Enabling High-Energy Solid-State Batteries with Stable Anode Interphase by the Use of Columnar Silicon Anodes

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All-solid-state batteries (ASSBs) with silicon anodes are promising candidates to overcome energy limitations of conventional lithium-ion batteries. However, silicon undergoes severe volume changes during cycling leading to rapid degradation. In this study, a columnar silicon anode (col-Si) fabricated by a scalable physical vapor deposition process (PVD) is integrated in all-solid-state batteries based on argyrodite-type electrolyte (Li₆PS₅Cl, 3 mS cm⁻¹) and Ni-rich layered oxide cathodes (LiNi₀.9Co₀.05Mn₀.05O₂, NCM) with a high specific capacity (210 mAh g⁻¹). The column structure exhibits a 1D breathing mechanism similar to lithium, which preserves the interface toward the electrolyte. Stable cycling is demonstrated for more than 100 cycles with a high coulombic efficiency (CE) of 99.7–99.9% in full cells with industrially relevant areal loadings of 3.5 mAh cm⁻², which is the highest value reported so far for ASSB full cells with silicon anodes. Impedance spectroscopy revealed that anode resistance is drastically reduced after first lithiation, which allows high charging currents of 0.9 mA cm⁻² at room temperature without the occurrence of dendrites and short circuits. Finally, in-operando monitoring of pouch cells gave valuable insights into the breathing behavior of the solid-state cell.

1. Introduction

The revolutionary breakthrough of Li-ion batteries (LIBs) has transformed our daily lives by enabling portable electronic devices in the past three decades, owing to their high specific energy, great cyclic and rate performance. An increasing demand in the global electric vehicle (EV) market enforces development of high energy and power density LIBs. However, two main drawbacks of current LIBs reveal that they have reached their optimization limits; 1) restricted energy density and 2) safety, particularly due to the ignition of volatile electrolyte components. Solid-state batteries are expected to overcome those limitations by enabling a safe use of lithium metal anodes. The volumetric capacity of metallic lithium (2162 mAh cm⁻³) significantly exceeds the restricted volumetric capacity of commercial graphite anodes (747 mAh cm⁻³) translating to a gain of up to 65% in volumetric energy density on cell level.[3] However, high reactivity of metallic lithium and its morphological changes upon cycling lead to fast degradation of cells. Diffusion limitations in metallic lithium lead to the formation of pores during discharge and dendrite growth during charge of full cells at reasonable current rates. [2] Due to this fundamental issue, practical current rates and areal capacities for lithium metal batteries are typically achieved at elevated temperatures >60 °C. Hence, high energy rechargeable batteries based on pure lithium metal anodes have not reached mass applications and consumer markets yet. Recently published C-Ag composite seeding layers could help mitigate the dendrite formation and show promising results in terms of energy density and cycling stability.[3]

Alternatively, silicon based anodes exhibit great potential due to high Si-abundance, reasonable electrochemical potential (0.4 V vs Li/Li⁺) and high volumetric energy density (2190 mAh cm⁻³ for the lithiated LiₓSi₄ phase), which makes them favorable in terms of costs and energy requirements. [4] However, silicon anodes undergo severe mechanical degradations, due to their huge volume expansion (contraction) (±320%) upon (de-)lithiation. This volume fluctuation generates a vulnerable silicon surface every cycle exposing to liquid electrolyte, resulting in rapid capacity decay and poor cyclic life due to continuous solid electrolyte interphase (SEI) formation. [5]

Various silicon structures have been studied to mitigate the issue of volume expansion ranging from nanoparticles,[6] hollow structures,[7] nanotubes,[8] composites,[9] and nanowires,[10] to thin films.[10] Reduction of particle size to nanoscale and introduction of pores (or voids) in the silicon structure suppress volumetric and morphological degradation, respectively.[12] Although these strategies improve cyclic life and capacity retention, other criteria are often overlooked but essential for developing silicon anodes for practical LIBs. High tap
density (=1.6 g cm\(^{-3}\)) and areal loadings (>3.0 mAh cm\(^{-2}\)) are crucial to surpass the volumetric energy density of graphite.[13] Also, the initial coulombic efficiency (ICE) should be above 90% to minimize lithium loss caused by SEI formation in full cells. Finally, rate capability (>0.5 mA cm\(^{-2}\)), temperature range (−20 to 70 °C), and safety should be considered.

Promising reports were published about combining silicon anodes with liquid electrolytes fulfilling above criteria.[15] Especially, columnar silicon films were reported to be a prospective high energy anode material.[16] These Si films are known to have low surface-area-to-volume ratio resulting in a high ICE and can be fabricated reaching several micrometers (1–6 µm) in thickness and multiple square meters via various deposition techniques.[17,18] With hierarchical structuring of col-Si films, areal capacities up to 75 mAh cm\(^{-2}\) with ICE over 90% have been already achieved.[19]

Nevertheless, adoption of col-Si anodes is still challenging in liquid electrolyte systems as such expensive electrolyte additives like fluoroethylene carbonate (FEC) are required and safety limitations are present.[20]

Sulfidic solid electrolytes (SSEs) with competitive ionic conductivities (≈3.0 × 10\(^{-3}\) S cm\(^{-1}\)) are ideal candidates and can mitigate the safety risk, since they ensure enhanced thermal and mechanical stability.[21] By applying SSEs, columnar silicon thin film electrodes can be confined under a rigid SE layer via external pressure ensuring mechanical integrity of the SEI film and suppressing deformations and volume expansion of the silicon anode.

Motivating results have been already reported for SSEs coupled with Si electrodes in half-cell configuration showing ICE around 95% and performing excellent at areal capacities of 2.5–4.4 mAh cm\(^{-2}\) over 100 cycles with capacity retention about 70%.[22,23]

However, only few publications show extensive full-cell studies with actual cathode materials. In this study, we aim to close this gap and demonstrate the utilization of silicon anodes in solid-state half and full cells. Therefore, we combined an argyrodite-type solid electrolyte (SE) Li\(_3\)PS\(_4\)Cl with a columnar silicon anode with practical areal capacity of 3.5 mAh cm\(^{-2}\).

To our knowledge, this is the highest areal capacity reported so far for a silicon structure that shows stable cycling in an NCM full cell and the first time silicon columns were utilized in sulfide based solid electrolytes.[24] Furthermore, we demonstrate high charging rate (0.9 mA cm\(^{-2}\)) and rate stability (up to 1.5 mA cm\(^{-2}\)) at room temperature, while lithium based solid-state cells are usually cycled at low currents (<0.1 mA cm\(^{-2}\)) or higher temperatures (>60 °C).[25] The approach implies intrinsic differences to common liquid electrolyte setups, which enhances full-cell capacity retention. The solid electrolyte is in intimate contact with the anode but does not penetrate in the gaps between single columns reducing the surface area for side reactions. Hence, a 2D lateral solid electrolyte interface is formed, which is mechanically stabilized by external pressure (Figure 1). Usually, such a 2D contact can cause high contact resistance, but lithiated silicon exhibits high Li\(^+\) ion conductivity. Furthermore, copper dendrites of the substrate guarantee a good electronic conductivity along the columns and a strong adhesion to the current collector, simplifying also cell design (no binder and conductive additive).[26] During cycling, the columns revealed a 1D breathing behavior in vertical direction similar to Li metal anodes. This 1D breathing can be compensated by intrinsic porosity of the silicon columnar structure and an external pressure on the cell stack, which also stabilizes the 2D SEI. The herein applied external pressure (20 MPa) also suppresses delamination of the Si columns from the current collector while maintaining compactness of the silicon film.

During cycling, the columns revealed only a 1D breathing behavior in vertical direction similar to Li metal anodes. This 1D growth and contractions can be compensated by an external pressure on the cell stack, which also stabilizes the 2D SEI. In contrast to Li metal anodes, silicon columns eliminate the risk of dendrite formation, short circuiting and most importantly dead material loss. The combination with a solid electrolyte leads to enhanced capacity retention in full cells compared to liquid electrolytes.

2. Results and Discussion

2.1. Columnar Silicon Anode Characterization

The macroscopic structure of as-produced col-Si was analyzed via SEM Imaging (Figure 2A,B). In the top view (Figure 2A) a compact columnar morphology is seen and some columns appear to be more bulky than others, which creates a certain surface roughness. Si columns demonstrate intimate adhesion to the Cu foil and the film thickness (Si column height) measured to be 6–8 µm in average as estimated from the cross section (Figure 2B).

Figure 1. Reversible volume changes of columnar silicon anode systems upon (de-)lithiation under ASSB cell configuration. The dendritic substrate ensures excellent adhesion of silicon film on current collector while promoting electric conductivity. The solid electrolyte (SE), which is in 2D contact with silicon electrode, maintains mechanical integrity of SEI layer and accommodates 1D growth of silicon columns.
The X-ray diffraction (XRD) pattern (Figure 2C) reveals that silicon is present in amorphous phase, since almost all peaks match with copper reference (Cu-Ref.) peaks originating from Cu foil used as current collector of Si anode. A tiny peak is observable at $2\theta = 69.13^\circ$ that corresponds to (400) of crystalline Si-wafer which is utilized as sample holder.

In the Raman spectrum (Figure 2D), no band at 520 cm$^{-1}$ is visible, which is an indication for the absence of crystalline silicon phase. Instead, a number of peaks are detected around 150, 318, 386, and 486 cm$^{-1}$. These are characteristic vibrational modes of amorphous silicon (a-Si) and are attributed to transversal acoustic (150 cm$^{-1}$), longitudinal acoustic (318 cm$^{-1}$), transversal optic (386 cm$^{-1}$), and longitudinal optic (486 cm$^{-1}$) phonons.[29] The bands centered at 630 cm$^{-1}$ are ascribed to a combination of transversal optic and acoustic phonons.

2.2. Electrochemical Performance of Columnar Silicon Anodes in Half Cells

Initially, the electrochemical characterization of columnar silicon anodes is carried out in half-cell configuration via galvanostatic cycling with potential limitation (GCPL), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) techniques (Figure 3A–C). In the initial cycle (Figure 3A), upon discharging (lithiation) a sudden voltage drop from open circuit voltage (OCV = 1.8 V) to 0.22 V was observed. Thereafter, the cell voltage increases again to a potential of around 0.25 V versus Li/Li$^+$, when pristine a-Si begins the alloying with lithium, forming Li-Si binary phases.[30] Afterward, the anode is lithiated at a second plateau around 0.1 V reaching more than 2000 mAh g$^{-1}$Si. At the end of discharge step, col-Si reaches a specific capacity of 3459 mAh g$^{-1}$Si, ≈96% of theoretical capacity (3579 mAh g$^{-1}$Si). The rapid voltage drop at the beginning of discharge correlates with the poor ionic conductivity of silicon in the pristine state that might govern sudden local lithiation, more specifically, growth of some Si columns. This local expansion in col-Si structure can partially push SE layer outward that leads to a more pronounced voltage drop for some samples and contact loss between surrounding pristine Si columns and SE layer in the beginning of the first charge (Figure 3D). Thus, these silicon sites that lost mechanical integrity with the SE layer are not addressed anymore, resulting in ≈20% reduced specific capacity (Figure S1, Supporting Information). Hence, a low current should be chosen during first lithiation to avoid an extreme voltage drop and contact loss. During charging (delithiation), the extracted capacity was calculated to be 2912 mAh g$^{-1}$Si giving a reasonable ICE ≈84% (Figure 3A). Here, it is worth noting that the counter electrode Li metal exhibits strong breathing behavior as well affecting ICE severely. The silicon anodes were further examined ex situ by SEM to depict morphological changes during cycling. Test cells were disassembled and the electrodes were cut in half to record a top and a cross view (Figure S2, Supporting Information). After first charge, the electrode still exhibits a flat surface and a clear morphology change is observable as the entire layer seems more distorted. Due to the applied pressure, solid electrolyte particles are sticking to the surface of the columns. Both, Young’s modulus and hardness were found to decrease as a-Si was lithiated.[31] Hence, the volume change cannot be
clearly monitored. The stress is compensated by the cell casing of the solid-state electrode, which maintains the high pressure in contrast to conventional liquid electrolyte cell casings. Hence, the electrode only expands in vertical direction toward the electrolyte. Comparable electrodes that were charged in a pouch cell with liquid electrolyte show massive deformation of the current collector.[17,19] After discharge, the silicon anode contracts to its initial volume. The columns shrink and form isles of agglomerated columns. It is obvious that the enormous pressure during first charge also induces a deformation of silicon columns, which become more ductile during lithiation.[32] Due to the contraction of the columns, the cell stack experiences a pressure drop and the torque cell setup cannot preserve the initial pressure. Hence, columns also contract in the horizontal plane forming isles. Significant area (≈43%) of the electrode (Table S1 and Figure S3, Supporting Information) seems be uncovered with silicon after delithiation and contraction, which shows that the silicon anode experiences immense mechanical stress during charging and expanding.

In the CV measurement (Figure 3B) two distinctive peaks are observable in the cathodic scan at 0.16 and 0.04 V through first lithiation (black curve), which shift their positions toward 0.21 and 0.05 V in subsequent cycles, respectively. The appearance of the cathodic peaks at lower potentials is a sign for higher resistance in the first cycle in comparison with the consecutive cycles, in agreement with the voltage drop observed during the first cycle. In the pristine state, a-Si is a poor ion conductor and therefore hampers Li$^+$ insertion which accounts for enhanced resistance through initial a-Si→a-Li$_x$Si phase transformation. The peaks at 0.05 and 0.21 V are commonly ascribed to alloying of a-Si with lithium and formation of various binary a-Li$_x$Si phases.[33] It is also noteworthy that only a low background current is visible in the potential range from 2.0 to 0.16 V through initial cathodic scan (first lithiation). Normally, current peaks are observable at 0.5 V versus Li, which originate from decomposition of electrolyte (SEI formation)[34,35] reaction of lithium with Si dangling bonds[36] and reduction of surface contaminants such as SiO$_2$.[37] The current density at 0.5 V (~8.5 × 10$^{-4}$ mA cm$^{-2}$) is in the same range as for a reference nickel foil electrode with the same electrode size and peaks are merely present (Figure S4, Supporting Information). Hence, the electrolyte does not penetrate the voids between the columns, which would result in a pronounced SEI formation peak. Here, 2D contact at SE|col-Si interphase reduces reactive...
contact area which assists to suppress SEI formation significantly, revealing an advantage of columnar silicon anodes.

In the cathodic scan, a-Si exhibits three phase transformations, i.e., from a-Si to PI phase (Li-50 at% Si; LiSi) at 0.21 V, in parallel with the formation of PII phase (Li-30 at% Si; Li2Si) from PI and formation of PIII (Li-24 at%; Li1.16Si) from PII at 0.05 V.[38] In the anodic scan two peaks appear at 0.29 and 0.49 V, which are simply reverse transformation processes; PIII-PII, PII-I, and formation of a-Si, respectively.[39]

EIS was performed in order to examine charge transfer kinetics of amorphous columnar silicon anodes in half-cell configuration versus Li. EIS data were recorded upon first lithiation at various equilibrium potentials ranging from 1.0 to 0.01 V with a voltage interval of 0.05 V. The fit parameters and ionic conductivity values in Table 1 were used to fit the impedance spectra. Here, Qgb, Qct, and Qw are constant phase elements (CPE, Q), which are formulated by $Q = C \alpha F^{-1}$, where $C$ is the capacitance, $\alpha$ is the resistance and $\alpha$ is the fit factor. $R_{gb}$ (for 0.25–0.2 V) and $R_{ct}$ (for 0.15–0.01 V) could not be resolved due to overlapping of respective semicircles.

| Potential [V] | $R_{gb}$ [Ω cm²] | $R_{ct}$ [Ω cm²] | $C_{gb}$ [F cm⁻²] | $Q_{ct}$ [F cm⁻²] | $\sigma$ [$\mu$S cm⁻¹] |
|--------------|------------------|------------------|------------------|------------------|------------------|
| 0.25         | 32.1             | -                | -                | -                | 2.0×10⁻⁴         | 2.35             |
| 0.20         | 32.1             | -                | -                | -                | 1.5×10⁻⁴         | 2.35             |
| 0.15         | 31.0             | 1.6              | 4.1×10⁻²         | -                | -                | 2.43             |
| 0.10         | 29.6             | 2.1              | 2.2×10⁻²         | -                | -                | 2.54             |
| 0.05         | 26.4             | 2.5              | 2.0×10⁻²         | -                | -                | 2.85             |
| 0.01         | 26.3             | 2.7              | 1.8×10⁻²         | -                | -                | 2.86             |

The equivalent circuit $R_{gb}(Q_{gb})(R_{ct}(Q_{ct}))Q_{w}$ was used to fit the impedance spectra. Here, $Q_{gb}$, $Q_{ct}$, and $Q_{w}$ are constant phase elements (CPE, Q), which are formulated by $Q = C \alpha F^{-1}$, where $C$ is the capacitance, $\alpha$ is the resistance and $\alpha$ is the fit factor. $R_{gb}$ (for 0.25–0.2 V) and $R_{ct}$ (for 0.15–0.01 V) could not be resolved due to overlapping of respective semicircles.

The EIS spectra (Figure 3C) basically can be divided into two regions, i.e., potential range I (PRI) and potential range II (PRII), whose Nyquist plots differ each other remarkably in terms of resistance and characteristic frequencies (time constants). In PRI (at 0.25 V) we attribute the semicircle with the frequency minima of 0.5 kHz to the charge transfer resistance ($\approx 570 \Omega$ cm²) that originates from SEI formation at a-Si|SE interface and rigid phase boundary between a-LiSi and a-Si (Figure 3D) while ascribing the second widening semicircle in LF to the Li⁺ diffusion resistance ($\approx 2666 \Omega$ cm², Warburg Impedance, $Q_{w}$) in the bulk a-Li,Si phases and a-Si. In both regions, the intersection point on the x-axis at the highest frequency gives the bulk resistance of the SE ($R_{bulk}$). At 0.20 V both semicircles are depressed since binary a-Li,Si phases keep forming at lower potentials that are more ionically conductive than pristine a-Si. Further Li⁺ insertion below 0.2 V drives EIS spectra to PRII, where above-mentioned semicircles completely vanished and the overall impedance of the anode suddenly decreases drastically. This event corresponds to the first lithiation peak at 0.16 V in the CV measurement (Figure 2B). Instead, an arc with the frequency minima of 10 kHz is formed together with a diffusion tail in LF. In liquid electrolytes, a further semicircle is well recognized in the LF region originating from promoted SEI formation at the column surface. In the solid system, SEI formation is minimized due to the 2D contact and a further semicircle is barely resolved in the Nyquist plot (Figure S8, Supporting Information). The tiny arc resembles the grain boundary resistance ($R_{gb}$) of the SE which keeps relatively constant (2.0 ± 0.5 Ω cm²) until the end of lithiation (0.01 V). Perhaps, such small $R_{gb}$ is embedded in $R_{ct}$ in the HF region at higher potentials (0.2 and 0.25 V) as well but cannot being deconvoluted due to overlapping of respective semicircles. The Li⁺ ion conductivity of SE layer ($\sigma_i$), calculated by the value of $R_{bulk} + R_{gb}$ increases from 2.12 to 2.59 mS cm⁻¹ over the course lithiation which in the range of ionic conductivity values reported in the literature.[39] This behavior is ascribed to 1D growth of Si columns that decreases $R_{bulk} + R_{gb}$ by repulsing the SE layer resulting in compact SE film. Consequently, $\sigma_i$ rises gradually from 0.25 to 0.01 V.

2.3. Electrochemical Performance of Columnar Silicon Anodes in Full Cells

In half-cell configuration, where Li metal is used as counter electrode, Li losses for, e.g., SEI formation can be accommodated significantly via excess lithium from Li anode. However, this compensation is not possible, when combining silicon anodes with Ni-rich NCM (LiNi0.9Co0.05Mn0.05) cathodes that yield the maximum capacity of 203 mAh g⁻¹ NCM. This value was determined in typical NCM|SE|Li-In half cells as a reference measurement. Li-In anodes allow a reliable characterization of cathode material, since the risk of short circuits is minimized and excess lithium is present to compensate lithium losses. Silicon anodes were oversized by 30% (n/p = 1.3) to avoid undesired lithium plating on top of the electrode. The 2D interface leads to a special effect, which is observed during the first charge plateau. In its pristine state, the columnar anodes exhibit a very low lithium ion conductivity, which increases rapidly once first
lithium is inserted in the silicon lattice. The same effect was observed in the half-cell setup and leads to a voltage peak at the beginning of the first charge. At an n/p ratio of 1.3, the voltage of the anode at the end of the charge is 90 mV versus Li, which was determined by a 3-electrode setup (Figure S9, Supporting Information). Hence, the NCM cathode is charged to 4.34 V versus Li at a cut-off voltage of 4.25 V versus Si. Consequently, the voltage plateau at the end of the charge step looks slightly different to the NCM|SE|Li-In half cell.

The discharge voltage profile is also influenced by the voltage profile of the silicon anode, which can be delithiated up to 1.0 V versus Li or even higher (section 2.2) instead of delivering a constant voltage plateau like lithium or indium. Hence, the lower cut-off voltage was reduced to 2.0 V to utilize the whole anode. During first discharge, 203 mAh g⁻¹ NCM was obtained (Figure 4A). Despite the fact that no lithium excess is present in the silicon anode, this value is similar to the cell with Li-In anode and hence surprisingly high (Figure S10, Supporting Information).

Furthermore, the first cycle CE (87.5%) is comparable to liquid electrolyte based full cells (87%).[17] Sulfide based solid electrolytes are known to show a comparatively low ICE originating from side reactions between the electrolyte and carbon additives or cathode material. Contrary to the liquid electrolyte system, this does not lead to lithium losses, as can be seen from the similar capacity that was extracted in the first cycle. In line with the Li-In anode, columnar silicon anode has only a 2D interface to the electrolyte, which drastically reduces the contact surface and the potential for side reactions at the anode side. Even at the highest discharge current of 1.4 mA, the discharge capacity remains at remarkably high 160 mAh g⁻¹ NCM, which is the same value as for the indium reference cell. Thus, the silicon anodes provide a reasonable power capability, despite the columnar architecture and the 2D interface.

During long-term cycling, a fresh cell was charged and discharged at a low current of 0.066 mA (0.03 C) for the first cycle and then discharged and charged with 0.19 mA (0.08 C) and 0.95 mA (0.4 C), respectively. The cut-off voltage was reduced to 4.0 V to compensate the high anode potential and conserve the NCM structure.[40] Noteworthy, the CE in the following cycles is 99.95% while a comparable cell with LP30 liquid electrolyte and 10 vol% FEC additive has a rather low CE of only 98–99% resulting from continuous SEI formation at the anode side (Figure 4B). The liquid electrolyte diffuses in the column structure and the high volume change of silicon during cycling leads the fresh silicon surface and electrolyte depletion in every cycle. In contrast, the 2D interface of silicon columns and the solid electrolyte leads to a stable SEI that remains intact during cycling. The liquid electrolyte cell has a similar balancing like the solid electrolyte cell and yields an initial capacity of 156 mAh g⁻¹ NCM. After 50 cycles, a capacity of 79 mAh g⁻¹ NCM is obtained from the liquid cell, representing low capacity retention of only 50.6%. The solid electrolyte full cell instead exhibits capacity retention of 92.8% after 50 cycles, which can be regarded as an outstanding result since the entire cell stack is breathing and no active pressure adjustment is applied on the test cell. Hence, the pressure cannot be preserved during cycling. This is a tremendous improvement compared to any liquid electrolyte system due to the 2D interface.[41] It is also noteworthy that the areal capacity of the silicon anode (3.5 mAh cm⁻²) is rather high compared to full cells in the literature (≤2 mAh cm⁻²).[23,42] Even after 100 cycles,
118 mAh g\(^{-1}\) (82% of the initial capacity) are still obtained from the cell (Figure 4C). For more than 350 cycles, no short circuits are observed. A continuous increase of the overvoltage is observed by time, which explains the steady decrease of the cell performance.

A second cell was switched to a symmetric test plan after 10 cycles and was charged/discharged with 0.4 C at room temperature (Figure 4D). Consequently, the capacity decreases slightly faster than before increasing the charge current, but no short circuits occur in 35 cycles before the cell was stopped. This is a huge benefit in terms of dendrite formation and safety compared to other high energy anodes like lithium. At room temperature, micro and macro short circuits occur very easily leading to capacity decay or complete cell failure, respectively (Figure S11, Supporting Information). Lithium metal anodes can only be charged at such high rates and loadings, when the operation temperature is increased to above 60 °C and even then, short circuits are a high risk. Contrary to lithium metal anodes, our silicon anodes combine high volumetric energy densities with the possibility to perform at ambient conditions.

Most particle based composites experience breathing behavior in all three dimensions, which easily leads to a mechanical deterioration of the cell stack. A 1D breathing, as it is observed also for Li anodes can be compensated by the cell housing, if a certain pressure is applied. In our small test cells, a pressure is applied by using a torque screw, which sets the cell casing under tension and applies a moderate pressure on the cell stack. Given the fact that the cell case is made from POM polymers, the value is expected to be rather low and the pressure cannot be preserved during cycling. However under these conditions, also other areal loadings were tested, but the increased breathing of the silicon anode lead to faster cell degradation for 4.5 and 9 mAh cm\(^{-2}\) (Figure S12, Supporting Information).

It is possible that higher loadings are achievable with an active pressure control in future.

To investigate the breathing behavior of columnar silicon anodes under constant pressure, a small pouch cell was fabricated by stacking a dry-film NCM-cathode with a columnar silicon anode. The small pouch cell had a nominal capacity of 8 mAh calculated from the theoretical capacity of NCM. A test setup was designed that is able to measure pressure and thickness changes in operando and put the cell under constant pressure by a spring. The pouch cell was placed in the test setup at 4.2 MPa and charged up to 4.0 V (Figure 5A). During first charge, the pressure increases constantly up to 4.3 MPa. The pressure change is caused by an expansion of the cell stack, enhancing pressure by 0.1 MPa, which compresses the spring element in the setup. This pressure increase can be translated into a thickness change of 11 µm meaning that the electrode expanded to ≈250% of its initial volume. This is a realistic value because the anode is not fully utilized at 4.0 V
with an n/p of 1.3. At 3.5 V, a plateau region is observed in the thickness and pressure signal. According to the three electrode measurement, the silicon anode has a potential of 0.2 V versus Li and a-Li$_x$Si is formed at this point. The columns become more ductile and deform under the pressure. Impedance measurements indicate also the SE layer to further compact, since the ionic bulk conductivity decreased slightly. It is important to see that the cell thickness reaches its initial value after the discharge is completed. This supports our hypothesis of a 1D breathing mechanism that can be compensated by an external pressure. If the pressure is too low, the discharge step leads to a partial contact loss between anode and solid electrolyte, which is seen from the delayed pressure drop in the discharge step of a second pouch cell pressurized at only 1 MPa and the fact that the initial thickness of the cell is not reached again after discharge (Figure S13, Supporting Information). A deformation of columns is not observed in the first charging step at 1 MPa. However, both pouch cells, pressurized at 1 and 4.2 MPa, showed micro short circuits and fast degradation after 25 cycles and the cells were stopped. For a larger cell format, it becomes more difficult to homogeneously apply the pressure. Hence, partial delamination took place and the local current density exceeded a critical value resulting in lithium plating and cell degradation.

Since a pressure of 4.2 MPa is not high enough to preserve the interface between anode and electrolyte, a new set of pouch cells was prepared and pressurized at 20 and 25 MPa in the same setup. First charge and discharge voltage plateaus are similar to the results obtained by the torque screw setup in the same setup. First charge and discharge voltage plateaus of pouch cells was prepared and pressurized at 20 and 25 MPa. However, both pouch cells, pressurized at 1 and 4.2 MPa, showed micro short circuits and fast degradation after 25 cycles and the cells were stopped. For a larger cell format, it becomes more difficult to homogeneously apply the pressure. Hence, partial delamination took place and the local current density exceeded a critical value resulting in lithium plating and cell degradation.

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4. Experimental Section

Material Preparation: To prepare cathode active material (AM), a LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (particle size 4–5 µm; see the Supporting Information) was coated with Li$_2$O-ZrO$_2$ (LZO) by the sol–gel method. The LZO coating sol was synthesized from 2-propanol, lithium methoxide (equivalent of 10 wt% lithium methoxide in methanol solution) and zirconium(IV) tetrapropoxide (Zr(OCH$_3$)$_4$) in the molar ratio 200:2:1. NCM (LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$) was dispersed in the solution above and stirred for 1 h for homogenous wetting of NCM particles by the coating precursors. The 2-propanol was evaporated in vacuum at 50 °C (water bath) assisted by ultrasonic treatment, in order to avoid agglomeration of the NCM particles. After filtration, the precursor was heated at 350 °C for 1 h under air, and the LZO coated NCM was obtained. The crystal structure of NCM was found to be α-NaFeO$_2$ with R3m space group and did not change even after the coating procedure. A uniform LZO coating with a thickness of ~3.8 nm had formed in (X-Ray) amorphous phase (Figure S16, Supporting Information).

The solid electrolyte powder (particle size: 3–4 µm; Supporting Information), crystalline LiP$_2$S$_3$Cl with high purity, was synthesized by mechanical milling in accordance with the previous studies (Figures S17 and S18 and Table S2, Supporting Information). Appropriate amounts of Li$_2$S (Alfa Aesar, 99%), LiCl (Alfa Aesar, 99%), and P$_2$S$_3$ (Sigma-Aldrich Co., 99%) were weighed and mixed in an agate mortar for about 20 min. The mixture was transferred in a zirconia (Zr) bowl with Zr spheres (10 mm) and sealed in an argon-filled box. High-energy ball milling was carried out by using the planetary mill P5 (Fritsch, Germany) for 16.5 h with a rotational speed of 380 rpm. After the milling, the mixture powder was wrapped in a gold foil and placed in a carbon crucible. Thereafter, the carbon crucible was set into a quartz tube and the tube was then vacuum sealed. The quartz tube was heated to 550 °C and annealed for

3. Conclusions

Columnar silicon anodes fabricated by a scalable PVD process show excellent cycling performance in solid-state half- and full cells. An intimate contact with the current collector assures the lithiation of the silicon material leading to good electronic/ionic conductivity after first lithiation. This concept enables higher charging rates at room temperature without short circuits compared to lithium metal anodes. Despite the large volume expansion during cycling, the 2D interface toward the solid electrolyte reduces the active contact area for side reactions and effectively eliminates the depletion of electrolyte in repeated cycling. The result is higher capacity retention and ICE compared to liquid electrolyte systems.

To the best of our knowledge, no other publication shows stable cycling of pure silicon thin film anodes with a high areal capacity of 3.5 mAh cm$^{-2}$. Such silicon film anodes were investigated in half cells to analyze morphological changes and phase transitions during lithiation of the anode. Potential-dependent EIS measurements demonstrated that the rigid phase boundary between a-Si and a-Li$_x$Si formed upon first lithiation impedes Li$^+$ insertion and diffusion, increasing inner cell resistance considerably ($R_{CT} + Q_N = 3236$ Ω cm$^{-2}$) while 1D vertical growth of col-Si promotes ionic conductivity of SE (from 2.35 to 2.86 mS cm$^{-1}$) by consolidating SE the layer. Full-cell tests revealed an outstanding capacity retention of 82% after 100 cycles and reversible cycling without short circuiting for more than 350 cycles. Even at relatively high charging rates (1 mA cm$^{-2}$) and room temperature no short circuits were observed, clearly outperforming conventional lithium metal anodes. Finally, small pouch cells were fabricated and it was shown that the capacity retention is even further enhanced by pressure control. An operando test setup gives insights into the thickness change during charge and discharge providing a valuable methodology for future mechanistic studies. Understanding the role of pressure evolution and active pressure control will be crucial for the commercialization of col-Si based solid-state batteries in electric vehicles and stationary storage systems.
1 h using a muffle furnace. After the heat treatment, the quartz tube was slowly cooled down to room temperature.

For the anode material, a columnar silicon film with approximately silicon loading of 1.00 mg cm$^{-2}$ corresponding to the areal capacity of 3.5 mAh cm$^{-2}$ was synthesized via a magnetron sputtering (see ref. [19] for details). Lithium and indium foils were purchased with a thickness of 50 and 100 µm, respectively.

**Electrode Preparation:** A powdered composite electrode was manually prepared by mixing the NCM, conductive carbon additive vapor-grown carbon nanofibers (VC-CNFF), and solid electrolyte (Li$_2$PS$_5$Cl, particle size: 1-2 µm, Supporting Information) in the mass ratio of 85:2:13 for 30 min in an agate mortar. To fabricate a free-standing and flexible dry-film, the above prepared powder electrode was mixed with 0.3 wt% of polytetrafluoroethylene (PTFE, emulsion polymerized fine powder; particle size 300–700 µm; softening point 320–330 °C; molecular weight $10^5$–$10^6$ g mol$^{-1}$) in a mortar at 100 °C.[45] After 1 min of mixing and shearing, a single flake was formed. The flake was placed on a hot plate and rolled out to the desired thickness (≈100 µm). Each sample was prepared at least twice to confirm the reproducibility of the process. To prepare a free-standing electrolyte film, the solid electrolyte was mixed with 0.15 wt% of PTFE and treated in the same way as the cathode film.

**Preparation of a test-cell:** Test cells were prepared in half- and full-cell configurations for investigating the basic characteristics of the cathode composite and a-Si film such as the charge/discharge potential profiles, rate discharge capability, and the cell internal resistance.

The full cell was prepared by using a die with a diameter of 13 mm as described previously.[46] The cell had a stainless steel outer casing with a Teflon liner (Figure S19, Supporting Information). For a typical test cell, 150 mg (750 µm) of the electrolyte Li$_2$PS$_5$Cl powder (particle size: 3–4 µm, Supporting Information) was uniformly spread inside the die by a microspatula. Next, the powder was once temporally compressed and compacted into a pellet. Then, 15 mg of cathode composite powder was homogeneously distributed across the compacted electrolyte surface in the die. Then the cathode layer was temporarily compressed. On the opposite side of the cell stack, a lithium–indium alloy anode (Li-In) was placed and compressed as described.[46] All the cell components were again pressed together and completely pelletized by using a hydraulic press (4 tons for 30 s were applied).

After compression, the cell stack was placed inside the outer steel casing; were a screw maintains the electric contact in the cell. The screw was fastened at 3.0 Nm using a preset torque.

Above procedures were applied to assemble half cells. Instead of cathode composite and Li-In electrodes, silicon anode and Li metal (50 µm) were placed at the both sides of the SE pellet as working and counter electrode, respectively.

To assemble the pouch cell, positive electrode (2.5 × 2.5 cm$^2$) was laminated on a primer coated aluminum foil. Positive and negative electrodes were separated by a free-standing bespoke SE membrane. The cell stack was placed inside a pouch bag and sealed under vacuum. Afterward, the cell was compressed under 300 MPa. All above mentioned processes were carried out in an Ar-filled glove box (≤0.1 ppm H$_2$O and O$_2$). After compression, the cell was placed in a pressurized setup. The pressure was applied from the top by a spring, which could be adjusted precisely by screws. The pressure sensor was placed below the pouch cell monitoring pressure changes during cycling by a CMU system (Basylec, Germany). At the same time, contraction of the cell was measured by a length sensor. The breathing of the cell had only a minor influence on the pressure applied by the spring.

**Characterization:** The powder XRD (CuK$\alpha$, 40 kV, 40 mA) pattern was measured using a D5005 XRD system (Siemens, Germany) for verifying crystallinity of silicon anodes and crystalline side products of dry-film preparation at room temperature. Kapton tape (3M) was used to prevent degradation due to moisture.

SEM images were obtained using a scanning electron microscopy JSM-6060 (JEOL, Japan). Raman spectroscopy was conducted to identify crystallinity of columnar silicon anodes using a Raman microscope (micro-Raman Spectrometer, Renishaw inVia PLC) with an excitation laser wavelength of 514 nm and a 50x lens. The laser beam density at the specimen was 0.44 mW µm$^{-2}$ and the acquisition time was 5 × 60 s.

EIS was performed at various equilibrium potentials using a VSP-300 (Bio-Logic, France) controlled by a computer. The half cell was cycled within the potential window of 0.01–1 V with a current density of 0.05 mA cm$^{-2}$ per voltage interval of 0.05 V. A constant voltage step was performed for each step until the applied current reached 0.01 mA to equilibrate the given potential. At the end of each potential step, EIS was carried out with an amplitude of 10 mV in a frequency range of 0.1 Hz–1 MHz at 40 °C under ambient pressure. The EIS results were analyzed using EC-Lab (ver. 11.20).

For the full cells, the standard rate performance test plan consisted of three different discharge currents ranging from 0.07 to 1.5 mA cm$^{-2}$ while the charging rate was kept constant at 0.15 mA cm$^{-2}$ including a CV step. The standard cutoff voltages for the cycle test were set at 3.63 and 1.93 V for charge and discharge, respectively. The cycle and rate performances of the cell were measured by a battery tester CTS-Lab (BaSyTec, Germany).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

all-solid-state batteries, columnar silicon anodes, in situ investigation, thioephosphate solid electrolytes, volumetric energy density
