Multiple images were stitched together to get an approximately 1 mm cross-section for better representation of electrode variability (though a 1 mm cross-section is still a very small segment of the total anode). As can be seen in the stitched images, porosity and electrode thickness vary

greatly throughout the electrode for both foils. The roughened copper foil (C70A) appears to have a rougher silicon surface than the H70A electrode. Also notable are the significant regions with gaps evident between the silicon and copper interface in the H70A electrode, indicating the active material is poorly adhered to the current collector for this foil and drying condition combination. Cross-sections of all the electrodes, and thickness measurements, are shown in Figures S5 and S6. All electrodes show significant variability in porosity and thickness.

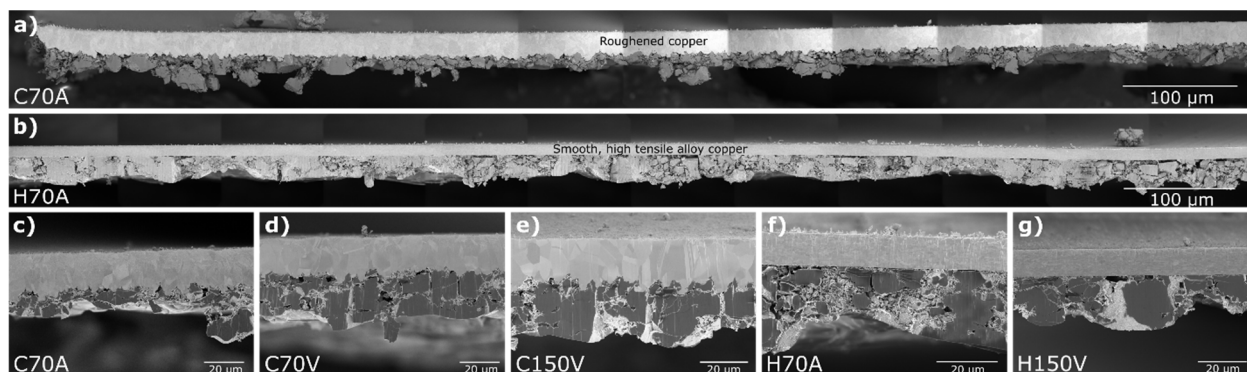


Figure 2. (a) Stitched BSE-SEM images of fs-Laser-cut cross-section of C70A. (b) Stitched SE-SEM fs-Laser-cut cross-section of H70A. (c–g) SE-SEM images of PFIB polished cross-section of each electrode. Images were all collected on pristine electrodes before any cycling.

The fs-Laser-cut cross-sections result in a rougher cross-sectional surface compared to the PFIB polished surface due to the formation of laser-induced periodic surface structures (LIPSS) that form from the interference of the laser and the material's surface electromagnetic waves. Therefore, LIPSS were removed from smaller areas of the cross-sections using the PFIB (which was more time-intensive) to reveal details of the electrode microstructure. Representative images are shown in Figure 2c–g for each foil and drying condition. The poor adhesion at the silicon–copper interface, as seen in Figure 2b, is consistent with the H70A PFIB image in Figure 2f, and can also be seen in the H150V sample. The higher temperature, vacuum-drying electrodes (C150V and H150V) seem to have less porosity than the other electrodes, though these images represent a very small section of the electrode. However, this lower porosity can also be seen in scanning spreading resistance microscopy (SSRM) and optical images, as shown in Figure S7, for these higher-temperature electrodes. This supports the expected result that a higher temperature, vacuum-dry process, which would be the most aggressive of the drying conditions, results in a denser electrode than a slower, lower-temperature process. However, the differences in porosity are not substantial, and due to the variability of the electrodes, as seen in Figure 2a,b, it is hard to conclude that the different drying conditions significantly impact porosity, so this qualitative argument would need to be verified by porosity measurements to make this conclusion with certainty. The choice of current collector, on the other hand, does seem to impact the morphology of the silicon–copper interface, with the rougher copper surface producing a better adhered active material than the smooth alloy surface.

To see how these drying conditions and foils impacted electrochemical performance, these electrodes were tested in full cells with a prelithiated anode paired with a NMC 811 cathode. Images of the silicon and copper sides of electrodes, taken after prelithiation and before reassembly into full cells, are shown in Figure 3a. The roughened copper foil exhibits wrinkling after three prelithiation cycles, regardless of drying condition. The C70A electrode appears to have less wrinkling amplitude, which might indicate this drying condition lowers the stress in the material [29–32]. The HTA electrodes do not wrinkle, but rather delaminate, regardless of drying condition, indicating that the interfacial adhesion between

the coating and the current collector becomes the point of failure to relieve stress instead of the current collector deforming. Half-cell areal and specific capacities versus mass loading tested between 50 and 700 mV during the prelithiation step prior to full-cell cycling are shown in Figure 3b. Electrode-specific capacities and mass loadings varied more punch to punch within a given drying condition than between drying conditions, so there was no clear trend in capacities corresponding to anode foil or drying condition, though the C70V electrode produced punches that had slightly lower capacities and masses than the others.

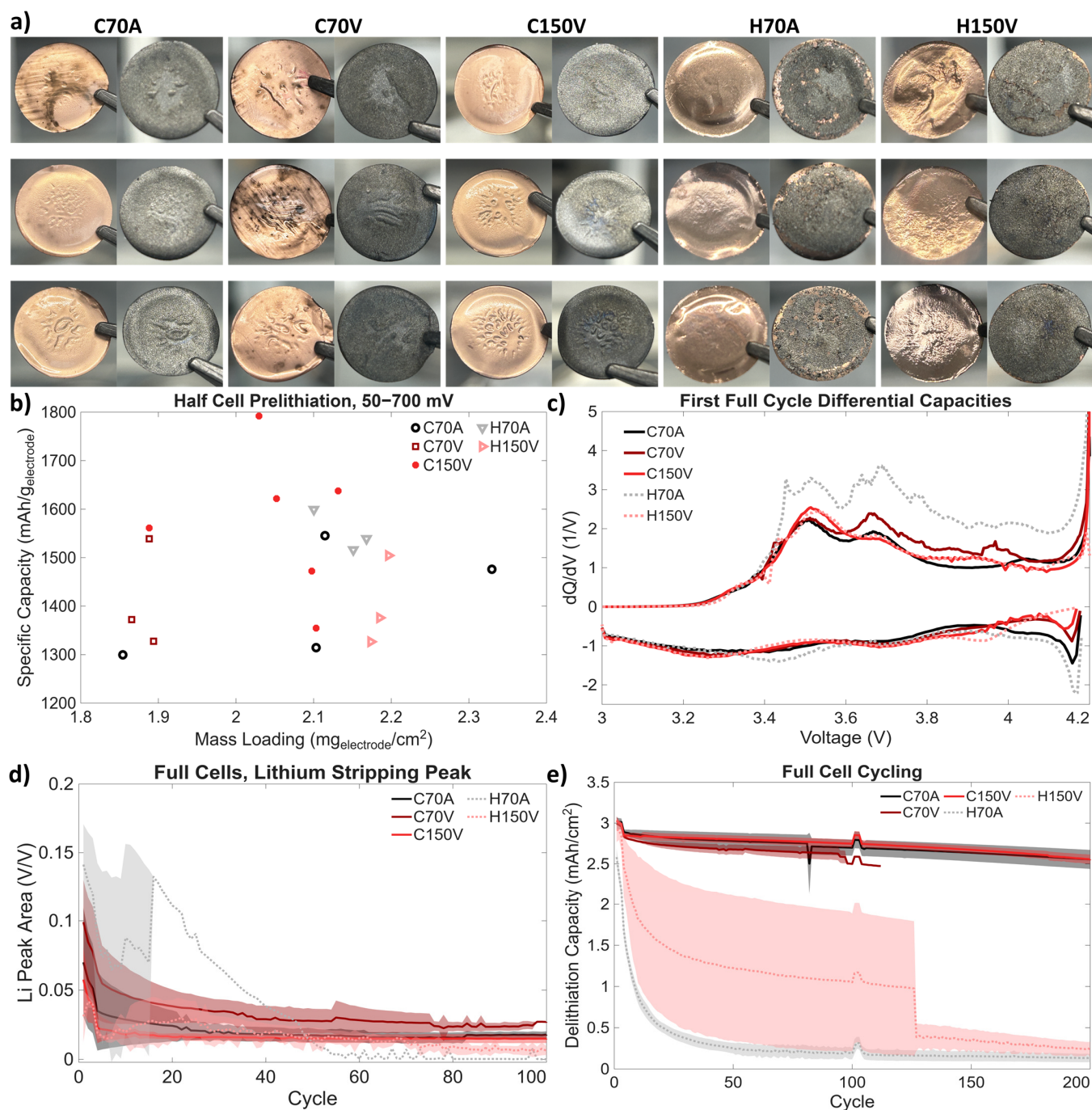


Figure 3. (a) Images of electrodes (Cu back side of electrodes on left and Si side on right) after electrochemical prelithiation, with three replicate electrodes for each condition. (b) Half-cell specific capacities between 50 and 700 mV versus total electrode mass loadings on the third prelithiation cycle. (c) First-cycle differential capacity in a full cell against NMC 811 after prelithiation of the Si in a half cell. (d) Lithium stripping peak area as a function of cycle number in full cells (shaded regions indicate one standard deviation, for at least three coin cells). (e) Full-cell capacity retention for each electrode.

The differential capacities of the anodes against NMC811 are shown in Figure 3c. The peaks during discharge at around 4.1 V indicate lithium stripping behavior, evidenced by correlating to the three-electrode results (Figure S1), suggesting that this N/P ratio was not ideally matched for all of the anodes. Anode punches with higher specific capacities, like the C70A cell in Figure 3c, had smaller lithium stripping peaks that went away after a few cycles. The area under this lithium peak, estimated as the area under the dQ/dV curve from 4.1 to 4.2 V, with a mean dQ/dV value between 4 and 4.1 V subtracted for normalization, was calculated for cells during full-cell cycling, and is shown in Figure 3d. For most cells, this peak disappears after the first ~20 cycles, though the lower capacity C70V electrode and the H70A electrode experience lithium stripping behavior that continues throughout cycling.

Figure 3e shows the capacity retention of the cells. Both HTA (H) electrodes experience significant capacity fade, with H70A losing most of its capacity within the first few cycles. The electrodes coated on the roughened copper foil (C) did not have significant capacity fade for the first few hundred cycles, though the C70V electrode performs slightly worse than the other copper foil electrodes, potentially due to the N/P mismatch. Cells were also cycled between 3 and 4.1 V, to see if the lithium plating and stripping behavior present in the 3 and 4.2 V experiment significantly impacted cycle performance, but a similar trend was observed (see Supplemental Figure S8) where the copper foil electrodes cycled well without significant capacity loss, while the HTA alloy electrodes rapidly lost capacity.

As seen in the images in Figure 3a, the H70A electrode exhibits much more severe delamination, which correlates with this electrode's more rapid capacity loss in full-cell cycling compared to the H150V electrode. The less severe delamination in the H150V electrode suggests that a faster drying condition might help with adhesion to this foil; however, delamination is still visible on the edges of the H150V anode punches, and this electrode performed much worse in full-cell cycling than the roughened copper foil electrodes, so the drying condition was not sufficient to overcome the mechanical issues.

It is worth noting that this significant delamination in the HTA electrodes might have been exacerbated by the need to disassemble and reassemble the coin cell after half-cell prelithiation. However, prelithiation is needed for high-loading silicon electrodes due to significant first-cycle losses, which are around 60% for these electrodes, and is consistent with other results using similar electrode formulations [10,12]. Accommodating this first-cycle loss must be achieved with either an oversized cathode, which sacrifices energy density and increases cost, or some type of prelithiation of the silicon, which might affect the mechanical stability of the material. Regardless, even without the need for handling of the electrode due to cell assembly requirements, it is clear that the mechanical stability of the electrode is closely tied with its electrochemical performance, and any electrode that experiences the level of delamination that the HTA electrodes have is likely to exhibit limited cycle life.

The images after prelithiation in Figure 3a indicate there is a tradeoff between wrinkling and delamination, and the solution to silicon anode mechanical problems is not as simple as substituting a stronger current collector. This finding is consistent with prior literature showing that wrinkling and delamination behavior depend on the specific substrate and film properties [31,32]. Above we identify that a major mechanical culprit is the high stress at the silicon–copper interface; this stress causes Cu to stretch upon lithiation and then wrinkle during delithiation if the adhesion of the electrode to the Cu is strong. If the adhesion is weak, it causes electrode delamination from the Cu if the Cu cannot stretch enough to accommodate the stress (e.g., HTA). While slower drying conditions at 70 °C under ambient pressure seem to result in a slightly more porous electrode, and thus less severe wrinkles, these parameters cannot sufficiently reduce interfacial stress to eliminate mechanical degradation.

Since drying conditions and higher-strength foils did not fully solve the mechanical degradation issues due to silicon volume changes, a new slurry was formulated with lower

silicon content (75 wt% active material) to limit the amount of total volume change of the anode. Both copper and HTA foils were tested with this 75% silicon content anode. A few different formulations were tested that varied the amount of binder and conductive carbon additives. Slurries that were made with high binder content (75:1:2:22 Si NP/SWCNT/PVDF/P84) did not have good dispersion of the polyimide binder and active material (visible non-uniformity was evident in the cast electrode, and the electrochemical performance in half cells was poor). A slurry with a higher amount of conductive carbon (75:5:10:10 Si NP/SWCNT/PVDF/P84) was chosen, as the viscosity of the slurry still allowed for proper mixing but was viscous enough that the electrode could be cast with a thick wet gap. A drying condition of 70 °C ambient was chosen because this condition reduced wrinkling in the roughened copper foil, as shown in Figure 3a, and a vacuum drying condition is challenging for roll-to-roll processes and would hinder scalability of these electrodes.

Though 75% silicon is still much higher than common commercial Si-carbon composite electrodes that are typically reported, optimizing the amount of active material higher than 75 wt% could be beneficial for maximizing energy density. Therefore, electrodes with a multilayer architecture were also tested. Multilayer electrodes have been previously demonstrated in the literature, ranging from varying the percentage of Si between cast layers to alternating Si layers with other species or other forms of Si [33–43]. Some of these architectures have been shown to reduce stresses at the anode-current collector interface and improve cycle performance [33,34]. Gradient architecture, for a bilayer electrode, places the lower-silicon-content layer next to the copper to act as a buffer for stresses, and the higher-silicon-content layer is coated on top. The top layer is the majority, by weight, of the electrode to maximize energy density. Note that this layering structure contrasts with a more common approach of coating a higher-porosity layer near the separator to reduce the tortuosity of the electrode and facilitate faster charging, because the focus of this work is on mitigating mechanical stress near the current collector.

The morphologies of these gradient architecture electrodes are shown in Figure 4. Electrodes are labeled with the current collector used (H for HTA or C for copper) and the layer silicon content, in order; for example, the electrode H75-92 is a bilayer electrode with a 75 wt% silicon first layer (nearest to the current collector) and a 92 wt% silicon second layer (nearest to the separator) on HTA. Figure 4a,b are stitched SEM laser-cut cross sections of H75 and H75-92. There is no obvious interface between the 75% and 92% layers for H75-92, indicating that the annealing step is sufficient to strongly adhere the bilayer together. There is also no obvious significant change in average thickness between these two electrodes, though there is significant inhomogeneity in thickness across both, indicating no significant change in volumetric energy densities would be expected if similar capacities were achieved.

Figure 4c,d show PFIB polished cross-sections and representative EDS maps of H75. The carbon seems to accumulate around pores (see Figure S7). Figure 4e,f show a PFIB cross-section and a representative EDS map of H75-92. Here, the carbon is primarily located at the silicon-copper interface, as the layer closest to the copper is higher in carbon (the 75 wt% active material layer has 5 wt% carbon nanotubes and 20 wt% polymer binder). This could account for the better adhesion of this layer to the copper, as this carbon is not expected to be electrochemically active and would not expand or contract significantly during cycling, creating a buffer layer between the volume-changing silicon and the copper. The H75-92 electrode also appears to be denser than the H75 electrode, though the sections shown in Figure 4 represent a very small segment of the anode.

Electrochemical prelithiation in half cells was performed, like with the drying conditions and foil electrode group that are shown in Figure 3. After prelithiation and imaging of the silicon and copper current collector, anodes were re-assembled into full cells. Figure 5a shows the wrinkling and delamination seen after prelithiation. No interfacial problems between the

two cast layers in the multilayer electrodes were observed; the two layers were well adhered, and EIS measurements revealed no additional impedance due to the extra interface (Figure S9). The authors note that the absence of rate capability or galvanostatic/potentiostatic titration technique testing of the multilayer electrodes is a limitation of this study and would be valuable in future work to help understand any changes in transport that could be caused by the interface.

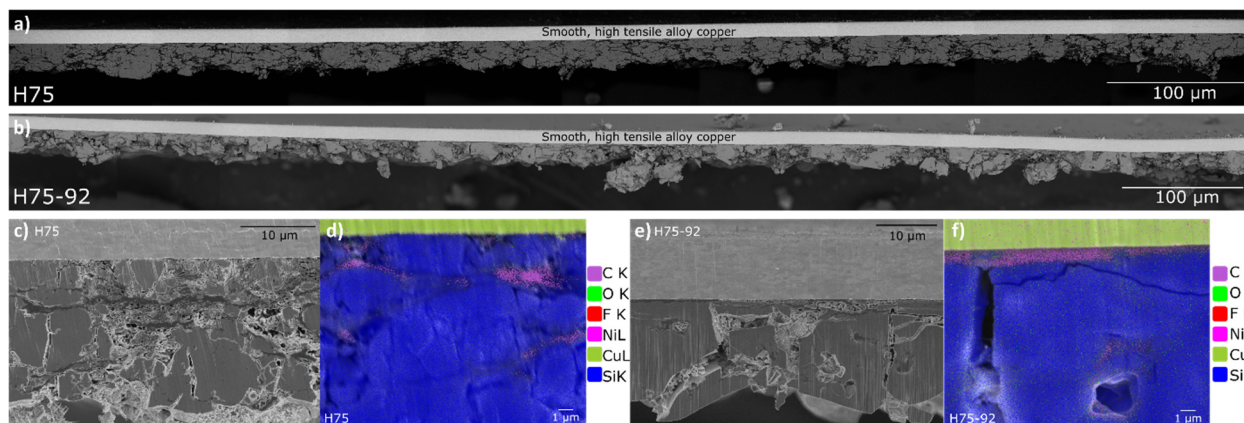


Figure 4. (a) Stacked BSE-SEM images of laser-cut cross-sections of H75. (b) Stacked BSE-SEM images of laser-cut cross-sections of H75-92. (c) PFIB cross-section of H75. (d) Representative EDS map of H75. (e) PFIB cross-section of H75-92. (f) Representative EDS map of H75-92. All images were collected before electrodes were assembled into coin cells.

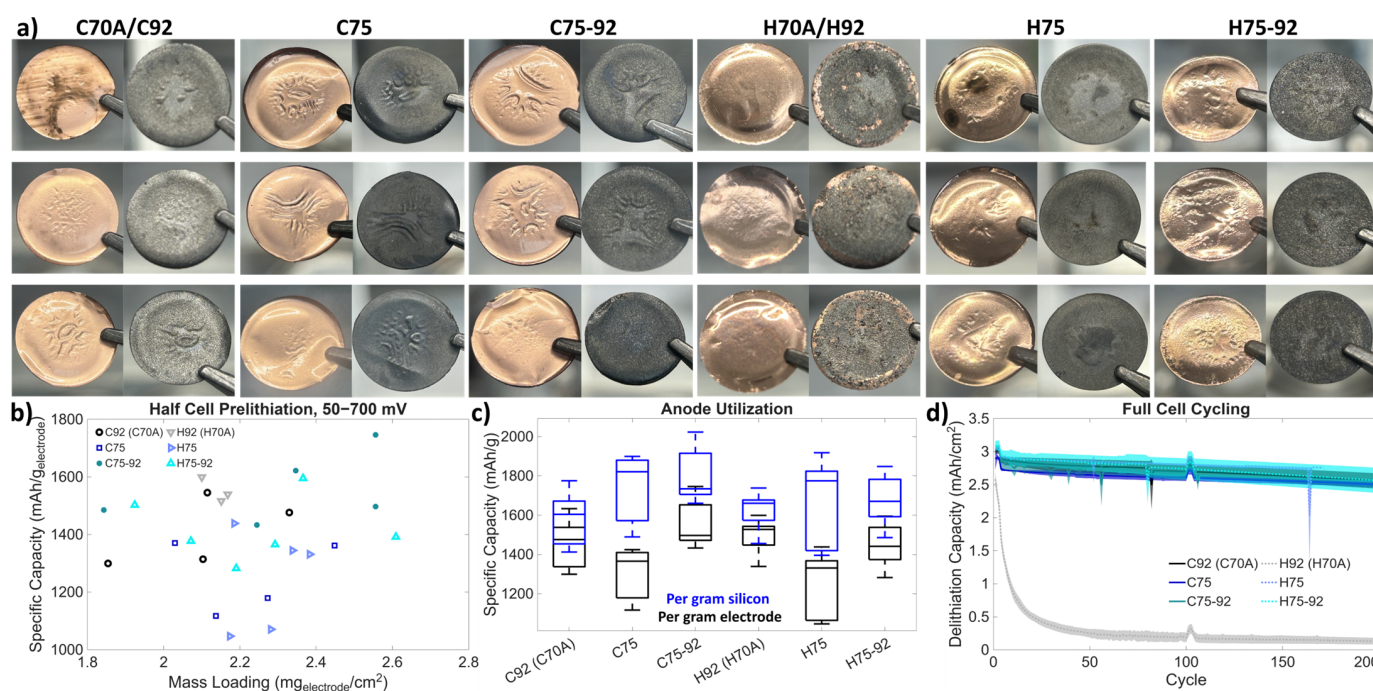


Figure 5. (a) Images of electrodes (Cu back side of electrodes on left and Si side on right) after electrochemical prelithiation, with three replicate electrodes for each condition. (b) Specific capacities versus mass loadings per gram electrode in half cells for the multilayer electrodes. (c) Anode utilization, per gram electrode and per gram active material, for each electrode. (d) Capacity retention in full cells for each electrode.

The intimate bonding between the layers is not surprising, given the electrode processing conditions. When two layers are cast in the electrode, the first layer is dried at low temperature until visibly dry, and then the second layer is cast and dried on top of the first. The silicon nanoparticles are coated in PEO oligomer to enable nanoparticle dispersion in

the slurry. These PEO groups on the surface survive the initial drying step at modest temperature (150 °C), though they are completely thermally decomposed during the electrode curing step (420 °C), as evidenced by thermogravimetric analysis in our published paper [10]. The thermal decomposition of PEO leads to dangling bonds at the silicon nanoparticle surface that react with the polyimide binder and cause it to cross-link. This likely leads to significant structural rearrangement of the particles within the polyimide binder and chemical changes to the polyimide binder itself. This structural rearrangement and cross-linking, combined with softening of the polyimide binder at this 420 °C temperature (its glass transition temperature, T_g , is ~315 °C from the manufacturer's specification sheet), suggests that there is intimate chemical contact and some mixing at the interface of these layers—despite each initially having different silicon/polyimide ratios. Thus, the two layers become indistinguishable, as is demonstrated in Figures 4 and S7.

The C75 and C75-92 electrodes still experience wrinkling, suggesting that this multilayer architecture strategy did not completely solve the mechanical issues, though it represents an improvement from the 92% electrode. A more significant improvement can be seen with the H75 and H75-92 electrodes, which do not experience the severe delamination that is seen in the H70A/H92 electrodes, showing that a combination of higher-tensile strength current collector and a gradient architecture are a pathway to a more mechanically-robust silicon anode. It should be noted, however, that the H75 and H75-92 electrodes do have small dimples seen on the foil, which are not present in the H92 electrode images. These differences suggest that the tradeoff between delamination and wrinkling observed in Figure 3 still applies here. Literature on wrinkling in bilayer materials has shown that different wrinkling morphologies result from different strain mismatches; dimples indicate a lower biaxial strain than herringbone pattern wrinkles [29,30]. While not explicitly proven in this work, this prior literature suggests that the small dimples observed in the H75 and H75-92 HTA electrodes suggest a more limited strain in the current collector than C75 and C75-92 electrodes experience, likely due to the higher modulus of the material. However, at least in coin cell format up to 200 cycles at the low rates tested here, the wrinkling and dimpling of these electrodes do not appear to significantly affect electrochemical performance as long as delamination is avoided. Because the wrinkles and dimples likely lead to differences in Li^+ transport distances, we speculate that the current collector mechanical damage could lead to more significant cycling problems if higher rates were tested. Furthermore, because these coin cells are flooded with electrolyte, which reacts with plated lithium metal and can lead to dry out, cells tested here may be more tolerant to lithium plating than more practical lean electrolyte cells. The authors also note that the architecture mitigations developed in this study have not been tested at high rate or under fast-charging conditions, where increased current non-uniformity, and the risk of lithium plating, would be more likely. Testing varied architecture mitigations in cells with varied rate capability and lean electrolyte to 1000 cycles will be the subject of future work.

The mass loadings and half-cell specific capacities of the lower silicon content and multilayer electrodes are shown in Figure 5b. As with the different drying condition and foil anodes in Figure 3, variations between coin cell punches resulted in a range of mass loadings; however, most of the cells tested contained anode loadings that ranged from 2 to 2.4 mg/cm². For comparison, the C70A and H70A electrode mass loadings (as the same 70 °C ambient drying condition in those cells was used for all the multilayer electrodes) are also plotted.

The specific capacity in full cells of each electrode, normalized per gram electrode or per gram silicon, is shown in Figure 5c. This shows that the active material utilization in the electrodes with 75% silicon was higher, as the utilization of the silicon increases from around 1400 mAh/g_{Si} for the bilayer 75–92% electrodes, to 1700 mAh/g_{Si} for the 75% Si electrodes. However, due to cell variability, this difference is not statistically significant. Unsurprisingly,

the specific capacity per gram electrode of the 75% Si electrodes is lower than the 92% Si electrodes, as these electrodes contain more inactive material. However, the bilayer 75–92% electrodes have comparable specific capacities to the 92% silicon electrodes, confirming that a multilayer architecture still produces an electrode with high specific capacity.

It is worth noting that the H75 electrodes contain more inactive components and a different ratio of SWCNT:PI than electrodes with higher Si content, which is necessary to enable a castable slurry. PI and SWCNTs can both be lithiated, contribute reversible and irreversible capacity, and can change electrode structure and conductivity [44,45]; therefore, changing the inactive content and ratio could impact cycle life, utilization, and first-cycle losses without these changes being independently attributable completely to the mechanical response of the electrode. Because these compositional changes are necessary to cast the slurry and test electrodes with lower Si content, it is helpful to discuss the changes in mechanical and electrochemical performance holistically. It would be difficult to decouple mechanical impacts from inactive material changes to attribute them purely to stress changes from the lower Si content or to electrochemical behavior changes that then induce mechanical changes. However, within error of the measurements, there is not a large change in electrochemical behavior, and a positive improvement is observed in current collector damage when a lower Si content is used.

The cycle performance of each electrode is shown in Figure 5d. The roughened copper foil electrodes (C) perform similarly to the copper foil electrodes shown in Figure 3, with good capacity retention over 200 cycles. However, improvement is seen with the HTA multilayer electrodes, which do not experience the rapid capacity fade that the H70A/H92 electrode does. In particular, the H75 and H75-92 electrodes perform similarly.

Linear correlation analyses were performed for both groups of electrodes (the different foil and drying conditions, and the multilayer electrodes), and are shown in Figure 6a,b (additional correlation plots are shown in Figures S10 and S11). Each square is the linear correlation between a pair of variables, where the best-fit line is plotted, and each cell is color-coded to indicate which electrode it is from. Following the methods from previous work [12], the Pearson correlation coefficient was calculated (shown for each correlation). If the correlation was found to be statistically significant, the square is shaded gray, with a darker gray indicating greater significance. Correlations between mass loading and half-cell areal capacity are unsurprising, and appear in both datasets. It is worth noting that, while significantly correlated, the Pearson correlation coefficient is only 0.67, which indicates scatter in the data or that the relationship between mass loading and areal capacity varies with drying condition, such that it is not a simple relationship. It is worth noting that the correlation is positive (not inverse) and appears reasonably linear within the scatter of the data, which means that increased mass loading leads to increased areal capacity rather than increased mass loading leading to decreased capacity or nonlinear capacity changes that may be expected to result from increased stress at higher mass loading.

It is also helpful to examine mass loading correlations with other parameters to further understand how it impacts performance. Correlations between mass loading and full-cell areal capacities suggest that these cells are anode limited and that the cathode is oversized enough to enable capacity to be higher when there is more anode available. Mass loading and half-cell areal capacity are inversely correlated with full-cell specific capacity because more anode mass dictates that each gram of anode is utilized less when paired with a fixed cathode capacity cycled in a fixed voltage window; essentially, this is a function of varied matching between the electrodes when the Si mass loading varies slightly. Half-cell specific capacity and half-cell first-cycle CE do not correlate to full-cell specific capacity, which is reasonable since the areal capacity is more relevant for anode–cathode matching considerations that lead in turn to changes in Si full-cell specific capacity here. Mass loading is not

correlated with half-cell specific capacity or half/full-cell first-cycle coulombic efficiency (CE), indicating that Si utilization and first-cycle losses are not significantly impacted by the mass loading variations in these cells (though utilization does vary with electrode drying, current collector, and multilayer electrode configuration). First-cycle CE in full cells is not correlated with anything, suggesting that the prelithiation protocol used was sufficient to overcome the first-cycle inefficiencies seen in this silicon material.

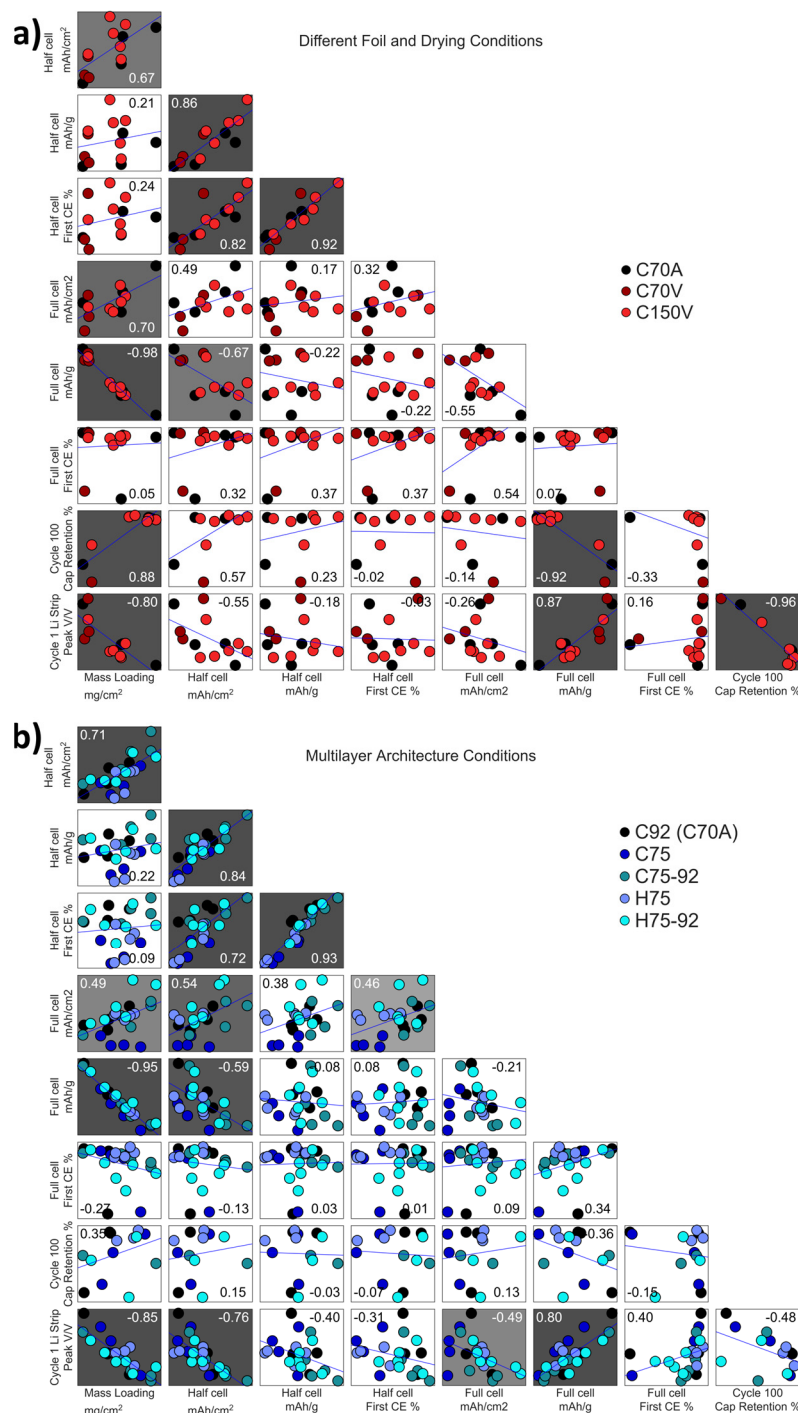


Figure 6. (a) Linear correlation plots for the varied drying condition and foil electrodes. (b) Linear correlation plots for the varied multilayer electrodes. Colors correlate to the colors used in Figures 3 and 5. Half-cell data is collected from cycle 2 charge and full-cell data is collected from cycle 3 discharge. Specific capacity is given per gram of Si electrode, and mass loading refers to mg of Si electrode including inactive components.

Given that mass loading correlates with half-cell areal capacity, as expected, one might also expect that mass loading and half-cell areal capacity would exhibit similar correlations with other parameters; however, the data do not always show similar correlations for mass loading and half-cell areal capacity with other parameters, indicating that architecture nuances may be a more significant factor in dictating performance metrics than simply causing changes in mass loading and that then lead to other performance impacts. For example, half-cell areal capacity is correlated with half-cell specific capacity and half-cell first-cycle CE; somewhat surprisingly, mass loading is *not* correlated with half-cell specific capacity or half-cell first-cycle CE despite mass loading correlating with half-cell areal capacity. This means that cells with higher mass loading (i.e., more Si in the anode that could enable higher half-cell areal capacity) do not lead to lower half-cell specific capacity or half-cell first-cycle CE due to potentially higher stresses degrading performance with increased loading within the mass loading variations in these data. Quite the opposite, these data show that when half cells achieve higher specific capacity and first-cycle CE, they also achieve higher half-cell areal capacity. Furthermore, cells with higher half-cell specific capacity also show higher half-cell first-cycle CE, further indicating that cells with improved half-cell specific capacity cycle more favorably across a broad range of metrics. Because improved half-cell specific capacity and first-cycle CE are positively correlated with half-cell areal capacity and are not correlated with mass loading, the conditions that lead to higher specific half-cell capacity are likely related to architecture changes that enable Si to cycle more effectively (i.e., higher half-cell specific capacity is also associated with higher half cycle areal capacity and first-cycle CE because the Si architecture is more favorable) rather than simply being related to cells with lower mass loading and lower resulting stresses.

It is also instructive to compare correlations that differ between the varied foil and drying study electrodes (Figure 6a) and the multilayer electrodes (Figure 6b). In Figure 6a, the full-cell areal capacity does not correlate strongly with half-cell areal capacity or half-cell first-cycle CE, despite full-cell areal capacity correlating to mass loading. In contrast, Figure 6b shows that full-cell areal capacity correlates with half-cell areal capacity and half-cell first-cycle CE for cells with multilayer architectures. This is likely related to the slightly higher mass loadings of the multilayer cells, which may enable better cell balancing with less lithium plating to frustrate correlation analysis in the foil and drying variation cells. Note that half-cell specific capacity does not correlate with full-cell areal capacity, which is reasonable because areal capacity of electrodes is more relevant for matching and affecting full-cell capacity directly.

To further understand the role of the higher mass loadings for multilayer electrodes on lithium plating, it is helpful to examine the capacity retention at cycle 100 in full cells and the size of the first-cycle peak associated with lithium plating and stripping. Interestingly, the capacity retention at 100 cycles is correlated with mass loading and full-cell specific capacity in the drying conditions and foils group, but not in the multilayer electrode group. This might be due to slight differences in mass loadings between the two populations, as the multilayer electrodes typically had slightly higher mass loadings than the drying condition electrodes, which might lead to worse N/P matching for the drying condition electrodes that affects cycle performance. For both datasets, this is corroborated by the inverse correlations seen between the full-cell first-cycle plating peak and mass loadings, which suggests that the lower loading cells did not have an ideal N/P ratio. The positive correlation between full-cell specific capacity and the first-cycle plating peak further confirms that higher Si utilization is correlated with increased lithium plating, as would be expected. It is also worth noting that the cells with foil and drying condition variation in Figure 6a show decreased capacity retention with increased lithium plating (decreased mass loading). In contrast, the multilayer cells with higher mass loadings show the lithium plating peak size is not correlated with

capacity retention, suggesting that a small amount of lithium plating in early cycles does not significantly degrade capacity long term. However, because these are anode-limited, electrolyte-flooded half cells, it is possible that cycle life in well-balanced full cells with limited excess lithium inventory and lean electrolyte addition would suffer more heavily from lithium plating in early cycles.

Most cells were removed from testing after 200 cycles, but Figure S12 shows a few cells cycled to 600 cycles: two different wet gaps of H75 (300 and 500 μm), a bilayer H75-92 cell, and C150V and H92 (H70A) cells for comparison. The H70A electrode, as shown in Figures 3 and 5, quickly loses capacity due to delamination. The C150V electrode cycles with stability initially but starts to lose capacity fast after about 300 cycles, possibly due to the extensive wrinkling that this electrode experiences (as shown in Figure 3a). The H75 and H75-92 cells are able to cycle for several hundred cycles without significantly losing capacity. This suggests that this 75 wt% layer on the HTA foil is mechanically stable for long periods, and that the interface between the 75% and 92% electrode layers in the bilayer is also robust.

4. Conclusions

Mechanical stability is crucial for silicon anode electrochemical performance due to the large volume changes experienced by the silicon during cycling. For high-loading ($>3 \text{ mAh/cm}^2$) and high wt% ($>92 \text{ wt\% Si}$ active material) electrodes, wrinkling occurs when the silicon electrode is well adhered to the Cu current collector and the Cu strength is weak enough to deform when the silicon cycles. The resulting wrinkles cause differences in ionic transport distances, leading to potential current hotspots, as well as active material cracking and degradation at wrinkle peaks and valleys from inhomogeneous silicon lithiation and the associated inhomogeneous volume expansion. In contrast, silicon delamination occurs when the electrode is poorly adhered to the Cu or the Cu strength is sufficient to prevent deformation. Delamination leads to loss of active material and catastrophic rapid capacity fade. Therefore, this paper investigated a few strategies to address the mechanical instability at the silicon–copper interface. Choice of current collector (roughened or smooth surfaces, tensile strengths) and processing conditions (drying temperatures and vacuum conditions) alone were not enough to lower the stress at the interface to completely avoid wrinkling or delamination and instead demonstrates that there is a tradeoff between delamination and wrinkling depending on the selected conditions. A promising multilayer architecture, using a lower silicon content layer (75 wt% Si active material) as a buffer layer next to the copper current collector, was tested and shown to be reasonably effective in improving mechanical stability without decreasing specific capacity. Because the 75 wt% Si electrode was optimized with a different ratio of inactive components than the 92 wt% Si electrodes (which was necessary to achieve a castable slurry), the observed mechanical stability improvement in lower Si wt% electrodes may be attributable to the reduced Si content, the change in inactive component ratios, or a combination of both factors. Regardless, the multilayer architecture demonstrated here enables use of high-strength foils without delamination and the resulting catastrophic capacity fade. These high-strength foils still exhibit evidence of mild mechanical damage (in the form of small wrinkles or dimples) during cycling, showing promise but also indicating that more work is needed to fully address this problem. Mechanical damage could possibly be eliminated by combining a high-strength, multilayer electrode with additional strategies beyond what was discussed in this paper; additional strategies may include structuring the current collector to alleviate stress, applying modest stack pressures to limit delamination, and other electrode architecture strategies that encourage pore formation or secondary particle agglomerations of the silicon nanoparticles.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/batteries12090352/s1>. The Supplementary Information describes additional method and results details and includes the following figures: Figure S1: Three-electrode cell measurement of a representative electrode (C75-92). (a) Full-cell, cathode, and anode voltages. Blue dashed lines indicate the desired 50–650 mV voltage window for the anode, and the red dashed line is 10 mV, below which silicon is at danger of plating lithium. (b) Zoomed-in anode voltage at the lower voltage cutoff. (c) Full-cell voltage versus capacity of cycle 1 and 5. (d) Differential capacities (normalized by first-cycle discharge capacity) of cycle 1 and cycle 5 of the full-cell voltage; Figure S2: Micro-CT image of a wrinkled electrode in a half cell, showing matching wrinkle patterns with the harvested anode after cell disassembly; Figure S3: (a) Half-cell capacities from cycle 6 delithiation (50–750 mV window). (b) Differential capacity plots for a C/20 50–750 mV cycle (cycle 6). (c) Half-cell rate testing and cycling results. (d) Post-mortem images of electrodes after rate test and cycling protocol; Figure S4: (a) Electrode images of a high-silicon content slurry, C70A, coated on the rough side of the CF-T8G-UN-18 foil and (b) H70A, coated on the smooth side of the HTA[®]-750 foil; Figure S5: Stitched SEM images of fs-Laser-cut cross-sections of electrodes. (a–e) Drying conditions and foil electrodes. (f–g) Lower Si wt% and multilayer electrodes; Figure S6: (a) Example stitched SEM image of fs-Laser prepared electrode cross section. (b) Corresponding segmentation of silicon anode. (c) Corresponding thickness profile of the C70A electrode. (d) Thickness measurements of all drying conditions and foils, as well as the bilayer electrode H75-92; Figure S7: (a–e) Optical images of cross-sections, structure components are indicated in (a). (f) SSRM results for C70A conditions, coated twice (first 100 μm wet gap, then 200 μm wet gap, following the same process as the multilayer drying and coating steps). (g) Corresponding AFM image for that C70A two-layer electrode cross-section. (h) SSRM image of a H70A electrode cross-section. (i) Corresponding AFM image of that H70A cross-section; Figure S8: (a) Areal capacity of electrodes cycling from 3 to 4.1 V compared to 3 to 4.2 V. (b) Differential capacity of electrodes cycling from 3 to 4.1 V. (c) Cycle performance of cells with a 4.1 V upper cutoff. (d) Comparison of HTA electrodes cycling from 3 to 4.1 V and 3 to 4.2 V; Figure S9: (a) Electrochemical impedance spectroscopy of half cells after prelithiation, delithiated to 750 mV, fit to an equivalent circuit. (b) Cell resistances of both semi-circles for 1–3 half cells per electrode; Figure S10: All cells, no delamination, correlations for 3–4.2 V cycling. Colors correlate to the colors used in Figures 3 and 5. Half-cell data is collected from cycle 2 charge, and full-cell data is collected from cycle 3 discharge. Specific capacity is given per g of anode, and mass loading refers to mg of anode including inactive components; Figure S11: H75 electrode-only correlations. Colors correlate to the colors used in Figures 3 and 5. Half-cell data is collected from cycle 2 charge, and full-cell data is collected from cycle 3 discharge; specific capacity is given per g of Si electrode, and mass loading refers to mg of Si electrode including inactive components. Figure S12: Extended cycling data for representative coin cells.

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