Li-ion Battery High-energy Silicon Anode Innovation & Patent Review

Table of Contents

Executive Summary
About the Author
Introduction
- Focus of This Review

Technology Decision Trees for High-energy Silicon Negative Electrodes
- Nanoscale Silicon (Synthetic Processes)
- Coating of Carbon with Nanoscale Silicon
- Nanoscale Silicon (Coatings)
- Porous Silicon Microparticles
- Silicon Alloys / Melts (Elemental Compositions / Coatings)
- Sphere-like Silicon-carbon or Silicon-MXene Composites Based on Solid Silicon Precursors
  - Synthetic Processes – Core
  - Non-silicon Precursors
  - Binders / Dispersants
  - Coatings
- Additives for Negative Electrodes
- Binders for Negative Electrodes
- High-energy Electrode Designs & Fabrication Methods
- Prospective Future Electrolyte Types for Sillicon Anode Materials by Companies Discussed in this Review (Liquid, Semi-solid or Solid)
- Silicon Anode Materials that are Used with Solid or Semi-solid Electrolytes

Predictions (5-10 Year Time Frame)
AI-based Identification of Commercially Relevant Patents
Assessment of Companies
- Advano (Nanostar) – USA
- Alkegen – USA
- Amprius – USA
- Aspen Aerogels – USA
- BTR – China
- BYD – China
- Cenate – Norway
- Contemporary Amperex Technology Limited (CATL) – China
- Daejoo Electronic Materials – South Korea
- E-magy – Netherlands

- Enevate – USA
- Enovix – USA
- Group14 Technologies / Cellforce – USA / Germany
- Ionic Mineral Technologies – USA
- Ionobell – USA
- LG Energy Solution / LG Chemical – South Korea
- LeydenJar Technologies – Netherlands
- Nanoramic – USA
- Neo Battery Materials – Canada
- Nexeon / Wacker Chemie – United Kingdom / Germany
- OneD Battery Sciences – USA
- Panasonic – Japan
- Paraclete (Kratos) – USA
- Posco – South Korea
- Putailai / Zichen – China
- Resonac – Japan
- Samsung – South Korea
- Shanshan – China
- Shin-Etsu – Japan
- Shinzoom – China
- Sila Nanotechnologies – USA
- StoreDot – Israel
- Umicore – Belgium
- Tesla – USA
- Toyota – Japan
- Zhide – China

Deep Dives
- Interfaces: Si-based Electrodes – Sulfide Electrolytes
- Interfaces: Si-based Electrodes – Polymer Electrolytes
- Interfaces: Si-based Electrodes – Oxide Composite Electrolytes
- Competing Technology Approach –
  Interfaces: Li Metal Electrodes – Polymer-based Electrolytes

Patent Analysis Methodology & Validation
List of Abbreviations
Disclaimer

About the Author

Pirmin Ulmann built b-science.net together with co-founders into a company with subscribers across America, Asia and Europe, ranging from startups to Fortune Global 500 companies, plus academic / government-affiliated organizations and investors. He obtained a diploma in chemistry from ETH Zurich (Switzerland) in 2004 and a PhD from Northwestern University (USA) in 2009. Thereafter, he was a JSPS Foreign Fellow in an ERATO academic-industrial project at the University of Tokyo (Japan). From 2010 to 2016, while working at a major battery materials manufacturer in Switzerland, he was a co-inventor of 7 patent families related to lithium-ion batteries. He also was in charge of a collaboration with the Paul Scherrer Institute. He holds the credential Stanford Certified Project Manager (SCPM) and has co-authored scientific articles with more than 1,900 citations.

Introduction

Focus of this Review

This review is designed for product development professionals that develop high-energy anode materials or anodes for Li-ion batteries and adjacent decision makers that wish to improve their decision-making quality towards enabling successful product launches (35-45% of high-tech product launches failed as of 2022).

Using a unique AI-supported approach, this review highlights commercially relevant technical and patent information that has been identified among the >100k battery patent documents published every year. Divergent technical decisions are visualized, which have been taken by key lithium-ion battery industry players to synthesize high-energy negative electrode materials and corresponding electrodes for battery cells with liquid, semi-solid and solid electrolytes.

Patents are classified according to these categories:

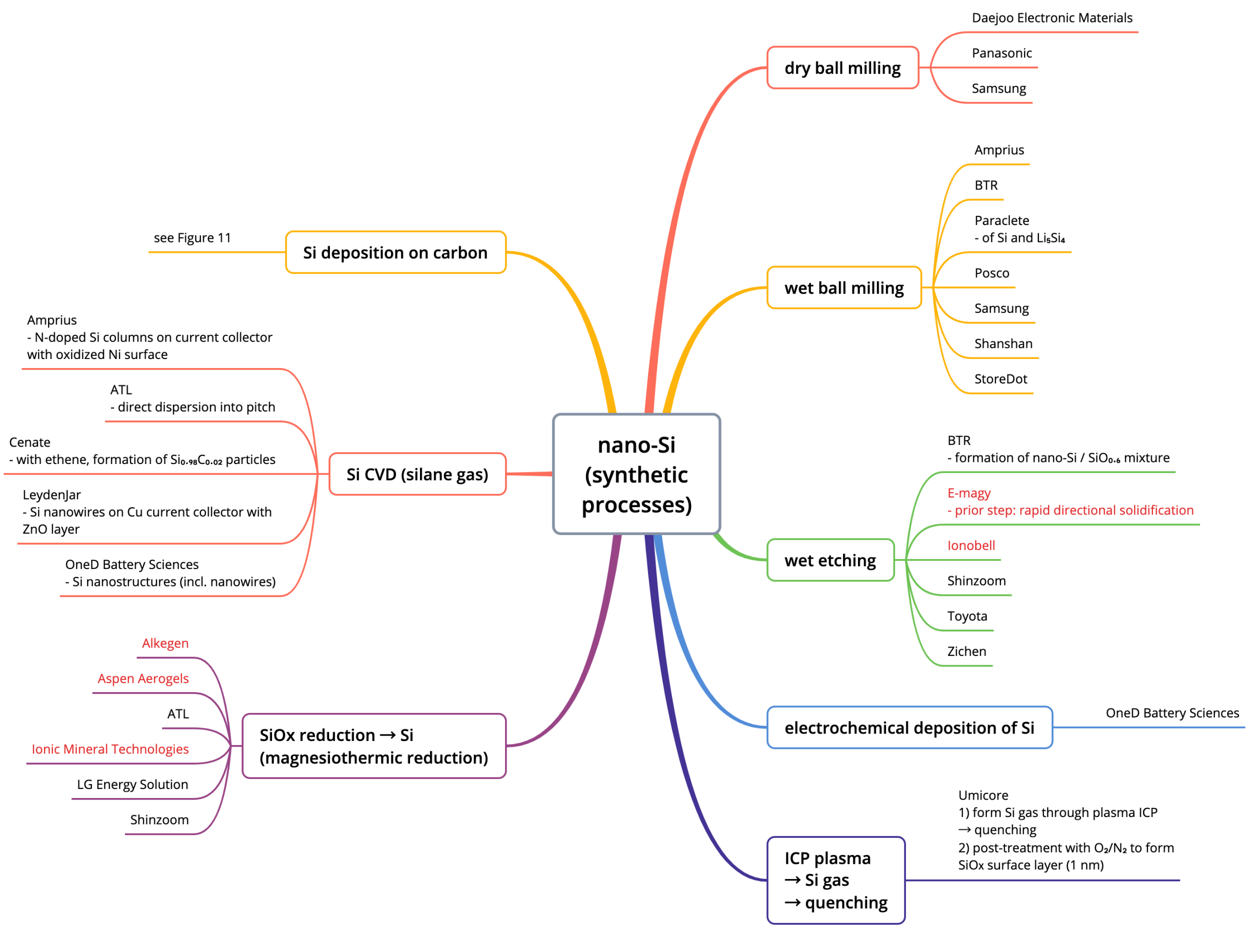
A) Active materials – chemical composition
B) Active materials – nano- & microarchitectures, composites
C) Active materials – surfaces & coatings
D) Active materials – large scale manufacturing, reliability
E) Negative electrodes for liquid electrolyte cells
F) Negative electrodes for solid-state or semi-solid cells

Patent portfolios are compared to public technical statements at conferences and in news reports about the characteristics of next-generation products and up-scaling timelines.

For tailored patent searches with prospective commercial relevance scoring, the AI models used for preparation of this review are available to users on b-science.net.

Technology Decision Trees for High-energy Silicon Negative Electrodes

Figure 10: decision tree - nano-Si (synthetic processes, in red: newly added branches as compared to prior review)



Proponents of CVD bottom-up Si nanostructure synthesis approaches (Figure 10: on current collector foils or particle deposition, Amprius, ATL, Cenate, LeydenJar, OneD Battery Sciences; Figure 11: on carbon support materials, Group14 Technologies, Nexeon, OneD Battery Sciences, Resonac, Sila Nanotechnologies) argue that to achieve improved energy densities, process technology transfer from high value-added industries (semiconductors, flat panel displays, solar cells) to the battery industry is necessary to better control nanoscale structures as compared to current processes. While hazardous monosilane is already employed in the range of 10k-100k tons/year in other industries, its large scale use requires tighter safety procedures as compared to many of the currently used large scale battery material manufacturing processes. A wide variety of nano-architectures can be achieved with this approach that are not accessible with other synthetic approaches, which is aided by the choice of catalysts and carbon or silicide support materials on which Si is deposited. Highly attractive process costs of around USD 19.7/kg Si (USD 1.67/kWh) have been claimed by OneD Battery Sciences to be feasible at large scale. A key milestone in relation to this monosilane 'technology track' was recently reached by Nexeon in the form of the homologation of its Si-carbon active material for EV battery cells by Panasonic (start of active material production in 2025 in new Kentucky plant), while up-scaling in high-value niches has been underway for a while and continues (wearables, unmanned drones, military applications).

The rest of this discussion and
13 additional decision trees are included in the full review.

AI-based Identification of Commercially Relevant Patents

b-science.net has developed a supervised AI methodology to assess the commercial relevance of patents, combined with an automatic translation framework that makes sure Non-English patents are identified. The methodology was validated as shown below. With this approach, we have comprehensively identified & classified patents by companies active in commercial R&D on Li-ion battery negative electrodes.

Table 2: number of commercially relevant high-energy Li-ion battery anode patent families / utility models (publication of first family member, without lithium metal electrodes, without patent filings by academic institutions)
Teal: companies discussed with a chapter

Company	Country	2020	2021	2022	2023	2020-2023	Joint patent filings
LG Chemical / LG Energy Solution	South Korea	72	64	61	142	**339**	

>200 additional companies are listed in the full review.

Assessment of Companies

Key commercially relevant patent filings and public technical statements are discussed in the company chapters below, which results in a projection by the author in the form of industrially plausible manufacturing processes that might allow for the synthesis of novel active materials. Material characteristics of novel active materials that might be launched into the market are projected.

Author comments are displayed in maroon.

Amprius – USA

Organization profile

Amprius (http://www.amprius.com) was founded as a spin-off from Prof. Yi Cui's labs at Stanford University in 2008. Based in Fremont (California, USA), Amprius operates a manufacturing site in Fremont (California, USA) and is building a USD 190M gigafactory (first phase, up to 5 GWh) in Brighton (Colorado, USA) that is targeted to be operational by 2025. Key aviation & defense customers include the US Army, Teledyne FLIR, AALTO Aribus and BAE Systems.

According to patent filings, Amprius also operates sites in Nanjing and Wuxi (China) that pursue a different technology approach (production of Si-carbon composites through spray-drying, while silane gas deposition is pursued in the US).

In May 2022, Amprius went public through a SPAC merger, which resulted in approximately USD 430M gross proceeds. Thereafter, plans for a post-IPO capital-raise of USD 202M were also announced.

Unique capability: commercial high-energy / high-power cells (current: 450 Wh/kg, 1,150 Wh/L, 6.8 Ah prototype cells: >504 Wh/kg / >1,321 Wh/L) with Si anodes that are deposited directly on the current collector foils from monosilane gas.

Leap of faith: roll-to-roll Si deposition on current collector foils leads to superior cell performance at competitive costs in aerospace, military and eventually EV applications.

Key differences as compared to 2022

Amprius raised >USD 430M of additional funding, which allows for the construction of a gigafactory and well-funded further technology and commercial development.

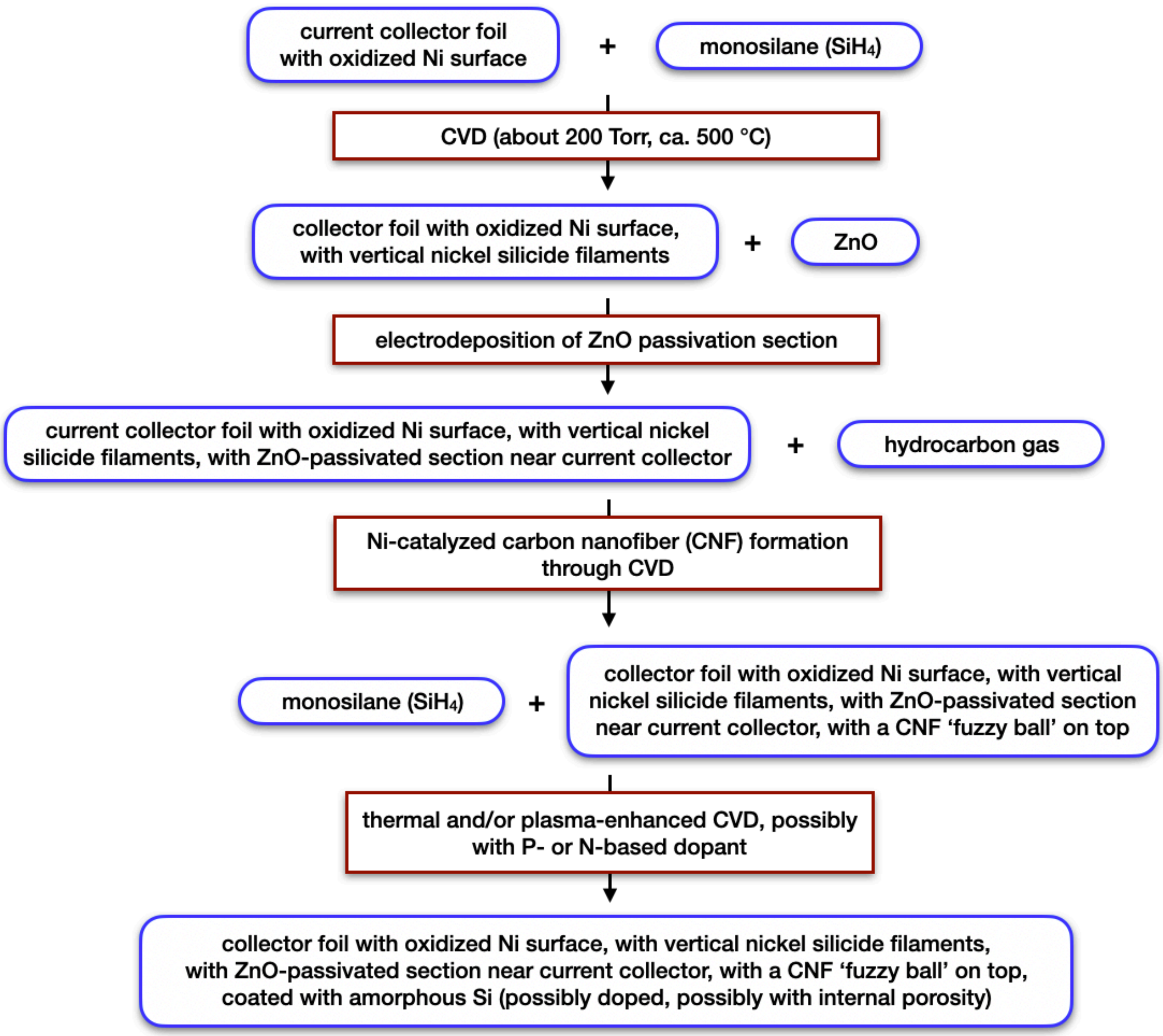
A patent for a new electrode nano-architecture through silane deposition has been filed (see Figures 91, 92) that can be seen as an evolution from the prior architecture (see Figures 93, 94), with favorable prospects for improved process efficiency (reduced number of process steps).

Possible composition of future silicon-based negative electrodes (for liquid, semi-solid or solid electrolyte cells, estimate based on public information)

- Si deposition on carbon nanofiber 'fuzzy balls' (Figure 92, **380**), which are attached on nickel silicide filaments (**370**).
- The nickel filaments are probably attached on the on the current collector with oxidized Ni surface layer.

- Figure 91 shows the corresponding process projection.

Figure 91: projected next generation manufacturing process option for Amprius (up-scaled implementation may vary)



Public technical statements & reports

In February 2024, Dr. Ionel Stefan (CTO) stated at the TechBlick 'Battery Materials & Solid-state Batteries' virtual conference:

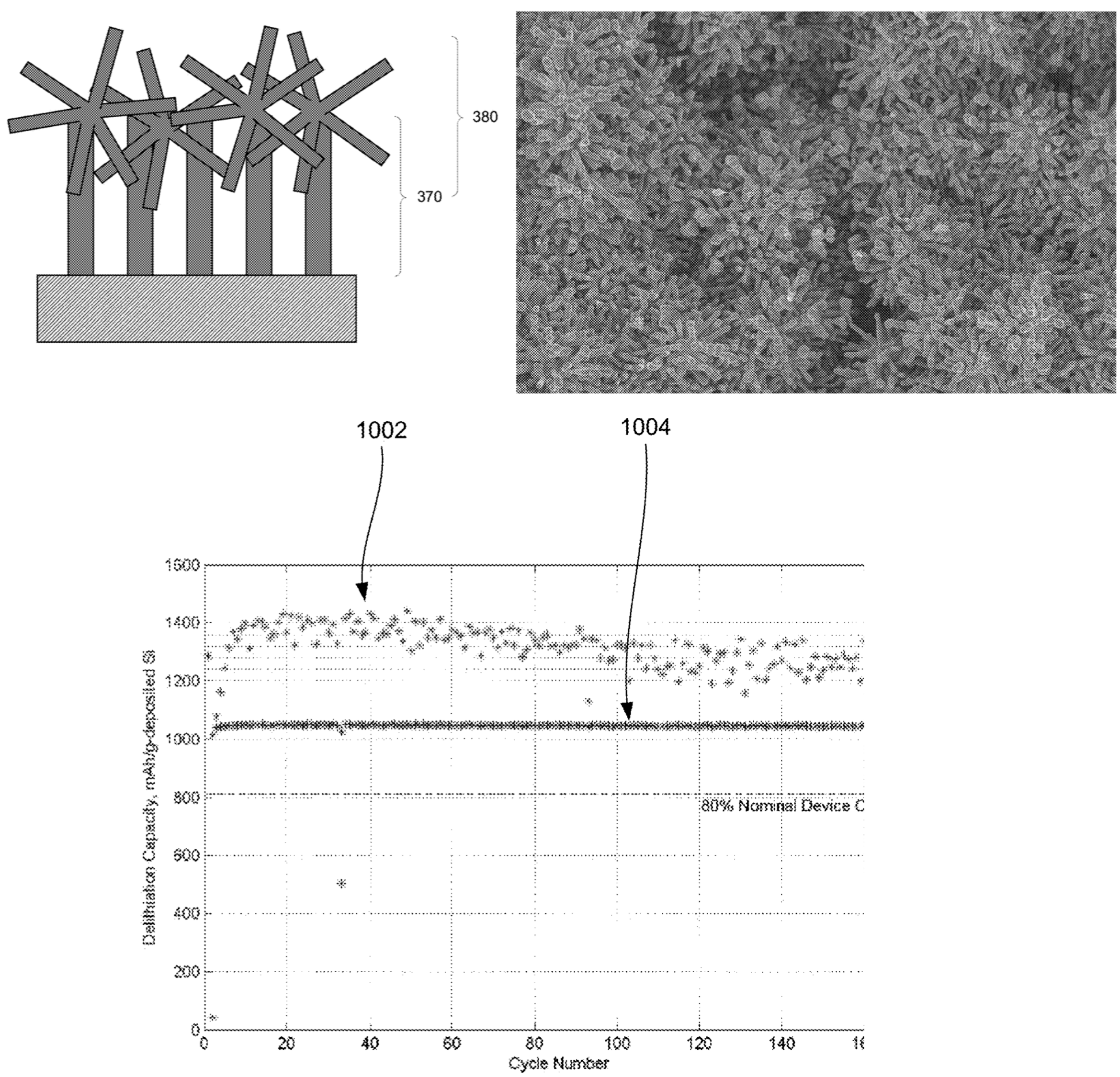
included in full version.

In March 2023, 3rd party test results were released that confirm an energy density of >504 Wh/kg / >1,321 Wh/L for Amprius 6.8 Ah cells (corresponding press release).

General patent portfolio characteristics

9 new patent families by Amprius have been published since 2022 that are related to high-energy Li-ion battery anodes (Amprius USA: 2 patent families, Amprius Nanjing & Wuxi: 7 patent families). No lithium metal anode patent families have been published since 2022.

Figure 92: top left – scheme of a current collector foil on which an initial silicide (probably nickel silicide) nanowire template layer (**370**) and an additional template layer (**380**, probably carbon nanofibers) have been deposited; top right – SEM image of an electrode in which amorphous silicon was deposited on the structure shown on the top left; bottom – corresponding half-cell electrochemical cycling data, **1002**: coulombic efficiency, **1004**: delithiation capacity (Amprius)



Example from the patent portfolio

B) Active materials – nano- & microarchitectures, composites; E) negative electrodes for liquid electrolyte cells

- **Process in Figure 91 –** HIGH CAPACITY BATTERY ELECTRODE STRUCTURES (Google, published in 2022, Amprius USA): orthogonal silicide (presumably nickel silicide) nanowires were first grown on current collector foil, referring to the patent listed immediately below. Carbon nanofibers (CNF) with 'fuzzy ball' shape were grown on top of these silicide nanowires (see Figure 92 – top left), followed by the deposition of amorphous Si using thermal or plasma-enhanced CVD (see Figure 92 – top right). Very stable electrochemical cycling was obtained in half-cells with a fist cycle efficiency of >96.5% (Figure 92 – bottom).
  It is understandable that very stable cycling in half-cells can be obtained with this approach, because volume changes during cycling of the silicon nanowires can be very well compensated without crack formation or loss of electrical contact to the current collector foil.
  To also achieve favorable cycling in full cells, the electrode / electrolyte interface area and chemistry will have to be carefully fine-tuned.
  Amprius already has extensive know-how on how to obtain doped anisotropic Si structures with comparably low electrolyte-electrode interface area (see below).
  Presumably, CNF nanofiber-based 'fuzzy balls' (**380**) can be formed on top of the initial template layer (**370**) because of the selective presence of catalytically active nickel at the top of nickel silicide filaments.
  With this new approach, some of the Si deposition process steps described in earlier patents (see Figure 94) might be facilitated to achieve process efficiency / cost advantages. Increased Si loading on negative electrodes might also be feasible (which could lead to increased energy density).

Key technical information from prior review edition that remains relevant

Possible composition of negative electrodes in current commercial 450 Wh/kg / 1,150 Wh/L liquid electrolyte cells

- baseball bat-shaped Si columns supported by nickel silicide filaments (Figure 93) on current collector with oxidized Ni surface layer.
- Si columns consist of low density N- or P-doped Si core and high density N- or P-doped Si shell.
- Figure 94 shows the process projection based on the Amprius patent portfolio analysis in the prior review edition.

Key earlier patent that might correspond to up-scaled commercial products

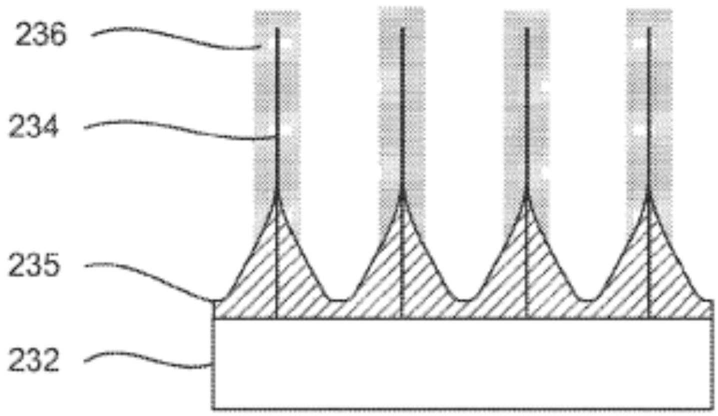
A) Active materials – chemical composition, B) particle nano- & microarchitectures, composites; E) negative electrodes for liquid electrolyte cells

- **Process in Figure 93 –** TEMPLATE ELECTRODE STRUCTURES FOR DEPOSITING ACTIVE MATERIALS (Google, published in 2022, Amprius USA, covered in patent update): nickel silicide nanowires (**234** in Figure 93 - top, varying composition along nanowire length: NiSi, Ni_2Si, $NiSi_2$) were formed on a current collector foil with a Ni surface (**232**, thickness of Ni surface layer: ≥20 nm, oxidation pretreatment of Ni layer with air, 50 Torr, 300 °C, 1 min) through a monosilane CVD treatment (about 1 volume% monosilane in carrier gas, such as nitrogen, 385-450 °C, about 100 Torr, about 10 min) using an STS MESC Multiplex CVD system (Surface Technology Systems, UK, used also for the PECVD step below). Nickel silicide nanowires with up to 20-25 μm length were formed and with about 20 nm thickness.

  A zinc oxide passivation section (**235**) was then electrodeposited, followed by deposition of P-doped Si active material (**236**) through PECVD (monosilane SiH_4 about 12 volume%, phosphine PH_3 about 2 volume%, carrier gas: helium, about 300 °C, about 1 Torr, radio frequency power: 50 W, about 15 min). As shown in Figure 93 - bottom, SEM exhibits the unique baseball bat shape of the Si columns (up to 1 μm thickness at free ends), which is very helpful for cycling stability (low mechanical strain because of thin connection to current collector).

  This work further elaborates several aspects that are crucial for the excellent cell performance at high energy density that Amprius has reported: 1) use of template (**235**) to limit Si formation close to the current collector; 2) oxidation pretreatment of current collector layer, which does not necessarily have to consist exclusively of nickel, but which should have a ≥20 nm nickel surface layer; 3) use P-doping instead of N-doping (disclosed in an earlier patent filing).

Figure 93: top: negative electrode structure with passivation section (**235**); bottom: corresponding SEM image with Si columns that are narrow near the substrate interface (Amprius)



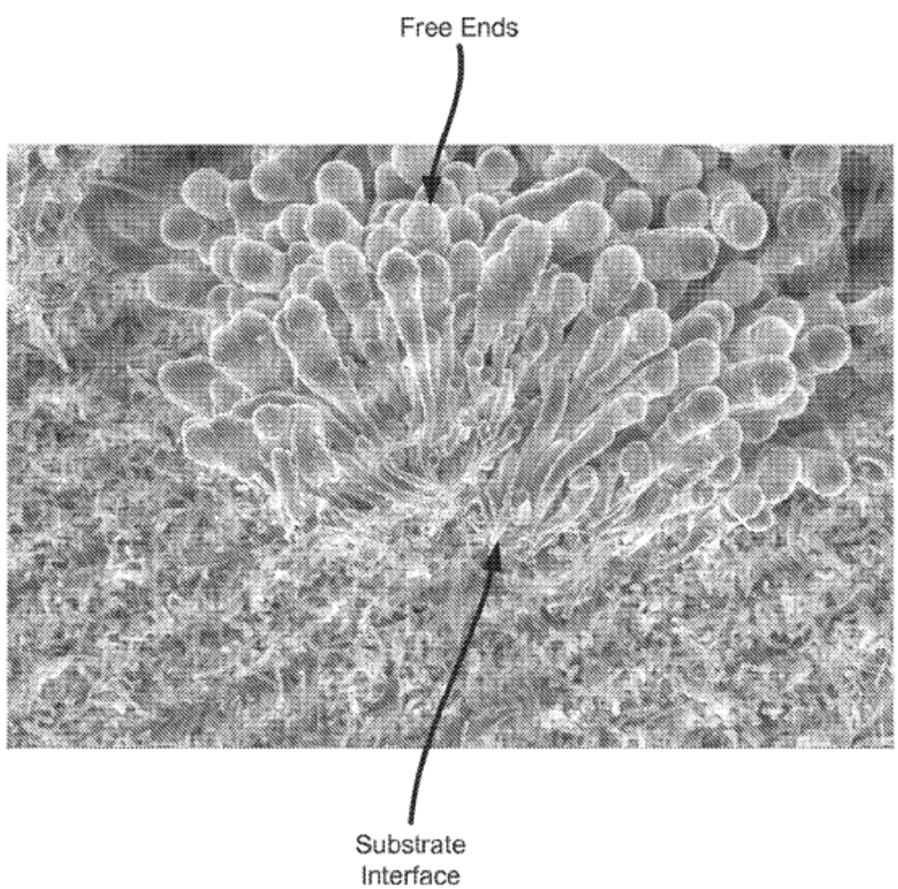
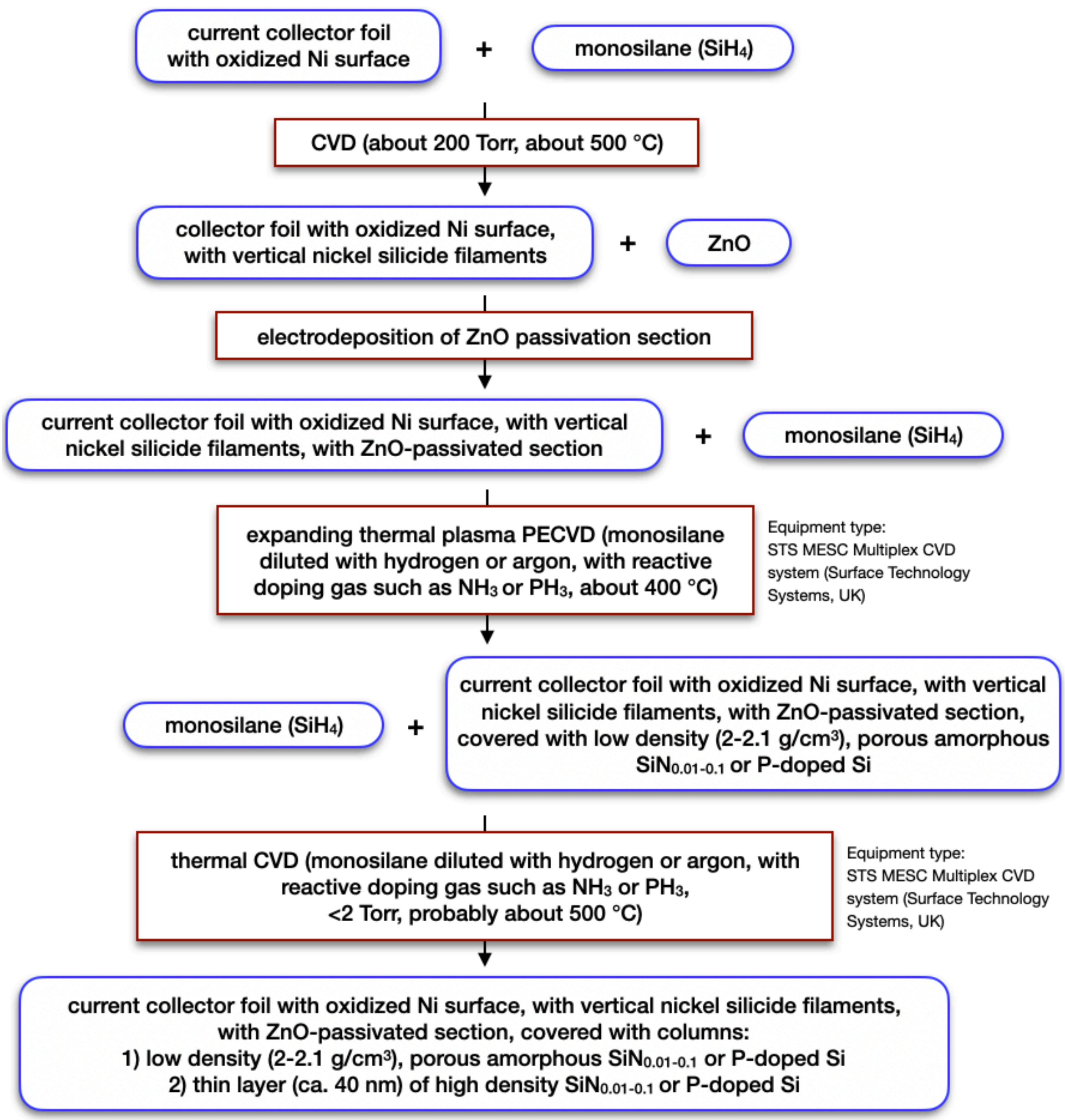


Figure 94: projected current generation manufacturing process option for Amprius (based on patent analysis, up-scaled implementation may vary)



Patent Analysis Methodology & Validation

The patent information source for this review is the European Patent Office (EPO), which covers patent filings from more than 100 patent offices around the world. >2.7 Mio. patent documents are included in the b-science.net database that were published since 1980, which either contain the words 'battery' or 'batteries' in the title or abstract, or were assigned to one of the energy storage-related CPC (cooperative patent classification) or IPC (international patent classification) codes: H01M (batteries & fuel cells) or H01G (capacitors). An AI model was defined for commercially relevant negative electrodes of Li-ion batteries (without Li metal electrodes). Patent documents were grouped into patent families and scored with the corresponding AI model. An AI relevancy score cutoff value of 40 was applied (100: very relevant, 0: not relevant). For companies listed in Table 2, scores between 35 and 45 were checked manually and false-positives / false-negatives were corrected if necessary. To generate Table 3, the AI model for solid / semi-solid Li-ion battery electrolytes was employed in combination with the AI model for Li-ion battery anode materials (without Li metal electrodes) to identify patent families with a connection to both of these categories. Only private / commercial companies are included in the statistics.

The **methodology was validated** with patent families by LG Energy Solution / LG Chemical published in 2023 (until November 29th). 129 patent families were manually classified as relevant. 123 of these patent families exhibit an AI score of ≥40 (correct AI classification). 1 patent with an AI score of 84 was manually classified as not relevant (1 false-positive). 6 patent families with AI scores of >30 were manually classified as relevant despite an AI score below 40 (6 false-negatives). 2,728 additional patent families were manually classified as not relevant and exhibit an AI score of <40 (correct AI classification).

Disclaimer

All warranties and liabilities on the part of b-science.net GmbH (LLC) and its affiliates are excluded, including, without limitation, guarantees as to fitness for a specific purpose, non-infringement, accuracy or completeness. Please check our Terms & Conditions and Privacy Policy, which apply to this document.

THIS SERVICE MAY CONTAIN TRANSLATIONS POWERED BY GOOGLE. GOOGLE DISCLAIMS ALL WARRANTIES RELATED TO THE TRANSLATIONS, EXPRESS OR IMPLIED, INCLUDING ANY WARRANTIES OF ACCURACY, RELIABILITY, AND ANY IMPLIED WARRANTIES OF MERCHANTABILITY, FITNESS FOR A PARTICULAR PURPOSE AND NONINFRINGEMENT.