

Advances in 3D silicon-based lithium-ion microbatteries



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14th Sep 23

Dear Mr Refino,

Thank you for submitting your manuscript, "From micro to mighty: How does 3D silicon microbattery achieve high applicability despite its small size?", to Communications Materials. It has now been seen by 4 referees, whose comments are appended below. You will see that while they find your work of interest, some important points are raised. We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

In particular, both Reviewers 1 and 4 suggest adding a discussion/perspective on new developments and the technological gap in current prototypes, in addition to what is needed for actual implementation. Both Reviewers 1 and 3 suggest discussions about advantages and disadvantages of certain components, such as the 3D architectures and cathode materials. Reviewer 4 requests to discuss the electrochemistry of silicon, challenges, and opportunities in the introduction, as well as points on LIPON and packaging.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

- A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.
- A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.
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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Dr Jet-Sing Lee
Associate Editor
Communications Materials
orcid.org/0000-0002-6740-8700

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In the submitted work, the authors present an extensive review paper about 3D-micro-Lithium-Ion batteries (LIBs) with the aim to address topics like “basic principles”, “materials”, “manufacturing methods” and “recent applications”.

Questions of the editor:

1) Do you think this Review is interesting and/or useful to other researchers working in the field?
Yes, the review is interesting for researchers in this field. Nevertheless, a major revision is needed.

2) Does the paper provide adequate critical discussion of the literature, or does it only summarize previous research efforts?

Basically, the paper provides critical discussion of the cited scientific works. It is recommended to carve out even more the application relevant differences, the advantages / disadvantages of the described 3D-architectures (chapter 3) and 3D-LIB variants (chapter 3.1-3.5). Background: Is every microbattery-design appropriate for every on-chip application (high energy demand-low energy demand, expected/desired lifetime of maybe weeks or maybe years, operating at room temperature or at elevated temperatures, etc.)

3) Do you think the paper is sufficiently forward-looking, and does it provide guidance for future research?

The conclusion (chapter 4) outlines the possible future and possible future success of 3D-LIBs primarily from the semiconductor manufacturing side. Important new developments related to material science like room temperature solid state electrolytes (LLZO, LATP, LGPS, etc.[1]), new liquid high voltage electrolytes [2-4], Ni-rich cathode materials (NMC 811, 955 or NiO₂) [5, 6] and their exciting impact on the energy density are not discussed. There are also new production techniques like femtosecond laser ablation with the potential to lower per piece production costs that are suggested to be mentioned.

4) Are there any parts of the paper that should be expanded, or parts that you think should be removed? For example, is the balance between topics appropriate?

Chapter 2 covers beside the “concept of microbattery” also possible cathode materials and the benefit of silicon as 3D-anode. The discussion of cathode materials focusses very much on the production of these materials but less on their individual properties that are important if applied in microbatteries (e.g. the high density of LCO enabling high volumetric charge densities, the tendency of LiMn₂O₄ to rapidly age at elevated temperatures (Mn-dissolution), the low electric conductivity and Li-diffusivity of undoped LFP and the need to add conductive agents, etc.). Important cathode materials like NMC 622 or 811 are not discussed at all. It is suggested to fundamentally revise the

“cathode part” (line 192-283).

The key material “silicon” is discussed with regards to its geometrical ambience inside the battery. It is suggested to cover crucial topics like the “ledge mechanism” [7] during lithiation and the anisotropic dilatation of crystalline Si during Li-uptake [8, 9] as these effects have an impact on the Si-material selection, the applied crystallographic orientation and ageing during cycling.

5) Are the figures and tables useful in communicating the author’s key points?

All figures, table 1 and 2 are useful and from appropriate quality. Table 3 benchmarking different microbattery technologies needs a major revision because of obviously mixing up values like “capacity retention” and “coulombic efficiency”. The quotation of specific- and areal capacity in the same row makes a direct comparison unfortunately difficult. It is suggested to introduce two dedicated rows. Please find attached further information under “detailed comments”.

Detailed comments:

Line 85: If intended so, a change to “...Si has a relatively low lithiation potential...” is suggested.

Line 139-142: The specific capacity (mAh/g) is always related to mass and therefore “gravimetric”. A “specific volumetric capacity” is unfamiliar to the reviewer. If charge is related to certain volume (mAh/cm³), it should be named “charge density” or “volumetric charge capacity”.

Line 142: The SI unit symbol for cubic centimeter is “cm³”, to a lesser extent “cc”

Line 194, Table 1: How is the “energy density” of a cathode material measured?

Line 229: Due to the low specific capacity, NMC 111 seems rather unattractive for microbatteries. The (additional) presentation of NMC 622 or 811 is suggested.

Line 300: The advantage of LiClO₄ over LiPF₆ is the absence of HF or HF-related electrolyte components. LiClO₄ enables so the application of Na-, K-containing glass cell components (BS 3.3 glass) that are available in semiconductor manufacturing processes.

Line 510: The cited colleague from Eindhoven is spelled “Baggetto”.

Line 578, table 2, “dry etching”: Reference [100] is missing.

Line 893: Wrong units. Reference [104] published values of “136 uAh.cm⁻²” and “181 uWh.cm⁻²”, not “136 Ah.cm⁻²” and “181 Wh.cm⁻²”.

Line 901-920: Introduced by a sentence about “Swiss-roll micro battery” (line 897), the text from line 901 to 920 is about a microbattery with vertical columns [76] that are discussed in chapter 3.2. It is suggested to insert this text block after removing redundancies at e.g. line 802.

Line 1025, table 3, row 3: The quotation of specific- and areal capacity in the same row makes a direct comparison difficult. It is suggested to introduce two dedicated rows.

Line 1025, table 3, row 5: Cited values like “capacity retention” and “coulombic efficiency” are obviously mixed up. Please check and revise.

Line 1025, table 3: The performance of cell in reference [76] that was cited several times as reference cell is missing. It is suggested to add two lines:

- “High-power” design: Vertical pillars, capacity 3.1 mAh.cm⁻², rate 181 mA.cm⁻¹, 200 cycles at 17% capacity retention, CE >99.9 %

- “High-energy” design: Vertical pillars, capacity 9.4 mAh.cm⁻², rate 0.78 mA.cm⁻¹, 100 cycles, CE >99.5 %

References:

[1] Krauskopf, T.; Richter, F. H.; Zeier, W. G.; Janek, J., Physicochemical Concepts of the Lithium Metal Anode in Solid-State Batteries. Chemical Reviews 2020, 120, (15), 7745-7794.

[2] Liu, Q. Q.; Xiong, D. J.; Petibon, R.; Du, C. Y.; Dahn, J. R., Gas Evolution during Unwanted Lithium

Plating in Li-Ion Cells with EC-Based or EC-Free Electrolytes. *Journal of the Electrochemical Society* 2016, 163, (14), A3010-A3015.

[3] Petibon, R.; Harlow, J.; Le, D. B.; Dahn, J. R., The use of ethyl acetate and methyl propanoate in combination with vinylene carbonate as ethylene carbonate-free solvent blends for electrolytes in Li-ion batteries. *Electrochimica Acta* 2015, 154, (0), 227-234.

[4] Fan, T.; Kai, W.; Harika, V. K.; Liu, C.; Nimkar, A.; Leifer, N.; Maiti, S.; Grinblat, J.; Tsubery, M. N.; Liu, X.; Wang, M.; Xu, L.; Lu, Y.; Min, Y.; Shpigel, N.; Aurbach, D., Operating Highly Stable LiCoO₂ Cathodes up to 4.6 V by Using an Effective Integration of Surface Engineering and Electrolyte Solutions Selection. *Advanced Functional Materials* 2022.

[5] Liu, Y.; Wu, H.; Wang, Y.; Li, K.; Yin, S.; Dahn, J. R., Impact of Shell Composition, Thickness and Heating Temperature on the Performance of Nickel-Rich Cobalt-Free Core-Shell Materials. *Journal of The Electrochemical Society* 2021, 167, (16), 160556.

[6] Liu, Y.; Harlow, J.; Dahn, J., Microstructural Observations of “Single Crystal” Positive Electrode Materials Before and After Long Term Cycling by Cross-section Scanning Electron Microscopy. *Journal of The Electrochemical Society* 2020, 167, (2).

[7] Liu, X. H.; Wang, J. W.; Huang, S.; Fan, F.; Huang, X.; Liu, Y.; Krylyuk, S.; Yoo, J.; Dayeh, S. A.; Davydov, A. V.; Mao, S. X.; Picraux, S. T.; Zhang, S.; Li, J.; Zhu, T.; Huang, J. Y., In situ atomic-scale imaging of electrochemical lithiation in silicon. *Nat Nano* 2012, 7, (11), 749-756.

[8] Lee, S. W.; McDowell, M. T.; Choi, J. W.; Cui, Y., Anomalous shape changes of silicon nanopillars by electrochemical lithiation. *Nano Lett* 2011, 11, (7), 3034-9.

[9] Goldman, J. L.; Long, B. R.; Gewirth, A. A.; Nuzzo, R. G., Strain Anisotropies and Self-Limiting Capacities in Single-Crystalline 3D Silicon Microstructures: Models for High Energy Density Lithium-Ion Battery Anodes. *Advanced Functional Materials* 2011, 21, (13), 2412-2422.

Reviewer #2 (Remarks to the Author):

1) Do you think this Review is interesting and/or useful to other researchers working in the field?

Yes

2) Does the paper provide adequate critical discussion of the literature, or does it only summarize previous research efforts?

Yes

3) Do you think the paper is sufficiently forward-looking, and does it provide guidance for future research?

Yes

4) Are there any parts of the paper that should be expanded, or parts that you think should be removed? For example, is the balance between topics appropriate?

None

5) Are the figures and tables useful in communicating the author's key points?

Yes

Reviewer #3 (Remarks to the Author):

In this review, the authors summarize the basic conception and the latest development of 3D silicon-based Li ion microbatteries according to the specific configurations. The review organizes the connections between the structure and performance of batteries, which is helpful for the future development of 3D Si-based Li ion batteries. I'd like to recommend it after some revisions.

1. Some sentences contain abbreviation typos like PVdF in line 317 and 320 and some unnecessary repeated full name like lithium-ion batteries in line 1030. The author should unify the expression.
2. In Section 2.1, many synthesis methods of cathode materials come along. More description about the structures and advantages of different cathodes may be more focused on the core of the part. Meanwhile, different anode materials like carbon or alloy material should also be included in this section to complete and enrich the introduction of microbatteries. The following works (doi: 10.1002/adma.202006229; 10.1038/s41467-020-15045-x) are suggested to include to inspire the readers.
3. The language and graphics of this manuscript need to be further polished.
4. In section 3, the author gave the title Recent emerging applications of 3D Si micro-LIB. However, in this chapter, the author discusses more about the structure of the 3D Li ion microbattery. The authors should give a more accurate title.
5. Some recent reviews on 3D microbatteries (such as doi:10.1002/adfm.201704880; 10.1021/accounts.mr.1c00175) are suggested to be included in the paper.

Reviewer #4 (Remarks to the Author):

The review covers various key aspects of the latest developments in 3D silicon-based lithium-ion microbatteries. It discusses their material compatibility, cell designs, fabrication methods, and performance across various materials and architectures. Authors highlight the critical relationship between device architecture and performance and provides comparisons between various fabrication technologies. This review can be a good reference work, however, I have several comments that may need to be addressed before recommending for publication.

General comments:

Since the focus of this review paper is Si anode based 3D microbatteries, it seems necessary to discuss the electrochemistry of silicon, (i.e. ion insertion reaction mechanisms, crystalline vs. Amorphous, etc.) challenges, and opportunities in the introduction section.

Authors took an effort to review the cathode materials in the introduction but do not really discuss. It would be interesting to include a column in Table 3 and see where the community is at (and possibly why). Without such discussion, the discussions involving cathode materials and synthesis approach in the introduction seem unnecessary.

Several state-of-the-art inorganic solid electrolyte systems depend on high stack pressures, sometimes exceeding 100 MPa, for optimal performance. However, it raises the question of whether such pressures are viable for 3D electrode architectures, given their high-aspect-ratio structures and the challenges associated with anisotropy.

The review mainly highlights inorganic solid electrolytes with a focus on LIPON-based chemistries. They are reported to exhibit considerably lower ionic conductivities compared to more recent systems. The adequacy of these conductivities for 3D microbatteries, where high ionic conductivity is crucial for uniform lithiation/de-lithiation of 3D electrodes and achieving the high power densities that make 3D microbatteries advantageous, needs consideration.

One of the biggest challenges for 3D micro batteries lies in their packaging. The discussion around how to package a non-planar battery, particularly when it involves liquid or gel electrolytes (which is the current state of the field) seems necessary. Addressing this challenge is a critical need within the community and should be thoroughly discussed.

Based on this review, the community has developed a number of different ways to achieve 3D Si micro-LIBs, particularly for the prototype demonstration. It would be good to get authors' perspective on what the technological gap is between these prototypes and the actual need for implementation.

Specific comments:

Ln 285 "For electrode making, those cathode materials will easily follow the usual fabrication methods for 3D Si micro-LIBs."

What are the usual fabrication methods for 3D Si micro LIBs? Is this in reference to Section 3? Examples included in Section 3, such as RF sputtering and ALD, are certainly not easy nor usual.

Ln 464 "the fabrication of a Si anode can be classified either as additive (bottom-up, see Figures 3a-c) or subtractive (top-down, see Figures 3d-f) methods"

Figure 3 includes examples that do not include 3D Si anodes. It may mislead readers.

Ln 1055-1060,

The nanostructuring approach may bring some performance improvement but it necessitates careful consideration.

Do we really need to further miniaturize our power sources? What are the power needs for integrated electronics? Can nanostructured silicon effectively sustain 3D configurations?

Response letter

Reviewer #1:

In the submitted work, the authors present an extensive review paper about 3D-micro-Lithium-Ion batteries (LIBs) with the aim to address topics like “basic principles”, “materials”, “manufacturing methods” and “recent applications”.

Questions of the editor:

1) Do you think this Review is interesting and/or useful to other researchers working in the field? Yes, the review is interesting for researchers in this field. Nevertheless, a major revision is needed.

Authors' response:

Thank you very much for your comments. We have revised the manuscript according to the points given by the reviewers.

2) Does the paper provide adequate critical discussion of the literature, or does it only summarize previous research efforts?

Basically, the paper provides critical discussion of the cited scientific works. It is recommended to carve out even more the application relevant differences, the advantages / disadvantages of the described 3D-architectures (chapter 3) and 3D-LIB variants (chapter 3.1-3.5). Background: Is every microbattery-design appropriate for every on-chip application (high energy demand-low energy demand, expected/desired lifetime of maybe weeks or maybe years, operating at room temperature or at elevated temperatures, etc.)

Authors' response:

Thank you very much for your recommendations. To accommodate the application relevant differences, we have dedicated an extra chapter: Chapter 3.6 “Applicability of 3D Si micro-LIBs”, and the following text has been added:

The currently existing 3D Si micro-LIB designs demonstrate their potential capabilities to provide energy in different ranges of applications. The resulting areal capacities differ from tens of $\mu\text{Ah cm}^{-2}$ up to several mAh cm^{-2} (see **Table 3**). Some reports use half-cell configuration with Li metal as the counter electrode, while some others already demonstrate the full-cell configuration with specific cathode materials. In particular, 3D Si micro-LIBs with full-cell configurations have good performances to fulfill the requirements of integrated microelectronics, considering their operating voltages, which translate to the energy densities between μWh to mWh^{116} . The thin-film structures exhibit relatively low areal capacities compared to 3D structures, for example the vertical pillar structures that have the highest areal capacity of nearly 10 mAh cm^{-2} . In terms of power, the rate capabilities that can be delivered by 3D structures are

comparable to thin films, which exhibit the ability of 3D structures to provide high energy density but at the same time can be designed to produce high power density.

Amongst 3D structures, the additive-manufacturing method, which produces interdigitated structures, benefits from the flexibility of shaping the Si anode geometry. The limitation comes from the structure size determined by the nozzle diameter that is used to deposit the materials. For example, the currently demonstrated interdigitated structures possess a smallest size of several hundreds of micrometers¹²⁴. Therefore, further miniaturization would be a challenge. In addition, the use of binder in the ink slurry obliges a fragmented Si content (*i.e.*, Si has to be a fraction of the total mass of the anode), which might limit the areal capacity. Nevertheless, the utilization of a carbon matrix can help to maintain the structural integrity of the Si anode, hence, contributes to capacity retention. Therefore, the use of an interdigitated structure might fit to the applications in case the capacity is less important than the capacity retention. The corresponding applications might be flexible and wearable devices, where low-power electronic devices are designed to be energized by multiple charge/discharge cycles without the risk of a quick capacity degradation.

The pillar-based structures (including vertical pillars and nanowires), which are more preferably fabricated using subtractive method, offer high robustness of Si. The way these 3D structures are fabricated also enables the utilization of a monolithic Si anode without the need of any binder. Moreover, the integration of such structures into on-chip applications (*e.g.*, microcomputers, sensors, and microrobots) can be straightforward since fabrication technologies (*e.g.*, lithography, dry etching, and various deposition methods) are widely used in semiconductor device production. In terms of performance, the areal capacities of pillar-based structures can achieve several mAh cm⁻², which are relatively high compared to those of other 3D structures. It indicates that the utilization of Si can be maximized. It is also possible to exploit the high power capability due to the transformation of *c*-Si to *α*-Si, as indicated by the high rate capability of hundreds of mA cm⁻². The high Coulombic efficiency over hundreds of cycles makes the utilization of such 3D structures even more promising for on-chip energy storage.

The *α*-Si anodes fabricated in coaxial pillars and Swiss-roll structures are promising alternatives in semiconductor processing technology. In principle, both structure types are aimed to utilize the conformity of all micro-LIB components (*i.e.*, current collectors, electrodes, and electrolyte) to result in a short Li⁺ diffusion pathway by increasing the interfacial-area sizes within the same areal footprint. In particular, Swiss-roll structure offers a simple and low-cost fabrication method to realize this aim. The resulting rate capability is comparable with the other 3D structures. Furthermore, it has been demonstrated that the full-cell prototype of a Swiss-roll structure with an areal footprint of 0.17 mm² is capable of powering a digital watch for 15 minutes, which is normally energized by a conventional AA battery, showing its potential as an alternative for a battery power supply⁹³.

Applications of 3D Si micro-LIBs may also be challenged by varying operating temperatures. Unfortunately, there is still limited information provided by published sources, especially

regarding the relation between temperature and structural integrity of the various 3D Si anodes. However, elevated temperatures can affect the kinetics of the battery. At elevated temperatures, the ionic conductivity of the solid electrolyte may decrease compared to a liquid electrolyte⁷¹. This may be an important criterion for material selection.

3) Do you think the paper is sufficiently forward-looking, and does it provide guidance for future research?

The conclusion (chapter 4) outlines the possible future and possible future success of 3D-LIBs primarily from the semiconductor manufacturing side. Important new developments related to material science like room temperature solid state electrolytes (LLZO, LATP, LGPS, etc.[1]), new liquid high voltage electrolytes [2-4], Ni-rich cathode materials (NMC 811, 955 or NiO₂) [5, 6] and their exciting impact on the energy density are not discussed. There are also new production techniques like femtosecond laser ablation with the potential to lower per piece production costs that are suggested to be mentioned.

Authors' response:

Thank you very much for your suggestions. To enhance the discussion of possible future success of 3D micro-LIBs, we have included the suggested references and added the following paragraph in Chapter 4 "Conclusions and outlook":

There is a growing need to investigate the synergies and compatibilities of these newer electrolyte solutions with existing semiconductor processes. Recently, material science breakthroughs have unveiled the potential of room-temperature solid-state electrolytes, such as LLZO, LATP, and LGPS¹⁶². These developments promise significantly enhanced safety and performance due to their inherent stability and potential for higher energy densities of micro-LIBs. Furthermore, new liquid high-voltage electrolytes are being explored, which can further push the boundaries of energy density and extend the lifespan of the battery by reducing degradation at high voltages^{163–165}. From the cathode side, the incorporation of materials with higher nickel content (*e.g.*, LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NCM-811) and LiNi_{0.9}Mn_{0.05}Co_{0.05}O₂ (NCM-955)), and other potential cathode materials (*e.g.*, LiNiO₂) pose great promises due to their demonstrated energy densities^{86,87}.

Moreover, an explanation about cathode materials that potentially match to 3D Si micro-LIB (including Ni-rich cathodes and LiNiO₂,) has been added into the part of cathode in Chapter 2.1 "Concept of microbattery":

A lithium nickel manganese cobalt oxide, specifically LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM-111), has emerged as a pivotal cathode material, particularly for mobile power sources, owing to its notable gravimetric and volumetric capacity. However, the automotive industry necessitates batteries with even higher energy density to propel the development of electric vehicles (EVs) with competitive or surpassing ranges compared to internal combustion engine automobiles⁷⁵. NCM-111 boasts several advantages, including a cell-level high energy density (>150 Wh kg⁻¹), a

robust power density (650 W kg^{-1} @ 25°C and 50% Depth of Discharge/DoD)⁷⁶, an exceptional rate capability, a substantial specific capacity (163 mAh g^{-1}), and a commendable thermal stability in the fully charged state⁷⁷. One strategy to enlarge energy density is by augmenting the nickel content in the NCM cathode material. Hence, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NCM-622) cathodes were fabricated using tape casting, incorporating 80 wt% of active material with a film thickness of $54 \mu\text{m}$. Additionally, to attain a 3D architecture, an ultrafast fiber-laser-driven ablation process was employed, creating line structures with a pitch of $200 \mu\text{m}$. This cathode material demonstrated an initial discharge capacity of 178 mAh g^{-1} at a C-rate of C/10. Notably, at a discharge rate of 10 C, the cell equipped with the structured cathode managed to maintain a discharge capacity of 35% of the initial value⁷⁸.

Moreover, well-established synthesis procedures^{75,79–85} and stability make cathode powder materials suitable for use in various electrode production methods. There is no distinct variation in the approach to achieving a 3D architecture, even with cathodes containing higher nickel contents such as $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NCM-811), $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (NCM-955), and other potential cathode materials like LiNiO_2 ^{86,87}. Various protocols, including conventional slurry-based techniques, tape casting, laser ablation, layer deposition synthesis (*e.g.*, ALD and MLD), as well as other thin-film fabrication and micro-architectural building methods, could be employed to design an advanced 3D cathode that complements the 3D Si micro-LIB^{47,88–90}.

To mention about the femtosecond laser ablation as a potential fabrication technique for Si anode in micro-LIBs, we have modified the following paragraph in Chapter 4 “Conclusions and outlook”:

Thirdly, the development of standard complete-cell fabrication and testing methods for micro-LIBs should be followed up. Differentiating from conventional LIBs that are usually fabricated as a coin cell and tested in a suitable electrochemical test setup, micro-LIB fabrication is based on the semiconductor processing technology, which is not directly compatible for the conventional and widely-used measurement methods. In terms of 3D Si fabrication for large-scale production, an alternative manufacturing method of femtosecond-laser ablation has yet to be more explored. Nevertheless, the use of this method to fabricate Si nano-/microstructures has been applied in many fields such as solar cells, sensors, optical detectors, and LIBs^{159,169–173}. This method offers high convenience and efficiency that can potentially lower the per-piece production cost of an LIB. The deployment of femtosecond-laser ablation in 3D Si micro-LIB fabrication can be directed towards the engraving of a planar Si anode to form 3D periodic nano-/microstructures. The versatility of this method to form a wide variety of shapes can enable quick, cost-effective, large-area processing of 3D Si anodes. Moreover, when the devices shall be made as products, they have to be verified in a standard industry setup. Although some efforts to build prototypes of complete micro-LIBs and their electrochemical tests have been well-demonstrated, there are still no standardized protocols to fabricate and test micro-LIBs. The formulation of best-practice guides could enable more comparable performance metrics, which in turn will drive and accelerate the study of micro-LIBs forward.

4) Are there any parts of the paper that should be expanded, or parts that you think should be removed? For example, is the balance between topics appropriate?

Chapter 2 covers beside the “concept of microbattery” also possible cathode materials and the benefit of silicon as 3D-anode. The discussion of cathode materials focusses very much on the production of these materials but less on their individual properties that are important if applied in microbatteries (e.g. the high density of LCO enabling high volumetric charge densities, the tendency of LiMn₂O₄ to rapidly age at elevated temperatures (Mn-dissolution), the low electric conductivity and Li-diffusivity of undoped LFP and the need to add conductive agents, etc.). Important cathode materials like NMC 622 or 811 are not discussed at all. It is suggested to fundamentally revise the “cathode part” (line 192-283).

Authors’ response:

Thank you very much for your valuable comments. The part of cathode materials in Chapter 2.1 “Concept of microbattery” have been totally revised to focus not only on the production sides but also their properties:

Table 1 Commercial lithium-ion battery cathode materials in different structures^{44–51}. A comparison of several key performance indicators (*i.e.*, average potential vs. Li/Li⁺, specific capacity range, and gravimetric energy density) of different cathode materials (*i.e.*, LiCoO₂ (LCO), LiFePO₄ (LFP), Li(Ni_{0.80}Co_{0.15}Al_{0.05})O₂ (NCA), LiMn₂O₄ (LMO) variants, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) variants, and LiNiO₂).

Cathode material	Structure	Average potential vs Li/Li ⁺ (V)	Specific capacity range (mAh g ⁻¹)	Gravimetric energy density range (Wh kg ⁻¹)	Cost	Safety	Material synthesis
LCO	Layered	3.90	140–160	530–550	High	Low	Easy
LFP	Olivine	3.45	150–170	520–590	Low	High	Medium
NCA	Layered	3.80	180–200	680–760	Medium	Medium	Medium
LMO variants	Spinel	4.10	100–120	410–490	Low	Medium	Easy
NCM variants	Layered	3.80	160–170	610–650	Medium	Medium	Medium
LiNiO ₂	Rocksalt	3.85	150–190	620–770	Medium	Low	Difficult

To maximize energy density, cathodes for LIBs are engineered to have higher average potentials relative to Li/Li⁺ compared to earlier materials like TiS₂ and vanadates designed for lithium metal batteries⁵¹. Moreover, cathode materials are typically limited to those containing first-row transition metals, including manganese (Mn), iron (Fe), cobalt (Co), and nickel (Ni), to meet the demand for high specific capacity⁴⁴. Presently, cathode materials for LIBs encompass metal oxides and poly-anionic compounds. Integrating cathodes into microbattery assemblies represents a notable challenge in microbattery development. Thus far, only a handful of instances have been documented regarding the use of 3D cathode architectures for microbatteries, as achieving a 3D cathode poses a severer difficulty than synthesizing 3D anodes or electrolytes.

This section provides an overview of potential cathode materials that can be paired with silicon-based anodes in 3D Si micro-LIBs (refer to **Table 1**). The suitability is assessed based on various parameters such as average potential, average specific capacity, gravimetric energy density, cost-effectiveness, safety consideration, and material synthesis. The gravimetric energy densities are obtained from the references, where those values were calculated as the product of average potential and specific capacity⁵⁰. **Figure 1** offers a qualitative comparison of these cathode materials.

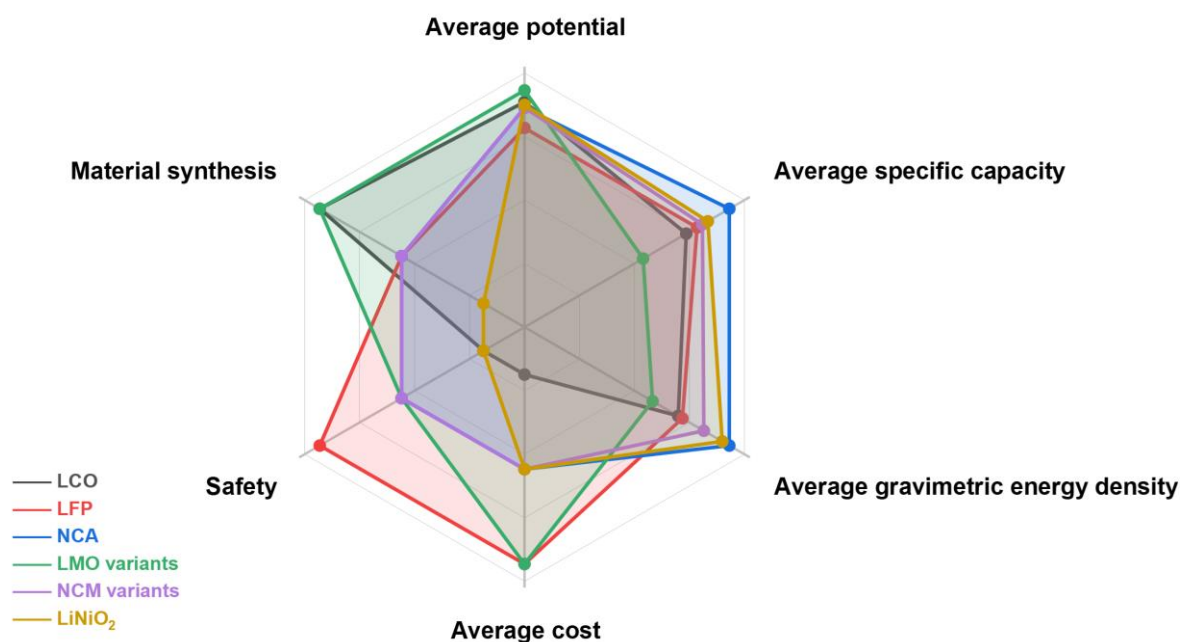


Figure 1 Cathode-material performance comparison for supporting 3D Si micro-LIBs. Different cathode materials have their own advantages and drawbacks in terms of lifespan, energy density, performance, cost, and safety.

A promising alternative approach involves the creation of 3D LIBs with thicker electrodes, surpassing 100 μm in thickness^{52–56}. The volumetric ratio of active to inactive materials within LIBs, and consequently their energy capacity, increases linearly with the electrode thickness for a given area. However, achieving efficient ionic and electronic transport through thicker electrodes presents challenges, leading to limitations in power density^{57–59}. To address this, recent research has concentrated on producing lithium-based cathodes with internal open channels perpendicular to current collector surfaces. This was accomplished through magnetic-field-induced alignment of anisotropic porogens, comprising either magnetic particle-coated polymer rods or particle-stabilized emulsion droplets. The result was sintered LiCoO₂ (LCO) cathodes, measuring 310 μm in thickness, exhibiting an impressive areal capacity of $\approx 12 \text{ mAh cm}^{-2}$ at a rate of 0.1 C⁶⁰. In the pursuit of enhancing electronic transport, highly porous metal foams have also been employed as 3D current collectors to develop high-performance LiFePO₄ (LFP) cathodes, 540- μm -thick, with an areal capacity of 8.8 mAh cm^{-2} at a current density of 1 mA cm^{-2} ⁵². It is worth noting that the use of thick electrodes introduces additional challenges, including issues with migration, cracking, and delamination during the drying process⁶¹, as well

as incomplete electrolyte infiltration⁶². Another strategy for achieving uniform deposition of LCO involves the thermal decomposition of sol-gel precursors spray-coated onto 3D-Al-nanorod current collectors directly grown on Al substrates. Additionally, it is important to recall that Ceder *et al.* have identified new cathode materials, in which non-transition metals are substituted for cobalt. Phases such as $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ have been reported, and an increase in cell voltage with Al substitution has been experimentally confirmed⁶³. Compared with a planar electrode presenting an equivalent nominal capacity, a 3D electrode exhibits improved capacity retention, retaining 68% of the nominal capacity at 8 C instead of 11%⁶⁴.

Recent studies have showcased the creation of micro-LIBs through the direct deposition of LFP cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode inks. The cathode inks are formulated by suspending LFP nanoparticles (with an average diameter of 180 nm) in a solution containing deionized water, ethylene glycol, glycerol, and viscosifiers derived from cellulose. This process involves multiple steps, including particle dispersion, centrifugation, and homogenization. Specifically, high-aspect-ratio, interdigitated LFP and LTO electrodes were printed with a wall thickness of approximately 60 μm and a height ranging from around 200 to 400 μm . These micro-LIBs, with a total volume of less than 1 mm^3 , demonstrated an areal capacity of roughly 1.5 mAh cm^{-2} when discharged at rates below 5 C. However, electronic transport constraints were observed, as LFP electrodes printed with eight layers (approximately 200 μm thick) displayed the same current density as those with 16 layers (approximately 400 μm thick)⁶⁵. Besides its promising performance, several challenges for LFP, such as low electronic conductivity and limited Li-ion diffusivity, especially for untreated/undoped LFP, which affect the overall properties of LFP, have to be addressed for future applications⁶⁶⁻⁶⁹.

In another investigation, $\text{Li}(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ (NCA) was employed as the active material for the positive electrode in a semiconductor-grade single-crystalline Si microbattery. The NCA cathode was created using a conventional slurry formulation, comprising 88% w/w NCA, 6% polyvinylidene fluoride (PVDF), 3% carbon black, and 3% graphite, mixed with an equal weight of N-Methyl-2-pyrrolidone (NMP). The slurry mixture was prepared using a planetary micro mill. The quantity of NCA within the cathode cavity was either 3.8 mg (for cells with a 0.5 mAh capacity) or 10.0 mg (for cells with a discharge capacity ranging from 1.0 to 2.0 mAh). The slurry was then dried at 60 °C for 12 hours in a temperature chamber without forced air circulation. The device exhibited a high current output power (200 mW cm^{-2} ; 30 mA peak current) and demonstrated robust charge/discharge stability for at least 100 cycles (equivalent to 10 mAh cm^{-2}). Additionally, it exhibited a high Coulombic efficiency, nearing 100%, making it highly suitable for integration into a wide array of intelligent, self-powered electric devices⁷⁰. Using a similar approach, the cathode slurry consisted of 75% NCA, 18.3% graphite, 1.7% PVDF, 2.8% lithium bis(trifluoromethane)sulfonimide (LiTFSI), 1.1% tetraglyme (TG), and 1.1% poly(ethylene oxide) (PEO), which were combined and assembled using a vacuum-infiltration protocol onto SU-8-coated Si arrays. The resulting rechargeable 3D microbatteries, fashioned on a 3 mm $\times$ 3 mm footprint, exhibited an areal capacity of nearly 2 mAh cm^{-2} . They operated at current densities of up to 0.66 mA cm^{-2} and maintained stability through 100 cycles⁷¹.

An innovative 3D micro-LIB is introduced, featuring sub-10 nm LiMn_2O_4 (LMO)/LTO nanocrystals synthesized through a solvothermal method and a novel copolymer gel electrolyte. This microbattery exhibits exceptional capacity retention (40% at 300 C) and boasts a high power density of $855.5 \mu\text{Wcm}^{-2} \mu\text{m}^{-1}$. The tailored microelectrodes are created via solvent-assisted imprint lithography, utilizing well-dispersed nanoparticle ink, and the battery cell is vertically integrated through layer-by-layer (LBL) assembly⁷². In a separate investigation, functional 3D LMO thin-film electrodes are produced, yielding a footprint capacity of 0.5 mAh cm^{-2} , employing an innovative process grounded in a solid-state reaction between electrolytic manganese dioxide (EMD) and Li_2CO_3 stacked-layers. These prepared thin films demonstrate electrochemical activity, achieving a volumetric capacity of 1200 Ah L^{-1} , closely approaching the theoretical capacity of spinel LMO. Moreover, a thin-film morphology, spanning a few hundred nanometers, allows for utilization of both 3 V and 4 V regions⁷³. Furthermore, a Mn-dissolution process of the LMO cathode at elevated temperatures⁷⁴ has to be a concern to achieve a more applicable 3D Si micro-LIBs.

A lithium nickel manganese cobalt oxide, specifically $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM-111), has emerged as a pivotal cathode material, particularly for mobile power sources, owing to its notable gravimetric and volumetric capacity. However, the automotive industry necessitates batteries with even higher energy density to propel the development of electric vehicles (EVs) with competitive or surpassing ranges compared to internal combustion engine automobiles⁷⁵. NCM-111 boasts several advantages, including a cell-level high energy density ($>150 \text{ Wh kg}^{-1}$), a robust power density (650 W kg^{-1} @ 25°C and 50% Depth of Discharge/DoD)⁷⁶, an exceptional rate capability, a substantial specific capacity (163 mAh g^{-1}), and a commendable thermal stability in the fully charged state⁷⁷. One strategy to enlarge energy density is by augmenting the nickel content in the NCM cathode material. Hence, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NCM-622) cathodes were fabricated using tape casting, incorporating 80 wt% of active material with a film thickness of $54 \mu\text{m}$. Additionally, to attain a 3D architecture, an ultrafast fiber-laser-driven ablation process was employed, creating line structures with a pitch of $200 \mu\text{m}$. This cathode material demonstrated an initial discharge capacity of 178 mAh g^{-1} at a C-rate of C/10. Notably, at a discharge rate of 10 C, the cell equipped with the structured cathode managed to maintain a discharge capacity of 35% of the initial value⁷⁸.

Moreover, well-established synthesis procedures^{75,79–85} and stability make cathode powder materials suitable for use in various electrode production methods. There is no distinct variation in the approach to achieving a 3D architecture, even with cathodes containing higher nickel contents such as $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NCM-811), $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (NCM-955), and other potential cathode materials like LiNiO_2 ^{86,87}. Various protocols, including conventional slurry-based techniques, tape casting, laser ablation, layer deposition synthesis (e.g., ALD and MLD), as well as other thin-film fabrication and micro-architectural building methods, could be employed to design an advanced 3D cathode that complements the 3D Si micro-LIB^{47,88–90}.

The key material “silicon” is discussed with regards to its geometrical ambience inside the battery. It is suggested to cover crucial topics like the “ledge mechanism” [7] during lithiation

and the anisotropic dilatation of crystalline Si during Li-uptake [8, 9] as these effects have an impact on the Si-material selection, the applied crystallographic orientation and ageing during cycling.

Authors' response:

Thank you very much for your suggestions. The following texts have been added into Chapter 2.1 "Concept of microbattery" along with the suggested references:

As a potential anode material in LIBs, Si had attracted the attention of many studies. In contrast with the intercalation of Li (*i.e.*, Li intercalates between adjacent atomic layers) in graphite, the lithiation mechanism of Li ions into Si occurs through insertion process. Lithiation mechanism of Si in general is a Li-Si alloying reaction, involving Si-Si bond breaking. Works have been done to investigate the electrochemical characteristics of crystalline Si (*c*-Si) with the aims of understanding the lithiation mechanism and improving Si anode performance in LIBs. Since the performance of a Si anode is limited by the mechanical disintegration of Si upon (de-)lithiation, studies are dedicated to demystify the lithiation-induced stresses. It was found that the strain evolution in *c*-Si is highly anisotropic³⁹. This non-uniform deformation drives gradient strain fields, which determine the material performance. Si nanopillars with three different axial orientations (*i.e.*, $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$) were used to investigate the morphological deformation of *c*-Si upon lithiation⁴⁰. The cross-sectional view of Si nanopillars after the first lithiation shows cross, oval, and hexagonal shapes of $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ oriented nanopillars, respectively. The results suggest an orientation-dependent nature of lithiation, in which Li prefers to enter into *c*-Si through $\langle 110 \rangle$ ion channels. Furthermore, atomistic insight into the (de-)lithiation mechanism of Si nanowires was obtained by reactive molecular dynamic simulation⁴¹ that confirms a Li penetration tendency along the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions. During lithiation, *c*-Si transforms into amorphous Li_xSi (*a*- Li_xSi) phases through Si-Si bond breaking caused by tensile stress between Si atoms. *In situ* transmission electron microscopy (TEM) was used to observe the dynamics of lithiation at atomic resolution in real time⁴². The study revealed the so-called ledge mechanism, in which an amorphization of *c*-Si during Li insertion occurs via a layer-by-layer peeling of $\{111\}$ atomic planes at the *c*-Si/*a*- Li_xSi interface. It was also demonstrated that the progression of the reaction front is atomically sharp (~ 1 nm), and its mobility depends on crystal orientation (*i.e.*, amorphizations through $\{111\}$ facets are much slower than the $\{110\}$ and $\{112\}$ facets). Besides *c*-Si, amorphous Si (*a*-Si) is also used as an anode in LIBs⁴³. Similar to *c*-Si, the first lithiation of *a*-Si is also characterized by a two-phase reaction with the progression of a sharp interface into the non-lithiated Si, followed by a single-phase mechanism in the delithiation process and the subsequent cycles. However, there are some differences including isotropic lithiation and volume change, lower Li concentration in the lithiated phase compared to the lithiated *c*-Si, and a relatively constant reaction rate (in contrast to the significant slowing of the reaction front in *c*-Si). The benefit of those characteristics is that *a*-Si has a more manageable morphological deformation than *c*-Si, which in some cases, makes *a*-Si more favorable as an anode material. For example, it was demonstrated that Si nanoparticles

in an amorphous phase have a larger critical radius for fracture compared to their crystalline counterparts.

5) Are the figures and tables useful in communicating the author's key points?

All figures, table 1 and 2 are useful and from appropriate quality. Table 3 benchmarking different microbattery technologies needs a major revision because of obviously mixing up values like "capacity retention" and "coulombic efficiency". The quotation of specific- and areal capacity in the same row makes a direct comparison unfortunately difficult. It is suggested to introduce two dedicated rows. Please find attached further information under "detailed comments".

Authors' response:

Thank you very much for your comments. **Table 3** has been revised accordingly as follows:

Table 3 Various structures of Si micro-LIBs and their performance. Comparison is made in terms of their architecture, materials, and performance metrics (*i.e.*, capacity, rate capability, and capacity retention, Coulombic efficiency, and cycle).

Architecture	Materials			Capacity		Rate capability	Capacity retention	Coulombic efficiency	Cycle	Ref.
	Anode	Electrolyte	Cathode	Areal capacity	Specific capacity					
Thin film	<i>a</i> -Si	LiPONB	Li metal	40 $\mu\text{Ah cm}^{-2}$	-	800 $\mu\text{A cm}^{-2}$	-	99.99%	1500	105
Thin film	<i>a</i> -Si	LiPON	VO-LiPO	15.7 $\mu\text{Ah cm}^{-2}$	-	-	49%	-	30	106
Thin film	Poly-Si	LiPON	LiCoO ₂	-	3000 mAh g^{-1}	40 mA cm^{-2}	-	-	60	118
Interdigitated structures	Si/C-graphite	LP30/FEC	Li metal	-	466 mAh g^{-1}	2C	75%	-	65	124
Vertical pillars	<i>c</i> -Si	SU-8	NCA	1.8 mAh cm^{-2}	-	0.66 mA cm^{-2}	-	92%	100	71
Vertical pillars	<i>c</i> -Si	LiClO ₄	NCA	9.4 mAh cm^{-2}	-	181 mA cm^{-2}	83%	99.9%	200	70
Vertical pillars	<i>c</i> -Si	LiClO ₄	Li metal	-	1093 mAh g^{-1}	-	-	98.9%	5	134
Nanowires	<i>c</i> -Si/PANI	LiPF ₆	Li metal	2 mAh cm^{-2}	-	2 mA cm^{-2}	-	~100%	346	121
Nanowires	<i>c</i> -Si	LiClO ₄	Li metal	3000 $\mu\text{Ah cm}^{-2}$	-	35 $\mu\text{A cm}^{-2}$	43%	-	20	91
Coaxial pillars	<i>a</i> -Si	LiPON	LiCoO ₂	25 $\mu\text{Ah cm}^{-2}$	-	27.6 $\mu\text{A cm}^{-2}$	-	-	20	130
Coaxial pillars	<i>c</i> -Si	LiPF ₆ /TiN/Sb	Li metal	400 $\mu\text{Ah cm}^{-2}$	-	200 $\mu\text{A cm}^{-2}$	-	~100%	500	120
Swiss-roll structures	Si-Ge	LiPF ₆	LiMn ₂ O ₄	1053 $\mu\text{Ah cm}^{-2}$	-	1.04 $\mu\text{A cm}^{-2}$	67%	85%	50	93
Mesoporous	<i>c</i> -Si	LiPF ₆	Li metal	-	2480 mAh g^{-1}	500 $\mu\text{A cm}^{-2}$	97%	-	70	135
Macroporous	<i>c</i> -Si	PVDF-HFP	LiCoO ₂	226 $\mu\text{Ah cm}^{-2}$	-	400 $\mu\text{A cm}^{-2}$	98%	99%	15	101
Honeycombs	<i>c</i> -Si/TiN/Ge	LiPF ₆	LiCoO ₂	0.15 mAh cm^{-2}	-	0.5 mA cm^{-2}	-	~100%	500	159

Detailed comments:

Line 85: If intended so, a change to "...Si has a relatively low lithiation potential..." is suggested.

Authors' response:

Thank you very much for your suggestion. The following changes have been made in the manuscript:

Moreover, Si has a relatively low lithiation potential (< 0.5 V) vs. Li/Li⁺, which makes it promising to provide a high energy density.

Line 139-142: The specific capacity (mAh/g) is always related to mass and therefore “gravimetric”. A “specific volumetric capacity” is unfamiliar to the reviewer. If charge is related to certain volume (mAh/cm³), it should be named “charge density” or “volumetric charge capacity”.

Authors’ response:

Thank you very much for your suggestion. The following changes have been made in the manuscript:

In battery research, commonly, the specific capacity of different materials is compared in terms of their weights (*i.e.*, specific capacity/gravimetric capacity (C_m)), which is usually represented by the unit mAh g⁻¹. Moreover, when the volume is considered to be more important, the specific capacity can also be converted into the charge density/volumetric charge capacity (C_v) that is usually represented by the unit mAh cm⁻³ based on the following relation:

Line 142: The SI unit symbol for cubic centimeter is “cm³”, to a lesser extent “cc”

Authors’ response:

Thank you very much for your suggestion. The following changes have been made in the manuscript:

Moreover, when the volume is considered to be more important, the specific capacity can also be converted into the charge density/volumetric charge capacity (C_v) that is usually represented by the unit mAh cm⁻³ based on the following relation:

Line 194, Table 1: How is the “energy density” of a cathode material measured?

Authors’ response:

Thank you very much for your question. The gravimetric energy densities in **Table 1** were obtained from the references as they are. They were calculated from the potential and specific capacity data. The following text has been added into the manuscript to give a clearer understanding about **Table 1**:

The gravimetric energy densities are obtained from the references, where those values were calculated as the product of average potential and specific capacity⁵⁰.

Line 229: Due to the low specific capacity, NMC 111 seems rather unattractive for microbatteries. The (additional) presentation of NMC 622 or 811 is suggested.

Authors' response:

Thank you very much for your suggestion. The following texts have been added into the manuscript:

A lithium nickel manganese cobalt oxide, specifically $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM-111), has emerged as a pivotal cathode material, particularly for mobile power sources, owing to its notable gravimetric and volumetric capacity. However, the automotive industry necessitates batteries with even higher energy density to propel the development of electric vehicles (EVs) with competitive or surpassing ranges compared to internal combustion engine automobiles⁷⁵. NCM-111 boasts several advantages, including a cell-level high energy density ($>150 \text{ Wh kg}^{-1}$), a robust power density (650 W kg^{-1} @ 25°C and 50% Depth of Discharge/DoD)⁷⁶, an exceptional rate capability, a substantial specific capacity (163 mAh g^{-1}), and a commendable thermal stability in the fully charged state⁷⁷. One strategy to enlarge energy density is by augmenting the nickel content in the NCM cathode material. Hence, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NCM-622) cathodes were fabricated using tape casting, incorporating 80 wt% of active material with a film thickness of $54 \mu\text{m}$. Additionally, to attain a 3D architecture, an ultrafast fiber-laser-driven ablation process was employed, creating line structures with a pitch of $200 \mu\text{m}$. This cathode material demonstrated an initial discharge capacity of 178 mAh g^{-1} at a C-rate of C/10. Notably, at a discharge rate of 10 C, the cell equipped with the structured cathode managed to maintain a discharge capacity of 35% of the initial value⁷⁸.

Moreover, well-established synthesis procedures^{75,79–85} and stability make cathode powder materials suitable for use in various electrode production methods. There is no distinct variation in the approach to achieving a 3D architecture, even with cathodes containing higher nickel contents such as $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NCM-811), $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (NCM-955), and other potential cathode materials like LiNiO_2 ^{86,87}. Various protocols, including conventional slurry-based techniques, tape casting, laser ablation, layer deposition synthesis (*e.g.*, ALD and MLD), as well as other thin-film fabrication and micro-architectural building methods, could be employed to design an advanced 3D cathode that complements the 3D Si micro-LIB^{47,88–90}.

Line 300: The advantage of LiClO_4 over LiPF_6 is the absence of HF or HF-related electrolyte components. LiClO_4 enables so the application of Na-, K-containing glass cell components (BS 3.3 glass) that are available in semiconductor manufacturing processes.

Authors' response:

Thank you very much for your valuable suggestion, we have added the following text to address your input:

The advantage of LiClO_4 over LiPF_6 is the absence of HF or HF-related electrolyte components. This distinction is critical because HF can be corrosive and damaging to various components⁹⁵.

LiClO₄ enables the application of Na-, K-containing glass cell components (BS 3.3 glass) that are available in semiconductor manufacturing processes. This compatibility offers a unique edge in integrating battery technology with semiconductor manufacturing⁷⁰.

Line 510: The cited colleague from Eindhoven is spelled “Baggetto”.

Authors’ response:

Thank you very much for your correction. The following changes have been made in the manuscript:

Baggetto *et al.* demonstrated the fabrication of a thin-film Si anode on a 3D substrate using LPCVD¹¹⁸.

Line 578, table 2, “dry etching”: Reference [100] is missing.

Authors’ response:

Thank you very much for your suggestion. The mentioned reference (Sternad, M., Forster, M. & Wilkening, M. The microstructure matters: Breaking down the barriers with single crystalline silicon as negative electrode in Li-ion batteries. *Sci. Rep.* **6**, 2–9 (2016).) has been added into **Table 2**, row “Dry etching”, as ref. 134:

Table 2 Fabrication methods of 3D Si micro-LIBs. Various fabrication methods including additive and subtractive processes possess their own advantages and disadvantages.

Method	Material	Advantages	Disadvantages	Reference
Sputtering	a-Si thin film	Wide variety of materials and substrates	High cost, low efficiency, low deposition rate, and low conformity	105,106,130–132
E-beam evaporation	a-Si thin film	Efficient process and possible deposition of materials with high melting point	High cost and low conformity	93
LPCVD	Poly-Si thin film	Conformal deposition, high purity, and high deposition rate	Limited material options based on the used precursors and high toxicity	118
VLS growth	c-Si nanowires	Low cost and feasible process of very small nanostructures	Irregular nanostructures and difficult-to-control uniformity	91
3D printing	Si/C nanoparticle – graphite blend slurry	Flexible design and fabrication capability for uncommon 3D structures.	Limited choice of ink materials	119,124

Dry etching	c-Si micro-/nanopillar arrays	Highly regular structure and well-established process in industrial scale	High investment for the equipment	70,71,125,126,133,134
MACE	c-Si nanowires	High density of nanowires, low production cost, and simple process	Irregular nanowires and hazardous etching substance	121
Electrochemical etching	Meso-/macroporous c-Si	Low production cost, fast process, and well-controlled nanostructure geometry	High surface roughness	92,101,135

Line 893: Wrong units. Reference [104] published values of “136 $\mu\text{Ah}\cdot\text{cm}^{-2}$ ” and “181 $\mu\text{Wh}\cdot\text{cm}^{-2}$ ”, not “136 $\text{Ah}\cdot\text{cm}^{-2}$ ” and “181 $\text{Wh}\cdot\text{cm}^{-2}$ ”.

Authors’ response:

Thank you very much for your correction. The following changes have been made in the manuscript:

With a footprint area of 0.11 mm^2 , the on-chip packaged Swiss-roll microbattery has a high capacity of up to $136\text{ }\mu\text{Ah cm}^{-2}$ and an energy density of $181\text{ }\mu\text{Wh cm}^{-2}$.

Line 901-920: Introduced by a sentence about “Swiss-roll micro battery” (line 897), the text from line 901 to 920 is about a microbattery with vertical columns [76] that are discussed in chapter 3.2. It is suggested to insert this text block after removing redundancies at e.g. line 802.

Authors’ response:

Thank you very much for your comment. The text has been moved into Chapter 3.2 “Vertical pillars” and modified accordingly:

Further work by Sternad *et al.* introduces wafer-grade monocrystalline Si not only as 3D active material for lithiation but also as a housing component, as displayed in **Figure 5g**⁷⁰. They demonstrated the fabrication of a complete cell with the same areal footprint as in their previous report (*i.e.*, $4 \times 4\text{ mm}^2$) but with higher Si towers (*i.e.*, with a lateral size of $50 \times 50\text{ }\mu\text{m}^2$ and a height of $60\text{ }\mu\text{m}$). A full-cell configuration was fabricated, which is mainly composed of three parts, two parts of electrode compartments (cathode and anode) and a separator. The anode part is a microstructured Si wafer (in the form of Si towers), with its backside deposited by Al as a current collector. The cathode part consists of thin Si on a glass. The glass is etched until the Si is exposed and then deposited by a polycrystalline NCA cathode material. The other side of Si is also sputtered by Al to act as the cathode’s current collector. The separator is a borosilicate glass fleece, immersed in a liquid electrolyte (propylene carbonate (PC) and LiClO_4). To complete the cell, both the cathode and anode compartments are glued together with an ultraviolet-cured adhesive, while the wetted separator is sandwiched between them. Here, Si also acts as a

packaging material which seals the whole inside of the cell. Fiber-like amorphous Si filaments draw through large areas of Si during the early stages of lithiation and activation cycles of single crystalline Si. The in-depth lithiation occurs through a complex 3D mechanism along cracks that run preferentially along the $\langle 110 \rangle$ directions. High but short-term discharge currents promote surface activation and, thus, the electrochemical performance of the monocrystalline Si surface. The authors studied the impact of various additives to the electrolyte (namely, vinylene carbonate (VC), 4-fluorophenyl isocyanate (4-FP), and 2,3,4-trifluorophenyl isocyanate (Tri-FP)) to optimize the cycling performance of the cell. VC additive, which form bulky oligomeric and polymeric layers, significantly improve the cycling durability of single-crystalline Si by maintaining the capacity almost twice as good as the other additives (4-FP and Tri-FP) (see **Figure 5h**). In contrast, additives that produce primarily thin inorganic SEI layers appear to have no benefit. The current Si micro-LIB can withstand more than 100 full cycles while fading capacity (only 17% after 200 cycles, 0.5 mAh, $4 \times 4 \text{ mm}^2$ electrode size). At power densities as high as 100 mW cm^{-2} , the small-format system has high Coulombic efficiencies ($>99.9\%$ for the first 180 cycles) and high energy densities (30 mWh cm^{-2}). These values are equivalent to discharge densities of up to 10 mAh cm^{-2} . The high-power cell design has a power density of 200 mW cm^{-2} (energy density of 10 mWh cm^{-2}). Notably, the 3D-patterned Si anode generates very high peak discharge currents ($>181 \text{ mA cm}^{-2}$ for 1 s) that are comparable to dedicated state-of-the-art (large-volume) high-power cells that commonly use graphite anodes. These parameters (full-cell design) allow for an easy powering of miniaturized data-transmission devices. Importantly, all components of the microbattery are manufactured at low per-piece costs, and the design is optimized for mass production in a semiconductor manufacturing environment⁷⁰.

Line 1025, table 3, row 3: The quotation of specific- and areal capacity in the same row makes a direct comparison difficult. It is suggested to introduce two dedicated rows.

Authors' response:

Thank you very much for your suggestion. **Table 3** has been revised accordingly as follows:

Table 3 Various structures of Si micro-LIBs and their performance. Comparison is made in terms of their architecture, materials, and performance metrics (*i.e.*, capacity, rate capability, and capacity retention, Coulombic efficiency, and cycle).

Architecture	Materials			Capacity		Rate capability	Capacity retention	Coulombic efficiency	Cycle	Ref.
	Anode	Electrolyte	Cathode	Areal capacity	Specific capacity					
Thin film	α -Si	LiPONB	Li metal	40 $\mu\text{Ah cm}^{-2}$	-	800 $\mu\text{A cm}^{-2}$	-	99.99%	1500	105
Thin film	α -Si	LiPON	VO-LiPO	15.7 $\mu\text{Ah cm}^{-2}$	-	-	49%	-	30	106
Thin film	Poly-Si	LiPON	LiCoO ₂	-	3000 mAh g^{-1}	40 mA cm^{-2}	-	-	60	118
Interdigitated structures	Si/C-graphite	LP30/FEC	Li metal	-	466 mAh g^{-1}	2C	75%	-	65	124
Vertical pillars	c-Si	SU-8	NCA	1.8 mAh cm^{-2}	-	0.66 mA cm^{-2}	-	92%	100	71
Vertical pillars	c-Si	LiClO ₄	NCA	9.4 mAh cm^{-2}	-	181 mA cm^{-2}	83%	99.9%	200	70
Vertical pillars	c-Si	LiClO ₄	Li metal	-	1093 mAh g^{-1}	-	-	98.9%	5	134

Nanowires	c-Si/PANI	LiPF ₆	Li metal	2 mAh cm ⁻²	-	2 mA cm ⁻²	-	~100%	346	121
Nanowires	c-Si	LiClO ₄	Li metal	3000 μAh cm ⁻²	-	35 μA cm ⁻²	43%	-	20	91
Coaxial pillars	α-Si	LiPON	LiCoO ₂	25 μAh cm ⁻²	-	27.6 μA cm ⁻²	-	-	20	130
Coaxial pillars	c-Si	LiPF ₆	Li metal	400 μAh cm ⁻²	-	200 μA cm ⁻²	-	~100%	500	120
Swiss-roll structures	Si-Ge	LiPF ₆	LiMn ₂ O ₄	1053 μAh cm ⁻²	-	1.04 μA cm ⁻²	67%	85%	50	93
Mesoporous	c-Si	LiPF ₆	Li metal	-	2480 mAh g ⁻¹	500 μA cm ⁻²	97%	-	70	135
Macroporous	c-Si	PVDF-HFP	LiCoO ₂	226 μAh cm ⁻²	-	400 μA cm ⁻²	98%	99%	15	101
Honeycombs	c-Si/TiN/Ge	LiPF ₆	LiCoO ₂	0.15 mAh cm ⁻²	-	0.5 mA cm ⁻²	-	~100%	500	159

Line 1025, table 3, row 5: Cited values like “capacity retention” and “coulombic efficiency” are obviously mixed up. Please check and revise.

Authors' response:

Thank you very much for your comments. **Table 3** has been revised accordingly as follows:

Table 3 Various structures of Si micro-LIBs and their performance. Comparison is made in terms of their architecture, materials, and performance metrics (*i.e.*, capacity, rate capability, and capacity retention, Coulombic efficiency, and cycle).

Architecture	Materials			Capacity		Rate capability	Capacity retention	Coulombic efficiency	Cycle	Ref.
	Anode	Electrolyte	Cathode	Areal capacity	Specific capacity					
Thin film	α-Si	LiPON	Li metal	40 μAh cm ⁻²	-	800 μA cm ⁻²	-	99.99%	1500	105
Thin film	α-Si	LiPON	VO-LiPO	15.7 μAh cm ⁻²	-	-	49%	-	30	106
Thin film	Poly-Si	LiPON	LiCoO ₂	-	3000 mAh g ⁻¹	40 mA cm ⁻²	-	-	60	118
Interdigitated structures	Si/C-graphite	LP30/FEC	Li metal	-	466 mAh g ⁻¹	2C	75%	-	65	124
Vertical pillars	c-Si	SU-8	NCA	1.8 mAh cm ⁻²	-	0.66 mA cm ⁻²	-	92%	100	71
Vertical pillars	c-Si	LiClO ₄	NCA	9.4 mAh cm ⁻²	-	181 mA cm ⁻²	83%	99.9%	200	70
Vertical pillars	c-Si	LiClO ₄	Li metal	-	1093 mAh g ⁻¹	-	-	98.9%	5	134
Nanowires	c-Si/PANI	LiPF ₆	Li metal	2 mAh cm ⁻²	-	2 mA cm ⁻²	-	~100%	346	121
Nanowires	c-Si	LiClO ₄	Li metal	3000 μAh cm ⁻²	-	35 μA cm ⁻²	43%	-	20	91
Coaxial pillars	α-Si	LiPON	LiCoO ₂	25 μAh cm ⁻²	-	27.6 μA cm ⁻²	-	-	20	130
Coaxial pillars	c-Si	LiPF ₆	Li metal	400 μAh cm ⁻²	-	200 μA cm ⁻²	-	~100%	500	120
Swiss-roll structures	Si-Ge	LiPF ₆	LiMn ₂ O ₄	1053 μAh cm ⁻²	-	1.04 μA cm ⁻²	67%	85%	50	93
Mesoporous	c-Si	LiPF ₆	Li metal	-	2480 mAh g ⁻¹	500 μA cm ⁻²	97%	-	70	135
Macroporous	c-Si	PVDF-HFP	LiCoO ₂	226 μAh cm ⁻²	-	400 μA cm ⁻²	98%	99%	15	101
Honeycombs	c-Si/TiN/Ge	LiPF ₆	LiCoO ₂	0.15 mAh cm ⁻²	-	0.5 mA cm ⁻²	-	~100%	500	159

Line 1025, table 3: The performance of cell in reference [76] that was cited several times as reference cell is missing. It is suggested to add two lines:

- “High-power” design: Vertical pillars, capacity 3.1 mAh.cm⁻², rate 181 mA.cm⁻¹, 200 cycles at 17% capacity retention, CE >99.9 %
- “High-energy” design: Vertical pillars, capacity 9.4 mAh.cm⁻², rate 0.78 mA.cm⁻¹, 100 cycles, CE >99.5 %

Authors’ response:

Thank you very much for your suggestion. The respective data have been added into **Table 3**. To unify the style of data presentation, we combine both “high-power” and “high-energy” designs by providing the highest capacity of 9.4 mAh cm⁻² (from high-energy design) and highest rate capability of 181 mA cm⁻² (from high-power design) into one line to show the possible values that can be achieved by the corresponding 3D design.

Table 3 Various structures of Si micro-LIBs and their performance. Comparison is made in terms of their architecture, materials, and performance metrics (i.e., capacity, rate capability, and capacity retention, Coulombic efficiency, and cycle).

Architecture	Materials			Capacity		Rate capability	Capacity retention	Coulombic efficiency	Cycle	Ref.
	Anode	Electrolyte	Cathode	Areal capacity	Specific capacity					
Thin film	<i>a</i> -Si	LiPONB	Li metal	40 μAh cm ⁻²	-	800 μA cm ⁻²	-	99.99%	1500	105
Thin film	<i>a</i> -Si	LiPON	VO-LiPO	15.7 μAh cm ⁻²	-	-	49%	-	30	106
Thin film	Poly-Si	LiPON	LiCoO ₂	-	3000 mAh g ⁻¹	40 mA cm ⁻²	-	-	60	118
Interdigitated structures	Si/C-graphite	LP30/FEC	Li metal	-	466 mAh g ⁻¹	2C	75%	-	65	124
Vertical pillars	<i>c</i> -Si	SU-8	NCA	1.8 mAh cm ⁻²	-	0.66 mA cm ⁻²	-	92%	100	71
Vertical pillars	<i>c</i> -Si	LiClO ₄	NCA	9.4 mAh cm ⁻²	-	181 mA cm ⁻²	83%	99.9%	200	70
Vertical pillars	<i>c</i> -Si	LiClO ₄	Li metal	-	1093 mAh g ⁻¹	-	-	98.9%	5	134
Nanowires	<i>c</i> -Si/PANI	LiPF ₆	Li metal	2 mAh cm ⁻²	-	2 mA cm ⁻²	-	~100%	346	121
Nanowires	<i>c</i> -Si	LiClO ₄	Li metal	3000 μAh cm ⁻²	-	35 μA cm ⁻²	43%	-	20	91
Coaxial pillars	<i>a</i> -Si	LiPON	LiCoO ₂	25 μAh cm ⁻²	-	27.6 μA cm ⁻²	-	-	20	130
Coaxial pillars	<i>c</i> -Si/TiN/Sb	LiPF ₆	Li metal	400 μAh cm ⁻²	-	200 μA cm ⁻²	-	~100%	500	120
Swiss-roll structures	Si-Ge	LiPF ₆	LiMn ₂ O ₄	1053 μAh cm ⁻²	-	1.04 μA cm ⁻²	67%	85%	50	93
Mesoporous	<i>c</i> -Si	LiPF ₆	Li metal	-	2480 mAh g ⁻¹	500 μA cm ⁻²	97%	-	70	135
Macroporous	<i>c</i> -Si	PVDF-HFP	LiCoO ₂	226 μAh cm ⁻²	-	400 μA cm ⁻²	98%	99%	15	101
Honeycombs	<i>c</i> -Si/TiN/Ge	LiPF ₆	LiCoO ₂	0.15 mAh cm ⁻²	-	0.5 mA cm ⁻²	-	~100%	500	159

References:

- [1] Krauskopf, T.; Richter, F. H.; Zeier, W. G.; Janek, J., Physicochemical Concepts of the Lithium Metal Anode in Solid-State Batteries. Chemical Reviews 2020, 120, (15), 7745-7794.

[2] Liu, Q. Q.; Xiong, D. J.; Petibon, R.; Du, C. Y.; Dahn, J. R., Gas Evolution during Unwanted Lithium Plating in Li-Ion Cells with EC-Based or EC-Free Electrolytes. *Journal of the Electrochemical Society* 2016, 163, (14), A3010-A3015.

[3] Petibon, R.; Harlow, J.; Le, D. B.; Dahn, J. R., The use of ethyl acetate and methyl propanoate in combination with vinylene carbonate as ethylene carbonate-free solvent blends for electrolytes in Li-ion batteries. *Electrochimica Acta* 2015, 154, (0), 227-234.

[4] Fan, T.; Kai, W.; Harika, V. K.; Liu, C.; Nimkar, A.; Leifer, N.; Maiti, S.; Grinblat, J.; Tsubery, M. N.; Liu, X.; Wang, M.; Xu, L.; Lu, Y.; Min, Y.; Shpigel, N.; Aurbach, D., Operating Highly Stable LiCoO₂ Cathodes up to 4.6 V by Using an Effective Integration of Surface Engineering and Electrolyte Solutions Selection. *Advanced Functional Materials* 2022.

[5] Liu, Y.; Wu, H.; Wang, Y.; Li, K.; Yin, S.; Dahn, J. R., Impact of Shell Composition, Thickness and Heating Temperature on the Performance of Nickel-Rich Cobalt-Free Core-Shell Materials. *Journal of The Electrochemical Society* 2021, 167, (16), 160556.

[6] Liu, Y.; Harlow, J.; Dahn, J., Microstructural Observations of “Single Crystal” Positive Electrode Materials Before and After Long Term Cycling by Cross-section Scanning Electron Microscopy. *Journal of The Electrochemical Society* 2020, 167, (2).

[7] Liu, X. H.; Wang, J. W.; Huang, S.; Fan, F.; Huang, X.; Liu, Y.; Krylyuk, S.; Yoo, J.; Dayeh, S. A.; Davydov, A. V.; Mao, S. X.; Picraux, S. T.; Zhang, S.; Li, J.; Zhu, T.; Huang, J. Y., In situ atomic-scale imaging of electrochemical lithiation in silicon. *Nat Nano* 2012, 7, (11), 749-756.

[8] Lee, S. W.; McDowell, M. T.; Choi, J. W.; Cui, Y., Anomalous shape changes of silicon nanopillars by electrochemical lithiation. *Nano Lett* 2011, 11, (7), 3034-9.

[9] Goldman, J. L.; Long, B. R.; Gewirth, A. A.; Nuzzo, R. G., Strain Anisotropies and Self-Limiting Capacities in Single-Crystalline 3D Silicon Microstructures: Models for High Energy Density Lithium-Ion Battery Anodes. *Advanced Functional Materials* 2011, 21, (13), 2412-2422.

Authors' response:

Thank you very much for your reference suggestions. We have added those references at the respective locations within the text. Their reference numbers are as follows:

39. Goldman, J. L., Long, B. R., Gewirth, A. A. & Nuzzo, R. G. Strain anisotropies and self-limiting capacities in single-crystalline 3D silicon microstructures: Models for high energy density lithium-ion battery anodes. *Adv. Funct. Mater.* 21, 2412–2422 (2011).

40. Lee, S. W., McDowell, M. T., Choi, J. W. & Cui, Y. Anomalous shape changes of silicon nanopillars by electrochemical lithiation. *Nano Lett.* 11, 3034–3039 (2011).

42. Liu, X. H. et al. In situ atomic-scale imaging of electrochemical lithiation in silicon. *Nat. Nanotechnol.* 7, 749–756 (2012).

86. Liu, Y., Harlow, J. & Dahn, J. Microstructural Observations of “Single Crystal” Positive Electrode Materials Before and After Long Term Cycling by Cross-section Scanning Electron Microscopy. *J. Electrochem. Soc.* 167, 020512 (2020).

87. Liu, Y. et al. Impact of Shell Composition, Thickness and Heating Temperature on the Performance of Nickel-Rich Cobalt-Free Core-Shell Materials. *J. Electrochem. Soc.* 167, 160556 (2020).

162. Krauskopf, T., Richter, F. H., Zeier, W. G. & Janek, J. Physicochemical Concepts of the Lithium Metal Anode in Solid-State Batteries. *Chemical Reviews* vol. 120 7745–7794 (2020).

163. Liu, Q. Q., Xiong, D. J., Petibon, R., Du, C. Y. & Dahn, J. R. Gas Evolution during Unwanted Lithium Plating in Li-Ion Cells with EC-Based or EC-Free Electrolytes. *J. Electrochem. Soc.* 163, A3010–A3015 (2016).

164. Petibon, R., Harlow, J., Le, D. B. & Dahn, J. R. The use of ethyl acetate and methyl propanoate in combination with vinylene carbonate as ethylene carbonate-free solvent blends for electrolytes in Li-ion batteries. *Electrochim. Acta* 154, 227–234 (2015).

165. Fan, T. et al. Operating Highly Stable LiCoO₂ Cathodes up to 4.6 V by Using an Effective Integration of Surface Engineering and Electrolyte Solutions Selection. *Adv. Funct. Mater.* 32, 2204972 (2022).

Reviewer #2:

1) Do you think this Review is interesting and/or useful to other researchers working in the field?

Yes

2) Does the paper provide adequate critical discussion of the literature, or does it only summarize previous research efforts?

Yes

3) Do you think the paper is sufficiently forward-looking, and does it provide guidance for future research?

Yes

4) Are there any parts of the paper that should be expanded, or parts that you think should be removed? For example, is the balance between topics appropriate?

None

5) Are the figures and tables useful in communicating the author's key points?

Yes

Authors' response:

Thank you very much for your comments. We appreciate your positive feedback. In addition, we have improved the manuscript quality according to the comments from the other reviewers.

Reviewer #3:

In this review, the authors summarize the basic conception and the latest development of 3D silicon-based Li ion microbatteries according to the specific configurations. The review organizes the connections between the structure and performance of batteries, which is helpful for the future development of 3D Si-based Li ion batteries. I'd like to recommend it after some revisions.

1. Some sentences contain abbreviation typos like PVdF in line 317 and 320 and some unnecessary repeated full name like lithium-ion batteries in line 1030. The author should unify the expression.

Authors' response:

Thank you very much for your comments and suggestion. We have checked the manuscript thoroughly to correct any abbreviation-related errors or inconsistencies. The following changes have been made in the manuscript:

A study by Chaudoy *et al.* demonstrated the application of a gel polymer electrolyte (GPE) based on polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) linear polymer for a macroporous Si anode¹⁰¹.

Miniaturized LIBs, or the so-called micro-LIBs, can answer the needs.

Additionally, we also correct some other abbreviation-related errors, for example:

It is reported that porous Nasicon (monoclinic structure) $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ was formed instead of the orthorhombic crystalline LiFePO_4 .

Another important note is to develop better cell packaging to overcome the volatility of the dimethyl carbonate (DMC) component in the ethylene carbonate (EC)/DMC electrolyte.

Using focused-ion beam (FIB) to prepare a cross-sectional view of the towers by scanning electron microscopy (SEM), it is clear that there are at least three different regions formed after 5 cycles (see **Figures 5e and 5f**).

The spiral structure of spiral microelectrode (sp- μ ED) displays a reversible capacity of $755 \mu\text{Ah cm}^{-2}$, indicating that it can withstand the significant volume changes in silicon and germanium without damage (**Figure 7c**).

2. In Section 2.1, many synthesis methods of cathode materials come along. More description about the structures and advantages of different cathodes may be more focused on the core of the part. Meanwhile, different anode materials like carbon or alloy material should also be included in this section to complete and enrich the introduction of microbatteries. The following

works (doi: 10.1002/adma.202006229; 10.1038/s41467-020-15045-x) are suggested to include to inspire the readers.

Authors' response:

Thank you very much for your input. It is indeed important to add more explanations regarding different type of anode materials. However, we believe that the explanations should be added earlier as in Chapter 2.1 the discussion of the anode is already aimed for 3D Si. Therefore, we added the explanations on different type of anode materials in Chapter 1 "Introduction" as follows:

The idea was to increase energy and power density by employing different materials and processing techniques to produce a three-dimensional (3D) structure^{22–26}. With regard to the anode, many researchers have explored materials such as TiO₂ due to their favorable operational potential, cost-effectiveness, and non-toxic properties²⁷. However, its notable drawbacks, that is poor conductivity, hinder its further application as it impedes charge transfer. Conversion-reaction anodes, such as transition-metal oxides and sulfides, can also store high concentrations of ions. However, their practical use in microbatteries is hindered by significant, typically 30% to 50%, irreversible capacity loss during the initial cycles²⁸. Metallic zinc (Zn) and aluminum (Al) can also be a potential candidate as they exhibit remarkable stability in atmospheric conditions due to the formation of protective oxide layers on their surfaces. This stability is a significant advantage for the large-scale production and processing of Zn and Al metal anodes, essential for achieving higher energy densities. However, the challenge of poor reversibility is a common issue in Zn anodes and various other metal batteries. Apart from previously mentioned anode materials, alloying-type anodes like Si, Sb, Ge, and Sn can also be considered as they provide high capacity and stability²⁹.

The following papers have been added to references:

26. Sun, P., Li, X., Shao, J. & Braun, P. V. High-Performance Packaged 3D Lithium-Ion Microbatteries Fabricated Using Imprint Lithography. *Adv. Mater.* **33**, 2006229 (2021).

29. Ni, J. *et al.* Rooting binder-free tin nanoarrays into copper substrate via tin-copper alloying for robust energy storage. *Nat. Commun.* **11**, 1–8 (2020).

3. The language and graphics of this manuscript need to be further polished.

Authors' response:

Thank you very much for your comment. We have revisited, read, and revised the manuscript thoroughly to improve the language. For example, the explanation of cathode materials in Chapter 2.1 "Concept of microbattery" has been polished and Figure 1 has been modified.

4. In section 3, the author gave the title Recent emerging applications of 3D Si micro-LIB. However, in this chapter, the author discusses more about the structure of the 3D Li ion microbattery. The authors should give a more accurate title.

Authors' response:

Thank you very much for your comments. We have added an additional chapter: Chapter 3.6 “Applicability of 3D Si micro-LIBs” to extend the discussion beyond the structural aspect of the 3D Si micro-LIB. We hope that the title of Chapter 3 “Recent emerging applications of 3D Si micro-LIB” is now contextually suitable:

The currently existing 3D Si micro-LIB designs demonstrate their potential capabilities to provide energy in different ranges of applications. The resulting areal capacities differ from tens of $\mu\text{Ah cm}^{-2}$ up to several mAh cm^{-2} (see **Table 3**). Some reports use half-cell configuration with Li metal as the counter electrode, while some others already demonstrate the full-cell configuration with specific cathode materials. In particular, 3D Si micro-LIBs with full-cell configurations have good performances to fulfill the requirements of integrated microelectronics, considering their operating voltages, which translate to the energy densities between μWh to mWh^{116} . The thin-film structures exhibit relatively low areal capacities compared to 3D structures, for example the vertical pillar structures that have the highest areal capacity of nearly 10 mAh cm^{-2} . In terms of power, the rate capabilities that can be delivered by 3D structures are comparable to thin films, which exhibit the ability of 3D structures to provide high energy density but at the same time can be designed to produce high power density.

Amongst 3D structures, the additive-manufacturing method, which produces interdigitated structures, benefits from the flexibility of shaping the Si anode geometry. The limitation comes from the structure size determined by the nozzle diameter that is used to deposit the materials. For example, the currently demonstrated interdigitated structures possess a smallest size of several hundreds of micrometers¹²⁴. Therefore, further miniaturization would be a challenge. In addition, the use of binder in the ink slurry obliges a fragmented Si content (*i.e.*, Si has to be a fraction of the total mass of the anode), which might limit the areal capacity. Nevertheless, the utilization of a carbon matrix can help to maintain the structural integrity of the Si anode, hence, contributes to capacity retention. Therefore, the use of an interdigitated structure might fit to the applications in case the capacity is less important than the capacity retention. The corresponding applications might be flexible and wearable devices, where low-power electronic devices are designed to be energized by multiple charge/discharge cycles without the risk of a quick capacity degradation.

The pillar-based structures (including vertical pillars and nanowires), which are more preferably fabricated using subtractive method, offer high robustness of Si. The way these 3D structures are fabricated also enables the utilization of a monolithic Si anode without the need of any binder. Moreover, the integration of such structures into on-chip applications (*e.g.*, microcomputers, sensors, and microrobots) can be straightforward since fabrication technologies (*e.g.*, lithography, dry etching, and various deposition methods) are widely used in semiconductor device production. In terms of performance, the areal capacities of pillar-based structures can achieve several mAh cm^{-2} , which are relatively high compared to those of other 3D structures. It indicates that the utilization of Si can be maximized. It is also possible to exploit the high power capability due to the transformation of *c*-Si to *a*-Si, as indicated by the high rate capability

of hundreds of mA cm^{-2} . The high Coulombic efficiency over hundreds of cycles makes the utilization of such 3D structures even more promising for on-chip energy storage.

The *a*-Si anodes fabricated in coaxial pillars and Swiss-roll structures are promising alternatives in semiconductor processing technology. In principle, both structure types are aimed to utilize the conformity of all micro-LIB components (*i.e.*, current collectors, electrodes, and electrolyte) to result in a short Li^+ diffusion pathway by increasing the interfacial-area sizes within the same areal footprint. In particular, Swiss-roll structure offers a simple and low-cost fabrication method to realize this aim. The resulting rate capability is comparable with the other 3D structures. Furthermore, it has been demonstrated that the full-cell prototype of a Swiss-roll structure with an areal footprint of 0.17 mm^2 is capable of powering a digital watch for 15 minutes, which is normally energized by a conventional AA battery, showing its potential as an alternative for a battery power supply⁹³.

Applications of 3D Si micro-LIBs may also be challenged by varying operating temperatures. Unfortunately, there is still limited information provided by published sources, especially regarding the relation between temperature and structural integrity of the various 3D Si anodes. However, elevated temperatures can affect the kinetics of the battery. At elevated temperatures, the ionic conductivity of the solid electrolyte may decrease compared to a liquid electrolyte⁷¹. This may be an important criterion for material selection.

Research in 3D Si micro-LIBs has successfully shown the capability of various structural designs from the level of proof-of-concept up until prototyping. Indeed, the demonstrated 3D designs have exhibited promising specific capacities, rate capabilities, as well as cyclabilities. Nevertheless, the implementation of these results into commercial use might pose different challenges.

Firstly, the main challenge comes from the upscaling of the 3D Si micro-LIBs fabrication process. As a roll-to-roll production has been established in the conventional LIB manufacturing, the current semiconductor processing technology should be able to accommodate mass production of micro-LIBs, too. The semiconductor industries have successfully automated large-batch production of microelectronic devices, which can deliver products with high throughput. When the process tries to integrate the production of micro-LIBs, the bottleneck might come from the fact that some steps involving the deposition of Li-containing materials have to be done inside a glovebox with low humidity and oxygen content. When manufacturing a prototype of 3D Si micro-LIBs can be carried out by human hands, the automated process has yet to be established in the current semiconductor processing line. The realization of such process is imperative to enable a higher throughput and thus lower the production cost.

Secondly, although the fabrication of 3D Si structures has already been well established for microelectronic devices, the fabrication of a complete 3D Si micro-LIB requires an optimized and reliable device performance before going to the real market. Most of the reported 3D Si micro-LIBs still show stable performance in hundreds of cycles, whereas the actual need usually

necessitates a stable and reproducible battery performance in thousands of cycles. Bridging this gap can be accomplished by pushing more research not only to a proof-of-concept, but further to the long-term reliability of 3D Si micro-LIBs. In fact, published results, specifically about the utilization of 3D Si anodes for micro-LIBs, is still very limited. This is in contrast with the results of nanostructured Si anodes for conventional LIBs.

Lastly, while many studies on 3D Si micro-LIBs focus on the development of performance metrics, there are still a few that are dedicated to include the packaging aspect. Packaging is a final step in 3D Si micro-LIB fabrication that requires special attention since it is related not only to performance aspects such as reliability of the device, but also safety issues. In general micro-LIB research, efforts are directed towards the utilization of solid electrolytes since the application of micro-LIB has to be compatible with solid-state electronics. Packaging for such type of electrolytes (*e.g.*, LiPONB and SU-8) in 3D Si micro-LIB has been done for example by epoxy encapsulations^{71,105}. Liquid electrolytes, which are used in 3D Si micro-LIBs such as LiClO₄ or LiPF₆, are mostly used in half-cell configurations resulting in packaging forms of Swagelok cells or CR2032 coin cells^{91,120,121,124,134,135,159}. However, some of the demonstrated full-cell prototypes using liquid electrolytes have already applied packaging techniques such as the employment of sandwiched c-Si/glass/c-Si glued with UV-cured adhesive⁷⁰ or capillary tubes sealed with photocurable epoxy⁹³. The scarcity of the reported packaging techniques in 3D Si micro-LIB fabrication should drive more studies about this crucial yet unexplored aspect in the future.

5. Some recent reviews on 3D microbatteries (such as doi:10.1002/adfm.201704880; 10.1021/accountsmr.1c00175) are suggested to be included in the paper.

Authors' response:

Thank you very much for your suggestion.
Both reviews have been added to references:

12. Ni, J. & Li, L. Self-Supported 3D Array Electrodes for Sodium Microbatteries. *Adv. Funct. Mater.* 28, 1704880 (2018).

25. Zhu, S., Sheng, J., Ni, J. & Li, Y. 3D Vertical Arrays of Nanomaterials for Microscaled Energy Storage Devices. *Accounts Mater. Res.* 2, 1215–1226 (2021).

Those references have been cited in Chapter 1 “Introduction” as ref 12 and 25, respectively.

The miniaturization of such devices can only be possible by realizing independent energy-storage systems that are not only fulfilling the energy requirement but also are small and could be integrated on-chip^{9–12}

The idea was to increase energy and power density by employing different materials and processing techniques to produce a three-dimensional (3D) structure^{22–26}.

Reviewer #4:

The review covers various key aspects of the latest developments in 3D silicon-based lithium-ion microbatteries. It discusses their material compatibility, cell designs, fabrication methods, and performance across various materials and architectures. Authors highlight the critical relationship between device architecture and performance and provides comparisons between various fabrication technologies. This review can be a good reference work, however, I have several comments that may need to be addressed before recommending for publication.

General comments:

Since the focus of this review paper is Si anode based 3D microbatteries, it seems necessary to discuss the electrochemistry of silicon, (i.e. ion insertion reaction mechanisms, crystalline vs. Amorphous, etc.) challenges, and opportunities in the introduction section.

Authors' response:

Thank you very much for your suggestions. We have added the following text in Chapter 2.1 "Concept of microbattery":

As a potential anode material in LIBs, Si had attracted the attention of many studies. In contrast with the intercalation of Li (*i.e.*, Li intercalates between adjacent atomic layers) in graphite, the lithiation mechanism of Li ions into Si occurs through insertion process. Lithiation mechanism of Si in general is a Li-Si alloying reaction, involving Si-Si bond breaking. Works have been done to investigate the electrochemical characteristics of crystalline Si (*c*-Si) with the aims of understanding the lithiation mechanism and improving Si anode performance in LIBs. Since the performance of a Si anode is limited by the mechanical disintegration of Si upon (de-)lithiation, studies are dedicated to demystify the lithiation-induced stresses. It was found that the strain evolution in *c*-Si is highly anisotropic³⁹. This non-uniform deformation drives gradient strain fields, which determine the material performance. Si nanopillars with three different axial orientations (*i.e.*, $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$) were used to investigate the morphological deformation of *c*-Si upon lithiation⁴⁰. The cross-sectional view of Si nanopillars after the first lithiation shows cross, oval, and hexagonal shapes of $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ oriented nanopillars, respectively. The results suggest an orientation-dependent nature of lithiation, in which Li prefers to enter into *c*-Si through $\langle 110 \rangle$ ion channels. Furthermore, atomistic insight into the (de-)lithiation mechanism of Si nanowires was obtained by reactive molecular dynamic simulation⁴¹ that confirms a Li penetration tendency along the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions. During lithiation, *c*-Si transforms into amorphous Li_xSi (*a*- Li_xSi) phases through Si-Si bond breaking caused by tensile stress between Si atoms. *In situ* transmission electron microscopy (TEM) was used to observe the dynamics of lithiation at atomic resolution in real time⁴². The study revealed the so-called ledge mechanism, in which an amorphization of *c*-Si during Li insertion occurs via a layer-by-layer peeling of $\{111\}$ atomic planes at the *c*-Si/*a*- Li_xSi interface. It was also demonstrated that the progression of the reaction front is atomically sharp (~ 1 nm), and its mobility depends on crystal orientation (*i.e.*, amorphizations through $\{111\}$ facets are much slower than the $\{110\}$ and $\{112\}$ facets). Besides *c*-Si, amorphous Si (*a*-Si) is also used as

an anode in LIBs⁴³. Similar to *c*-Si, the first lithiation of *a*-Si is also characterized by a two-phase reaction with the progression of a sharp interface into the non-lithiated Si, followed by a single-phase mechanism in the delithiation process and the subsequent cycles. However, there are some differences including isotropic lithiation and volume change, lower Li concentration in the lithiated phase compared to the lithiated *c*-Si, and a relatively constant reaction rate (in contrast to the significant slowing of the reaction front in *c*-Si). The benefit of those characteristics is that *a*-Si has a more manageable morphological deformation than *c*-Si, which in some cases, makes *a*-Si more favorable as an anode material. For example, it was demonstrated that Si nanoparticles in an amorphous phase have a larger critical radius for fracture compared to their crystalline counterparts.

Authors took an effort to review the cathode materials in the introduction but do not really discuss. It would be interesting to include a column in Table 3 and see where the community is at (and possibly why). Without such discussion, the discussions involving cathode materials and synthesis approach in the introduction seem unnecessary.

Authors' response:

Thank you very much for your comments. We have modified **Table 3** to include cathode and electrolyte materials, and discuss them in an additional chapter, Chapter 3.6 "Applicability of 3D Si micro-LIBs":

Table 3 Various structures of Si micro-LIBs and their performance. Comparison is made in terms of their architecture, materials, and performance metrics (*i.e.*, capacity, rate capability, and capacity retention, Coulombic efficiency, and cycle).

Architecture	Materials			Capacity		Rate capability	Capacity retention	Coulombic efficiency	Cycle	Ref.
	Anode	Electrolyte	Cathode	Areal capacity	Specific capacity					
Thin film	<i>a</i> -Si	LiPON	Li metal	40 $\mu\text{Ah cm}^{-2}$	-	800 $\mu\text{A cm}^{-2}$	-	99.99%	1500	105
Thin film	<i>a</i> -Si	LiPON	VO-LiPO	15.7 $\mu\text{Ah cm}^{-2}$	-	-	49%	-	30	106
Thin film	Poly-Si	LiPON	LiCoO ₂	-	3000 mAh g ⁻¹	40 mA cm ⁻²	-	-	60	118
Interdigitated structures	Si/C-graphite	LP30/FEC	Li metal	-	466 mAh g ⁻¹	2C	75%	-	65	124
Vertical pillars	<i>a</i> -Si	SU-8	NCA	1.8 mAh cm ⁻²	-	0.66 mA cm ⁻²	-	92%	100	71
Vertical pillars	<i>a</i> -Si	LiClO ₄	NCA	9.4 mAh cm ⁻²	-	181 mA cm ⁻²	83%	99.9%	200	70
Vertical pillars	<i>a</i> -Si	LiClO ₄	Li metal	-	1093 mAh g ⁻¹	-	-	98.9%	5	134
Nanowires	<i>a</i> -Si/PAN	LiPF ₆	Li metal	2 mAh cm ⁻²	-	2 mA cm ⁻²	-	~100%	346	121
Nanowires	<i>a</i> -Si	LiClO ₄	Li metal	3000 $\mu\text{Ah cm}^{-2}$	-	35 $\mu\text{A cm}^{-2}$	43%	-	20	91
Coaxial pillars	<i>a</i> -Si	LiPON	LiCoO ₂	25 $\mu\text{Ah cm}^{-2}$	-	27.6 $\mu\text{A cm}^{-2}$	-	-	20	130
Coaxial pillars	<i>a</i> -Si/TiN/Si	LiPF ₆	Li metal	400 $\mu\text{Ah cm}^{-2}$	-	200 $\mu\text{A cm}^{-2}$	-	~100%	500	120
Swiss-roll structures	Si-Ga	LiPF ₆	LiMn ₂ O ₄	1053 $\mu\text{Ah cm}^{-2}$	-	1.04 $\mu\text{A cm}^{-2}$	67%	85%	50	93
Mesoporous	<i>a</i> -Si	LiPF ₆	Li metal	-	2480 mAh g ⁻¹	500 $\mu\text{A cm}^{-2}$	97%	-	70	135
Macroporous	<i>a</i> -Si	PVDF-HFP	LiCoO ₂	226 $\mu\text{Ah cm}^{-2}$	-	400 $\mu\text{A cm}^{-2}$	98%	99%	15	101

Honeycombs				0.15 mAh cm ⁻²	-	0.5 mA cm ⁻²	-	~100%	500	159
										

Several state-of-the-art inorganic solid electrolyte systems depend on high stack pressures, sometimes exceeding 100 MPa, for optimal performance. However, it raises the question of whether such pressures are viable for 3D electrode architectures, given their high-aspect-ratio structures and the challenges associated with anisotropy.

Authors' response:

Thank you for your insightful comment regarding the application of high stack pressures. We would like to emphasize that the feasibility of employing high stack pressures on such systems has indeed been demonstrated. Previous studies, some of which we reference in our review, have successfully utilized inorganic solid electrolytes with 3D electrode architectures and achieved not only functional stability but also mechanical robustness. Moreover, the improvement of mechanical properties of Si by reducing the size to micro-/nanoscale 3D structures has also been demonstrated by some studies.

To underline this concern, we have added the following text to the electrolyte part in Chapter 2.1 "Concept of microbattery":

From the perspective of mechanical stability, the employment of a solid electrolyte into Si micro-LIBs should also consider the structural integrity of the Si anode. For example, some of the state-of-the-art solid electrolytes require high stack pressures for optimal device performance that are even surpassing 100 MPa^{110,111}. This might rise some questions about the viability of the Si anode to handle the pressure within the cell, especially when a 3D nano-/microstructure is utilized. It is because Si is known of its brittleness. In fact, a study showed the ability of microstructured Si of high surface quality to handle shear stress up to 4 GPa¹¹². In another report, a Si nanowire with a diameter of 30 nm can even sustain an extreme tensile stress of more than 12 GPa¹¹³. Moreover, the feasibility of employing high stack pressures on such systems has indeed been demonstrated, which shows the capability of Si to maintain not only functional stability but also mechanical robustness upon high pressure.

The review mainly highlights inorganic solid electrolytes with a focus on LiPON-based chemistries. They are reported to exhibit considerably lower ionic conductivities compared to more recent systems. The adequacy of these conductivities for 3D microbatteries, where high ionic conductivity is crucial for uniform lithiation/de-lithiation of 3D electrodes and achieving the high power densities that make 3D microbatteries advantageous, needs consideration.

Authors' response:

Thank you for your insightful comments and for pointing out the emphasis on LiPON-based chemistries in our review. The choice to focus on LiPON, despite some reports indicating its lower ionic conductivity compared to more recent systems, was deliberate and multifaceted. Historically, LiPON-based compounds have been at the forefront of solid electrolyte research,

offering a foundational perspective on the evolution of electrolytes in the realm of micro-LIBs. This historical depth allows readers to gauge the advancements and challenges of newer electrolytes based on an established benchmark.

Furthermore, LiPON exhibits commendable electrochemical stability and compatibility, especially with Si anodes, as our referenced studies have shown. This balance between stability and compatibility is crucial for ensuring longevity and safety in micro-LIB applications. Beyond its chemical attributes, the mechanical robustness of LiPON, particularly its ability to prevent crack initiation in Si anodes, is paramount, given the stresses micro-LIBs are subjected to during operation.

While we acknowledge the importance of high ionic conductivity for uniform lithiation/delithiation in 3D microbatteries, we believe that focusing solely on conductivity might overshadow other equally vital attributes. LiPON, despite its conductivity challenges, offers a suite of features making it a viable contender for 3D microbatteries. Moreover, by emphasizing its current limitations, we hope to inspire targeted research efforts to augment its properties by showing that some efforts have been done already to improve the ionic conductivity of LiPON.

To clarify this aspect, we have modified the following discussion in the electrolyte part in Chapter 2.1 “Concept of microbattery”:

LiPON-based compounds are the most developed glass electrolytes because they have high electrochemical stability and low electronic conductivity. Phan *et al.* evaluated LiPONB as a solid electrolyte in Li/LiPONB/Si micro batteries¹⁰⁵. Boron was added into LiPON electrolytes to improve chemical and thermal durability, while also maintaining the electrical performance¹⁰⁵. The most prominent finding from this study is the ability of LiPONB to prevent initiation of cracks in the Si anode thanks to its excellent mechanical stability and adhesion. It was also found that the reaction of the LiPONB electrolyte with the electrodes does not produce any byproduct at their interfaces, implying the compatibility of LiPONB with Si anodes.

Kanazawa and coworkers recently prepared thin-film batteries consisting of amorphous vanadium oxide with lithium phosphorus oxide (VO-LiPO), Si, and LiPON as cathode, anode, and electrolyte materials, respectively¹⁰⁶. The process involved the use of a three-target RF magnetron sputtering system, which had a mask moving system, to deposit multiple layers of VO-LiPO-cathode, LiPON-electrolyte, and Si-anode materials onto a substrate. It was discovered that the resulting thin-film LIBs exhibited a compact structure and well-defined boundaries between the LiPON electrolyte and both the cathode and anode layers, suggesting compatibility among them.

However, all-solid-state systems using LiPON-based electrolytes show a slightly reduced capacity for a given voltage window and a lower current density due to higher polarization caused by the lower ionic conductivity of LiPON solid electrolytes in comparison to a liquid one¹⁰⁵. There are studies which have been dedicated to improve the ionic conductivity of LiPON.

for example by the addition of molybdenum trioxide (MoO_3)¹⁰⁷ or by doping (B, Al, As, or Mg)^{108,109}. Implementation of such efforts in Si micro-LIBs should be aimed in the future. Additionally, the synthesis and deposition of high-quality LiPON thin films can be technically challenging and requires specialized equipment, which can increase the cost and complexity of the manufacturing process²⁴. Thus, these problems need to be resolved before their further applications for micro-LIBs.

One of the biggest challenges for 3D micro batteries lies in their packaging. The discussion around how to package a non-planar battery, particularly when it involves liquid or gel electrolytes (which is the current state of the field) seems necessary. Addressing this challenge is a critical need within the community and should be thoroughly discussed.

Authors' response:

Thank you very much for your comments. The following texts have been added into Chapter 3.6 “Applicability of 3D Si micro-LIBs”:

Lastly, while many studies on 3D Si micro-LIBs focus on the development of performance metrics, there are still a few that are dedicated to include the packaging aspect. Packaging is a final step in 3D Si micro-LIB fabrication that requires special attention since it is related not only to performance aspects such as reliability of the device, but also safety issues. In general micro-LIB research, efforts are directed towards the utilization of solid electrolytes since the application of micro-LIB has to be compatible with solid-state electronics. Packaging for such type of electrolytes (*e.g.*, LiPONB and SU-8) in 3D Si micro-LIB has been done for example by epoxy encapsulations^{71,105}. Liquid electrolytes, which are used in 3D Si micro-LIBs such as LiClO_4 or LiPF_6 , are mostly used in half-cell configurations resulting in packaging forms of Swagelok cells or CR2032 coin cells^{91,120,121,124,134,135,159}. However, some of the demonstrated full-cell prototypes using liquid electrolytes have already applied packaging techniques such as the employment of sandwiched c-Si/glass/c-Si glued with UV-cured adhesive⁷⁰ or capillary tubes sealed with photocurable epoxy⁹³. The scarcity of the reported packaging techniques in 3D Si micro-LIB fabrication should drive more studies about this crucial yet unexplored aspect in the future.

Based on this review, the community has developed a number of different ways to achieve 3D Si micro-LIBs, particularly for the prototype demonstration. It would be good to get authors' perspective on what the technological gap is between these prototypes and the actual need for implementation.

Authors' response:

Thank you very much for your suggestion. We have added Chapter 3.6 “Applicability of 3D Si micro-LIBs”, dedicated to the comparative discussion about different 3D structures and their challenges for implementation:

Research in 3D Si micro-LIBs has successfully shown the capability of various structural designs from the level of proof-of-concept up until prototyping. Indeed, the demonstrated 3D designs have exhibited promising specific capacities, rate capabilities, as well as cyclabilities. Nevertheless, the implementation of these results into commercial use might pose different challenges.

Firstly, the main challenge comes from the upscaling of the 3D Si micro-LIBs fabrication process. As a roll-to-roll production has been established in the conventional LIB manufacturing, the current semiconductor processing technology should be able to accommodate mass production of micro-LIBs, too. The semiconductor industries have successfully automated large-batch production of microelectronic devices, which can deliver products with high throughput. When the process tries to integrate the production of micro-LIBs, the bottleneck might come from the fact that some steps involving the deposition of Li-containing materials have to be done inside a glovebox with low humidity and oxygen content. When manufacturing a prototype of 3D Si micro-LIBs can be carried out by human hands, the automated process has yet to be established in the current semiconductor processing line. The realization of such process is imperative to enable a higher throughput and thus lower the production cost.

Secondly, although the fabrication of 3D Si structures has already been well established for microelectronic devices, the fabrication of a complete 3D Si micro-LIB requires an optimized and reliable device performance before going to the real market. Most of the reported 3D Si micro-LIBs still show stable performance in hundreds of cycles, whereas the actual need usually necessitates a stable and reproducible battery performance in thousands of cycles. Bridging this gap can be accomplished by pushing more research not only to a proof-of-concept, but further to the long-term reliability of 3D Si micro-LIBs. In fact, published results, specifically about the utilization of 3D Si anodes for micro-LIBs, is still very limited. This is in contrast with the results of nanostructured Si anodes for conventional LIBs.

Lastly, while many studies on 3D Si micro-LIBs focus on the development of performance metrics, there are still a few that are dedicated to include the packaging aspect. Packaging is a final step in 3D Si micro-LIB fabrication that requires special attention since it is related not only to performance aspects such as reliability of the device, but also safety issues. In general micro-LIB research, efforts are directed towards the utilization of solid electrolytes since the application of micro-LIB has to be compatible with solid-state electronics. Packaging for such type of electrolytes (*e.g.*, LiPONB and SU-8) in 3D Si micro-LIB has been done for example by epoxy encapsulations^{71,105}. Liquid electrolytes, which are used in 3D Si micro-LIBs such as LiClO₄ or LiPF₆, are mostly used in half-cell configurations resulting in packaging forms of Swagelok cells or CR2032 coin cells^{91,120,121,124,134,135,159}. However, some of the demonstrated full-cell prototypes using liquid electrolytes have already applied packaging techniques such as the employment of sandwiched c-Si/glass/c-Si glued with UV-cured adhesive⁷⁰ or capillary tubes sealed with photocurable epoxy⁹³. The scarcity of the reported packaging techniques in 3D Si micro-LIB fabrication should drive more studies about this crucial yet unexplored aspect in the future.

Specific comments:

Ln 285 "For electrode making, those cathode materials will easily follow the usual fabrication methods for 3D Si micro-LIBs."

What is the usual fabrication methods for 3D Si micro LIBs? Is this in reference to Section 3? Examples included in Section 3, such as RF sputtering and ALD, are certainly not easy nor usual.

Authors' response:

Thank you very much for your comment. We have removed the mentioned statement to prevent confusion. Moreover, the cathode material part in Chapter 2.1 "Concept of microbattery" has been totally revised to provide clearer information about the fabrication of each variety of cathode materials and is discussed in the context of 3D Si micro-LIBs:

Table 1 Commercial lithium-ion battery cathode materials in different structures^{44–51}. A comparison of several key performance indicators (*i.e.*, average potential vs. Li/Li^+ , specific capacity range, and gravimetric energy density) of different cathode materials (*i.e.*, LiCoO_2 (LCO), LiFePO_4 (LFP), $\text{Li}(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ (NCA), LiMn_2O_4 (LMO) variants, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) variants, and LiNiO_2).

Cathode material	Structure	Average potential vs Li/Li^+ (V)	Specific capacity range (mAh g^{-1})	Gravimetric energy density range (Wh kg^{-1})	Cost	Safety	Material synthesis
LCO	Layered	3.90	140–160	530–550	High	Low	Easy
LFP	Olivine	3.45	150–170	520–590	Low	High	Medium
NCA	Layered	3.80	180–200	680–760	Medium	Medium	Medium
LMO variants	Spinel	4.10	100–120	410–490	Low	Medium	Easy
NCM variants	Layered	3.80	160–170	610–650	Medium	Medium	Medium
LiNiO_2	Rocksalt	3.85	150–190	620–770	Medium	Low	Difficult

To maximize energy density, cathodes for LIBs are engineered to have higher average potentials relative to Li/Li^+ compared to earlier materials like TiS_2 and vanadates designed for lithium metal batteries⁵¹. Moreover, cathode materials are typically limited to those containing first-row transition metals, including manganese (Mn), iron (Fe), cobalt (Co), and nickel (Ni), to meet the demand for high specific capacity⁴⁴. Presently, cathode materials for LIBs encompass metal oxides and poly-anionic compounds. Integrating cathodes into microbattery assemblies represents a notable challenge in microbattery development. Thus far, only a handful of instances have been documented regarding the use of 3D cathode architectures for microbatteries, as achieving a 3D cathode poses a severer difficulty than synthesizing 3D anodes or electrolytes. This section provides an overview of potential cathode materials that can be paired with silicon-

based anodes in 3D Si micro-LIBs (refer to **Table 1**). The suitability is assessed based on various parameters such as average potential, average specific capacity, gravimetric energy density, cost-effectiveness, safety consideration, and material synthesis. The gravimetric energy densities are obtained from the references, where those values were calculated as the product of average potential and specific capacity⁵⁰. **Figure 1** offers a qualitative comparison of these cathode materials.

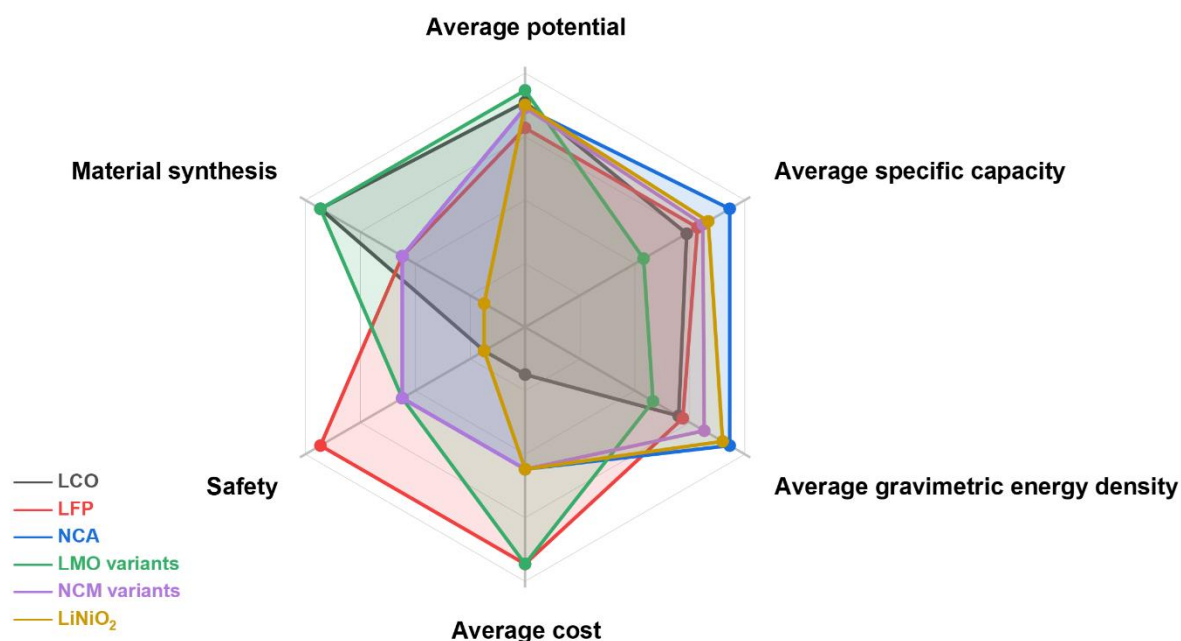


Figure 1 Cathode-material performance comparison for supporting 3D Si micro-LIBs. Different cathode materials have their own advantages and drawbacks in terms of lifespan, energy density, performance, cost, and safety.

A promising alternative approach involves the creation of 3D LIBs with thicker electrodes, surpassing 100 μm in thickness^{52–56}. The volumetric ratio of active to inactive materials within LIBs, and consequently their energy capacity, increases linearly with the electrode thickness for a given area. However, achieving efficient ionic and electronic transport through thicker electrodes presents challenges, leading to limitations in power density^{57–59}. To address this, recent research has concentrated on producing lithium-based cathodes with internal open channels perpendicular to current collector surfaces. This was accomplished through magnetic-field-induced alignment of anisotropic porogens, comprising either magnetic particle-coated polymer rods or particle-stabilized emulsion droplets. The result was sintered LiCoO_2 (LCO) cathodes, measuring 310 μm in thickness, exhibiting an impressive areal capacity of $\approx 12 \text{ mAh cm}^{-2}$ at a rate of 0.1 C⁶⁰. In the pursuit of enhancing electronic transport, highly porous metal foams have also been employed as 3D current collectors to develop high-performance LiFePO_4 (LFP) cathodes, 540- μm -thick, with an areal capacity of 8.8 mAh cm^{-2} at a current density of 1 mA cm^{-2} ⁵². It is worth noting that the use of thick electrodes introduces additional challenges, including issues with migration, cracking, and delamination during the drying process⁶¹, as well as incomplete electrolyte infiltration⁶². Another strategy for achieving uniform deposition of

LCO involves the thermal decomposition of sol-gel precursors spray-coated onto 3D-Al-nanorod current collectors directly grown on Al substrates. Additionally, it is important to recall that Ceder *et al.* have identified new cathode materials, in which non-transition metals are substituted for cobalt. Phases such as $\text{LiCo}_{1-x}\text{Al}_x\text{O}_2$ have been reported, and an increase in cell voltage with Al substitution has been experimentally confirmed⁶³. Compared with a planar electrode presenting an equivalent nominal capacity, a 3D electrode exhibits improved capacity retention, retaining 68% of the nominal capacity at 8 C instead of 11%⁶⁴.

Recent studies have showcased the creation of micro-LIBs through the direct deposition of LFP cathode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode inks. The cathode inks are formulated by suspending LFP nanoparticles (with an average diameter of 180 nm) in a solution containing deionized water, ethylene glycol, glycerol, and viscosifiers derived from cellulose. This process involves multiple steps, including particle dispersion, centrifugation, and homogenization. Specifically, high-aspect-ratio, interdigitated LFP and LTO electrodes were printed with a wall thickness of approximately 60 μm and a height ranging from around 200 to 400 μm . These micro-LIBs, with a total volume of less than 1 mm^3 , demonstrated an areal capacity of roughly 1.5 mAh cm^{-2} when discharged at rates below 5 C. However, electronic transport constraints were observed, as LFP electrodes printed with eight layers (approximately 200 μm thick) displayed the same current density as those with 16 layers (approximately 400 μm thick)⁶⁵. Besides its promising performance, several challenges for LFP, such as low electronic conductivity and limited Li-ion diffusivity, especially for untreated/undoped LFP, which affect the overall properties of LFP, have to be addressed for future applications^{66–69}.

In another investigation, $\text{Li}(\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05})\text{O}_2$ (NCA) was employed as the active material for the positive electrode in a semiconductor-grade single-crystalline Si microbattery. The NCA cathode was created using a conventional slurry formulation, comprising 88% w/w NCA, 6% polyvinylidene fluoride (PVDF), 3% carbon black, and 3% graphite, mixed with an equal weight of N-Methyl-2-pyrrolidone (NMP). The slurry mixture was prepared using a planetary micro mill. The quantity of NCA within the cathode cavity was either 3.8 mg (for cells with a 0.5 mAh capacity) or 10.0 mg (for cells with a discharge capacity ranging from 1.0 to 2.0 mAh). The slurry was then dried at 60 °C for 12 hours in a temperature chamber without forced air circulation. The device exhibited a high current output power (200 mW cm^{-2} ; 30 mA peak current) and demonstrated robust charge/discharge stability for at least 100 cycles (equivalent to 10 mAh cm^{-2}). Additionally, it exhibited a high Coulombic efficiency, nearing 100%, making it highly suitable for integration into a wide array of intelligent, self-powered electric devices⁷⁰. Using a similar approach, the cathode slurry consisted of 75% NCA, 18.3% graphite, 1.7% PVDF, 2.8% lithium bis(trifluoromethane)sulfonimide (LiTFSI), 1.1% tetraglyme (TG), and 1.1% poly(ethylene oxide) (PEO), which were combined and assembled using a vacuum-infiltration protocol onto SU-8-coated Si arrays. The resulting rechargeable 3D microbatteries, fashioned on a 3 mm $\times$ 3 mm footprint, exhibited an areal capacity of nearly 2 mAh cm^{-2} . They operated at current densities of up to 0.66 mA cm^{-2} and maintained stability through 100 cycles⁷¹.

An innovative 3D micro-LIB is introduced, featuring sub-10 nm LiMn_2O_4 (LMO)/LTO nanocrystals synthesized through a solvothermal method and a novel copolymer gel electrolyte. This microbattery exhibits exceptional capacity retention (40% at 300 C) and boasts a high power density of $855.5 \mu\text{Wcm}^{-2} \mu\text{m}^{-1}$. The tailored microelectrodes are created via solvent-assisted imprint lithography, utilizing well-dispersed nanoparticle ink, and the battery cell is vertically integrated through layer-by-layer (LBL) assembly⁷². In a separate investigation, functional 3D LMO thin-film electrodes are produced, yielding a footprint capacity of 0.5 mAh cm^{-2} , employing an innovative process grounded in a solid-state reaction between electrolytic manganese dioxide (EMD) and Li_2CO_3 stacked-layers. These prepared thin films demonstrate electrochemical activity, achieving a volumetric capacity of 1200 Ah L^{-1} , closely approaching the theoretical capacity of spinel LMO. Moreover, a thin-film morphology, spanning a few hundred nanometers, allows for utilization of both 3 V and 4 V regions⁷³. Furthermore, a Mn-dissolution process of the LMO cathode at elevated temperatures⁷⁴ has to be a concern to achieve a more applicable 3D Si micro-LIBs.

A lithium nickel manganese cobalt oxide, specifically $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM-111), has emerged as a pivotal cathode material, particularly for mobile power sources, owing to its notable gravimetric and volumetric capacity. However, the automotive industry necessitates batteries with even higher energy density to propel the development of electric vehicles (EVs) with competitive or surpassing ranges compared to internal combustion engine automobiles⁷⁵. NCM-111 boasts several advantages, including a cell-level high energy density ($>150 \text{ Wh kg}^{-1}$), a robust power density (650 W kg^{-1} @ 25°C and 50% Depth of Discharge/DoD)⁷⁶, an exceptional rate capability, a substantial specific capacity (163 mAh g^{-1}), and a commendable thermal stability in the fully charged state⁷⁷. One strategy to enlarge energy density is by augmenting the nickel content in the NCM cathode material. Hence, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NCM-622) cathodes were fabricated using tape casting, incorporating 80 wt% of active material with a film thickness of $54 \mu\text{m}$. Additionally, to attain a 3D architecture, an ultrafast fiber-laser-driven ablation process was employed, creating line structures with a pitch of $200 \mu\text{m}$. This cathode material demonstrated an initial discharge capacity of 178 mAh g^{-1} at a C-rate of C/10. Notably, at a discharge rate of 10 C, the cell equipped with the structured cathode managed to maintain a discharge capacity of 35% of the initial value⁷⁸.

Moreover, well-established synthesis procedures^{75,79–85} and stability make cathode powder materials suitable for use in various electrode production methods. There is no distinct variation in the approach to achieving a 3D architecture, even with cathodes containing higher nickel contents such as $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NCM-811), $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ (NCM-955), and other potential cathode materials like LiNiO_2 ^{86,87}. Various protocols, including conventional slurry-based techniques, tape casting, laser ablation, layer deposition synthesis (e.g., ALD and MLD), as well as other thin-film fabrication and micro-architectural building methods, could be employed to design an advanced 3D cathode that complements the 3D Si micro-LIB^{47,88–90}.

Ln 464 "the fabrication of a Si anode can be classified either as additive (bottom-up, see Figures 3a-c) or subtractive (top-down, see Figures 3d-f) methods"

Figure 3 includes examples that do not include 3D Si anodes. It may mislead readers.

Authors' response:

Thank you very much for your comments. We have replaced Figure 3c to refer the study that demonstrates 3D Si anode fabrication:

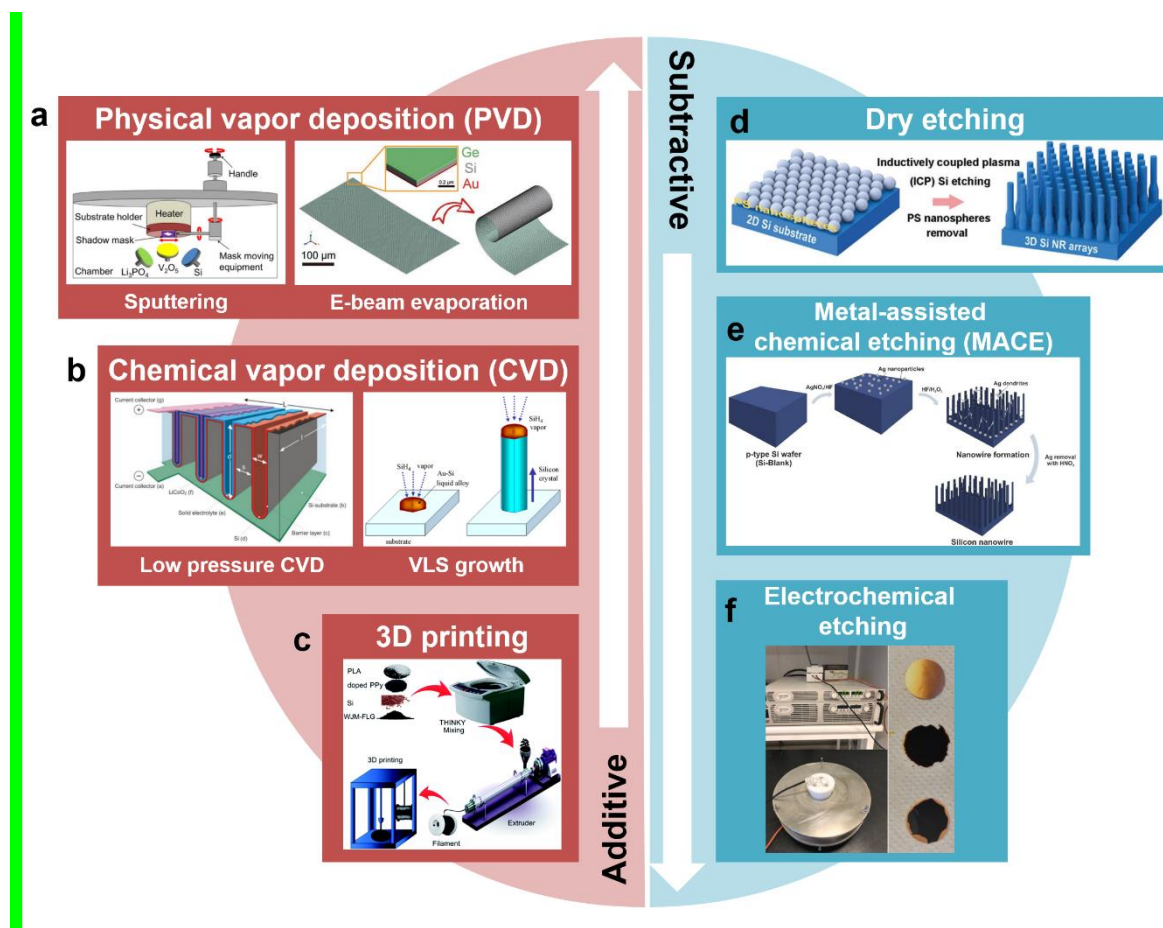


Figure 3 Fabrication methods of 3D Si anodes for micro-LIBs, classified as additive and subtractive techniques. Additive techniques used for fabricating Si anodes in a bottom-up manner include **a** physical vapor deposition (PVD) processes (*e.g.*, magnetron sputtering (adapted with permission from ref¹⁰⁵, Copyright 2020 Elsevier) and electron beam evaporation (adapted with permission from ref⁹², Copyright 2020 Wiley-VCH GmbH)), **b** chemical vapor deposition (CVD) processes (*e.g.*, low pressure CVD (LPCVD) (adapted with permission from ref¹¹⁷, Copyright 2008 Wiley-VCH GmbH) and vapor-liquid-solid (VLS) growth (adapted with permission from ref⁹⁰, Copyright 2008 Elsevier)), and **c** 3D printing (reproduced from ref.¹¹⁸, <https://doi.org/10.1039/D1RA06643A>, under the terms of the CC BY 3.0 license <https://creativecommons.org/licenses/by/3.0/>). On the other hand, subtractive techniques mainly involve etching techniques (top-down) including **d** dry etching (adapted with permission from ref¹¹⁹, Copyright 2020 Wiley-VCH GmbH), **e** metal-assisted chemical etching (MACE) (adapted with permission from ref¹²⁰, Copyright 2022 Wiley-VCH GmbH), and **f** electrochemical etching (adapted with permission from ref⁹¹, Copyright 2022 Elsevier).

Ln 1055-1060,

The nanostructuring approach may bring some performance improvement but it necessitates careful consideration.

Do we really need to further miniaturize our power sources? What are the power needs for integrated electronics? Can nanostructured silicon effectively sustain 3D configurations?

Authors' response:

Thank you very much for your comment and questions. We improved the following text in Chapter 4 “Conclusions and outlook” to better accommodate those concerns:

Secondly, a further miniaturization of the 3D Si anode geometry should be established. The current dimensions of 3D Si anodes in micro-LIBs are mostly in micrometer scale. However, the potential of nanoscale 3D Si to improve the micro-LIB performance is huge. At the moment, the required energy for integrated microelectronics with the areal footprint in the order of millimeters is within the range of μWh to mWh ¹¹⁶, while the devices commonly operate in the power range of nW to mW ¹⁶⁶. Reducing the structure of a Si anode to the nanometer scale may pack more accessible storage sites within the same areal footprint and at the same time improve the kinetics. This can enable 3D Si micro-LIB with higher energy and power density. Moreover, structural degradation of Si can be suppressed only in nanostructured Si, which can lead to better cycling stability as demonstrated in many studies^{167,168}. Indeed, there are some challenges in the adoption of Si nanostructures for large scale applications such as the complexity of fabrication technique, the potentially increased cost, and the possibly reduced homogeneity. Therefore, further studies need to also consider those issues in the development of nanostructured Si anodes for microbatteries. Anyhow, improving the energy and power of microbatteries by further miniaturization of Si anode structures is not only aimed to the existing microelectronic uses, but also would potentially trigger the opening of entirely new applications.

22nd Jan 24

Dear Mr Refino,

Your manuscript titled "From micro to mighty: How does 3D silicon microbattery achieve high applicability despite its small size?" has now been seen again by our referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

Dr Jet-Sing Lee
Associate Editor
Communications Materials
orcid.org/0000-0002-6740-8700

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

All questions/issues raised by the reviewer have been satisfactorily addressed by the authors in revision 1 ("1584_1_merged_1703181296.pdf").

Reviewer #3 (Remarks to the Author):

This revised version can be accepted now.

Reviewer #4 (Remarks to the Author):

I appreciate the authors' diligence and thoughtful consideration in responding to the comments. The revision is suitable for publication.