

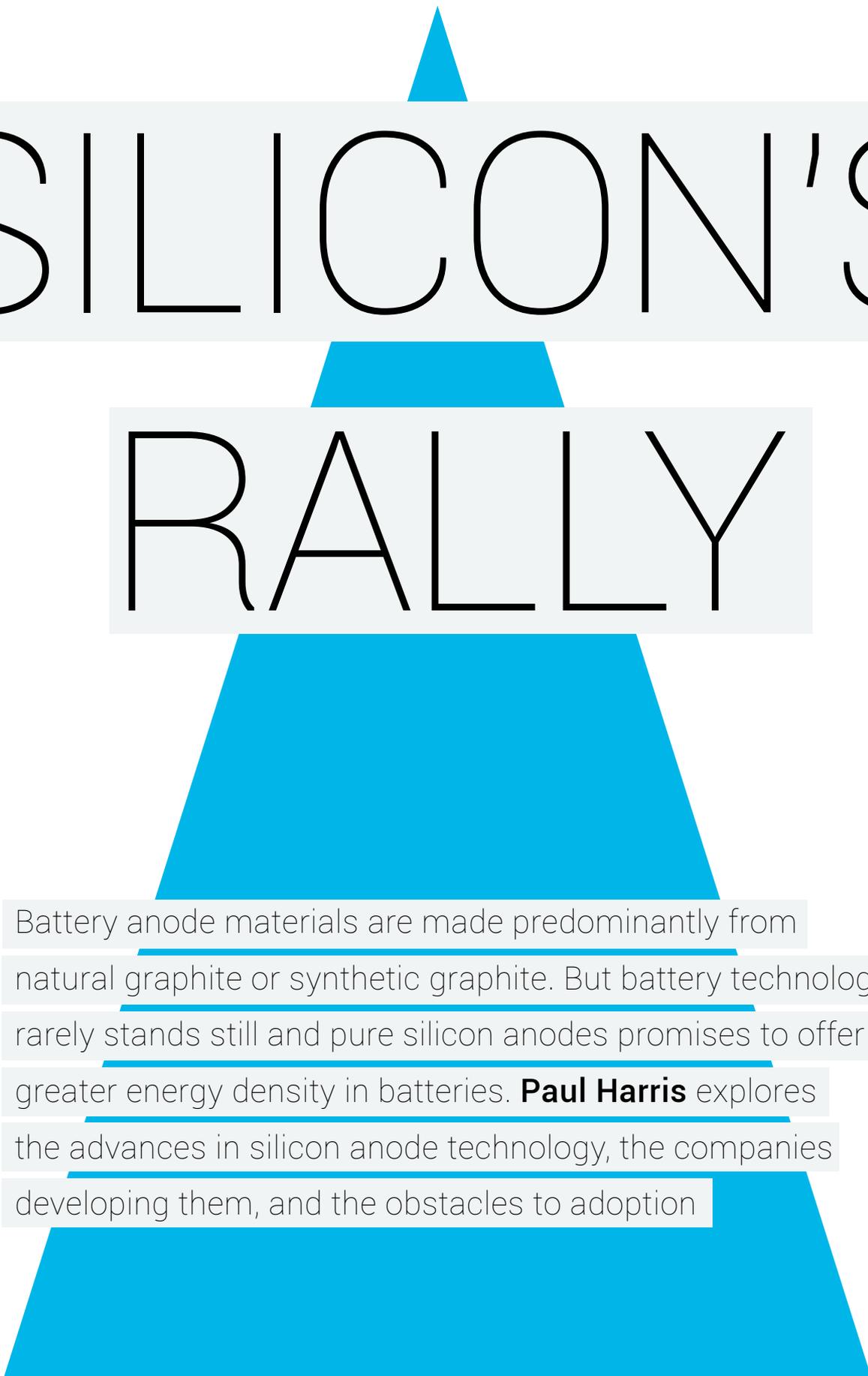
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SILICON'S RALLY



SILICON'S

RALLY

Battery anode materials are made predominantly from natural graphite or synthetic graphite. But battery technology rarely stands still and pure silicon anodes promises to offer greater energy density in batteries. **Paul Harris** explores the advances in silicon anode technology, the companies developing them, and the obstacles to adoption

The quest to improve lithium-ion battery performance seeks to produce batteries that can hold a greater charge to increase the time between charges, to decrease charging times, cost and other performance parameters. While much of the news has focused on cathode formulations and how much nickel or cobalt they will have, the next leap in battery performance looks set to come from changing the anode material from graphite to silicon.

With lithium-ion batteries using essentially the same chemistry as Sony developed in 1991, moving from graphite to silicon represents a fundamental transformation in battery chemistry and an opportunity to increase energy density in a cell as silicon can store much more energy than carbon sources such as graphite or graphene. In traditional lithium-ion batteries, the anode is made of graphite with lithium stored as LiC_6 (one lithium atom surrounded by six carbon atoms). Silicon combines with lithium to form $\text{Li}_{15}\text{Si}_4$. This 15:4 ratio means a smaller amount of anode material can store a lot more lithium and thus provide much larger capacities.

To put this another way, a commercially available graphite anode has a gravimetric capacity of 372 mAh/g (milliamp-hours per gram). Silicon has a much higher theoretical gravimetric capacity of 4,200 mAh/g. "Theoretically, silicon is the best material for anodes in batteries. It can store up to ten times more energy than graphite anodes in conventional lithium-ion batteries," according to Kiel University materials scientist Dr Sandra Hansen.

However, what is practically achievable is often overlooked in the glare of the 10x theoretical possibility. "While silicon can have 10x more lithium per gram than graphite, on a volumetric basis it is 3x better, but that only applies to the anode itself. The 10x figure can never apply to the whole lithium-ion battery. Our anode is 5x better than graphite on a weight basis, but we are talking about a 20% energy improvement at the whole cell level. The most credible mathematical estimate is to make a battery 40% better than the state-of-the-art battery available today using graphite. This is also the limit of lithium metal technology too," Gene Berdichevsky, CEO



Credit:
Nanotechnologies

Gene Berdichevsky, CEO, Sila Nanotechnologies

of Sila Nanotechnologies told **Benchmark Minerals**.

A rule of thumb is that about 1kg of graphite is needed per kWh of battery capacity so for example, about 80kg of graphite is needed for an 80kWh EV battery and about 30g for a 30Wh tablet battery. To get the same performance with silicon requires the use of a smaller amount of material allowing you to have a smaller battery. Or you could maintain the same battery size and increase the amount of power you have.

Projections from Persistence Market Research see lithium-silicon batteries growing in dominance through 2024 and beyond. It said the global silicon anode battery market was valued at US\$90 million in 2015 and is anticipated to register a compound annual growth rate of 21.5% in the 2016–2024 period.

By application, the silicon anode battery

market is segmented into consumer electronics, automotive, industrial and grid & renewable energy. Consumer electronics currently represents the largest market but EVs are expected to be a key growth segment. Geographically, North America leads the market followed by Asia Pacific.

Markets

Portable consumer devices like smartwatches, smartphones and tablets will be the first products to benefit from the commercialisation of silicon anodes, as they are less price sensitive. "We are focused on wearables, smartphones and notebooks where we can have a significant impact on performance and establish ourselves and work on bringing our production costs down. These are less price sensitive markets compared to EVs," said Bruce Pharr, senior director of marketing at Enovix.

The tipping point for widespread consumer

Credit:
Thomas
Hawk

Researchers in Silicon Valley are hoping to use pure silicon anode technology in electric vehicles

uptake of EVs is widely perceived to be cost over and above other factors, specifically when EVs are the same cost as internal combustion-engine vehicles (ICE). Battery pack costs (anode, cathode and separator, packaging, electrolyte, safety features and final testing) fell to around \$200 per kWh in 2018 from around \$1,000 per kWh in 2010, with Tesla claiming it is close to reaching a battery cell (anode, cathode and separator) cost of \$100/kWh this year with its battery pack costs expected to reach that level in 2020. The \$100 per kWh price tag for a battery pack is thought to be the tipping point where EVs and ICE costs are similar to each other.

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Dr Sandra Hansen
Kiel University

Silicon is a widely available material and silicon anodes have the potential to bring EVs closer towards the tipping point, especially since the cost of silicon could be set to fall if HPQ Silicon Resources is successful in developing its Purevap quartz reduction reactor plasma technology as an alternative to the traditional Siemens silicon metal furnace. “A full-size plant using our technology to produce solar grade silicon could cost US\$70-100 million and produce silicon at \$3,000-4,000 per tonne,” president and COO Patrick Levasseur told **Benchmark Minerals**, who is building a pilot plant in Montreal, Canada to produce 50 tonnes a year. This compares to

- ▶ a \$1 billion price tag on a Siemen's furnace which makes a product for \$11,000-12,000/t.

Simple but not easy

If silicon anodes promise such great benefits, why are people still using graphite? Silicon has not yet blown away graphite because of mechanical limitations engineers are working to resolve, which have so far limited its penetration.

When silicon accommodates lithium ions into its structure in the lithiation process it expands by up to 400%, which graphite does not. However, during discharge, it then shrinks again which causes some silicon particles to lose contact with the current collector. This causes the current collector to demand greater discharge from the silicon it is in contact with and these silicon particles then over discharge and crack. This cracking, or mechanical instability, can destroy a battery in just 20-30 cycles.

Scientists are looking at three different solutions to crack the silicon cracking problem: dilution, nanowires and architecture with much of the leading research being performed in California's Silicon Valley.

Dilution solutions stick with a graphite anode but introduce small amounts of silicon—typically 3-5%—to get some performance benefits while limiting silicon's expansion issue so it doesn't start breaking. This approach has been around for many years and is the basis of the Tesla battery, which contains about 5% silicon. "Adding silicon oxide to graphite is limited to only 5% because the oxygen is highly detrimental to the battery. It is used because the cathode carries extra lithium that reacts with the oxygen and makes it inert," said Berdichevsky. While an enhancement over straight graphite, dilution fails to capture much of the potential benefit of silicon due to the low amount used.

A second approach is to use silicon in the form of nanowires or nanoparticles, the idea being that when the small silicon thickness expands the stress created will not be high enough to cause breakage. This approach has also been under investigation for years and typically uses a graphite or graphene anode with a silicon coating. Many companies are researching this solution, which has the potential to increase the energy density of lithium batteries by 40%. "The challenge is that the silicon may be mechanically stable,



Credit: Enovix

Murali Ramasubramanian, Enovix co-founder and vice president of research and development

but it is not electrochemically stable. No one has been able to show this. It is the unsolved problem," said Berdichevsky.

Amprius, a manufacturer of high-energy lithium-ion batteries demonstrated a high-volume manufacturing tool for inline, continuous and roll-to-roll production of three-dimensional silicon nanowire anodes in May 2016. The company believes this will allow it to scale manufacturing and deliver lightweight and long-lasting batteries for EVs.

Developed in partnership with Meyer Burger of the Netherlands, a leader in high-throughput deposition systems and processes, the tool uses a multi-step, chemical vapour deposition (CVD) process to produce

silicon nanowire anodes. The company said its batteries achieve energies per unit volume of 800–1,000Wh/L depending on cell capacity and form-factor, and energies per unit weight of 325–400Wh/kg. "Inline, continuous, and roll-to-roll manufacturing will enable Amprius to transition high-energy batteries from lab to market, and from batch processing to pilot production," said Amprius CEO Dr Kang Sun in a statement.

Nanotubes are also the focus of researchers from the Institute for Materials Science at Kiel University in Germany in cooperation with RENA Technologies. Kiel's Dr Hansen said silicon behaves more flexibly when it is produced in the form of a thin wire. Porous

CHALLENGES OF A 100% SILICON ANODE

Comparing a graphite and silicon anode in a conventional Li-ion cell architecture

	Conventional graphite anode	Conventional silicon anode
Formation expansion	LOW Anode material expands by about 10%	HIGH Anode material can expand by over 100%
Formation efficiency	HIGH (90 - 95%) Pre-lithiation not needed for cathode limited cells	LOW (50- 60%) Without pre-lithiation, cells will be anode limited
Cycle swelling	LOW (< 10%) Relatively stable anode electrode	HIGH (>20%) Anode electrode repeatedly swells and shrinks
Cycle life	HIGH (500 - 1,000 cycles)	LOW (<100 cycles) Particles electrically disconnect on discharge Over-discharge and particle pulverization New Si surfaces open, SEI regenerates, rapid Li loss

Source: Enovix

silicon has more free volume which leaves more space for expansion to prevent contact with the electrode from breaking, Hansen co-developed and patented a method for a stable connection between the two, using a sulphur cathode to, “combine two materials that promise really high performance from the battery,” she said in a statement.

OneD Material is also following this route with its SiNANOde anode material where silicon nanowires are grown on graphite particles in CVD furnaces using silane gas. It has scaled its process to increase production capacity from 10 tonnes a year to over 100tpy in grades ranging from 4% to 32% silicon to carbon weight ratio. Its 10% Si/C SiNANOde product can store an amount of energy per kg which is twice that stored in graphite while its 20% Si/C SiNANOde is three times greater.

While the silicon doesn’t break, this method has the disadvantage of the silicon having to sit on something else which increases the surface area and causes other issues, and as with the dilution solution, it fails to deliver the full potential energy density benefit that silicon promises.

“The challenge is that the silicon may be mechanically stable, but it is not electrochemically stable. No one has been able to show this. It is the unsolved problem”
Gene Berdichevsky,
Sila Nanotechnologies

Architecture

Instead of looking at the materials per se, Enovix has looked at reworking battery architecture to overcome the mechanical issues of silicon that way. Murali Ramasubramanian, Enovix co-founder and vice president of research and development, and other company co-founders had previously used 3D architecture to increase density for read-write heads of high-density disc drives and high-density semiconductor test products and thought it could be applied to batteries to increase energy density. It has developed products that it is now bringing to market in consumer electronics.

“We solved the issue by adding an integrated constraint to the cell. We add a stainless-steel constraint that prevents silicon in the anode from cracking. This provides pressure which limits expansion and maintains the silicon’s contact with the collector, which stops over discharge and breakage,” he told **Benchmark Minerals**.

The constraint applies pressure to inhibit silicon swelling. A square millimetre of silicon needs about 1 kilogram-force (kgf) to push

back the expansion and maintain connection during discharge.

This created another issue. "A 20x20mm conventional lithium-ion battery needs 400 kilogram-force and a cell phone battery needs over 2,000 kilogram-force," he said.

To apply force without overly adding to the weight and size of a device, Enovix again looked at the architecture. "Instead of building batteries with electrode and separator sheets layered bottom to top we structure them left to right. The 90-degree change in orientation allows this to work as the anode has a smaller surface area. It is an elegant solution that looks really obvious in hindsight," said Ramasubramanian.

While the constraint takes up some volume, high-capacity silicon provides an anode with 97% active material (3% is binder and conductive aids), which more than makes up for the constraint volume.

Unlike graphite anodes, silicon needs to be pre-lithiated for first-cycle formation efficiency.

Enovix uses an unmodified 3-5-micron commercially available silicon powder such as silicon oxide or metallurgical grade silicon. Silicon oxide is what other companies use to add to graphite anodes. Metallurgical grade is used in photovoltaic solar cells. "We are experimenting with lower cost silicon grades which would be more cost effective. We believe there will be opportunities to use cheaper grades rather than using semiconductor grade silicon," he said.

Enovix says its EX1 wearable cell gets a 46% increase in energy density and 38% for its smartphone cell over a conventional lithium-ion cell and is achieving around 600 cycles for its wearable watch cell and is confident it can get above 1,000 in the future. "We see less than 2% swelling after 500 cycles. Even graphite swells 6-7% at the end of its life, so silicon is much better than graphite cells because of the constraint. We have done enough testing to know that our EX2 and EX3 cells [due for production in 2020 and 2021, respectively] will get 74-105% more energy density," said Ramasubramanian.

"To put this in context, since 1992, there has been about a 5% per year increase in energy density in lithium-ion batteries. With Enovix technology we can get 30 to 50 to 100% increases over the next few years," said Enovix's Pharr.



Credit: Nanotechnologies

Sila Nanotechnologies' production facilities in California

Also bringing an architectural-type solution to a silicon anode-based battery is Sila Nanotechnologies. Sila makes a structurally engineered material to replace graphite from commodity precursors in liquids and gases. "We synthesize and convert these through a series of chemical transformations in a vertically integrated production chain that has been through thousands of design iterations. You could say the silicon is engaged in a structure which has a porous scaffolding for the silicon to expand into within the internal structure, so the outside of the particle doesn't change shape or size during charging with an outer surface impermeable to the electrolyte."

Sila's material can achieve 500-800 cycles, works existing battery infrastructure and will provide an initial 20% energy gain as it starts the process of commercialisation, which it will subsequently seek to push up to 40%.

"We have an R&D line that we have developed over the last eight years. We developed a pilot line in the last year or so with which we have started to qualify material with battery manufacturers. We are commissioning a commercial production line and will have that running by the end of the year which will provide material to get into small consumer devices and we will have product selling later this year or early next," said Berdichevsky.

Berdichevsky says the consumer markets are very profitable and will give the company

time to scale up its production and finance the tens of millions building new factory capacity will cost.

"We plan to take this production line and scale it up further for larger factories. We will supply the consumer market for the next two to four years. It is all to do with volume. The amount of material we need to produce for one EV is the same as for 10,000 cell phones. It won't be until the mid-2020s that we can produce for hundreds of thousands of cars. We have a lot of production scaling to do. It takes two years to build a large-scale factory. We will take it in steps to get there," he said.

Sila has caught the attention of German automakers who are keen to see its benefits in batteries for their EVs. In March 2018, Sila announced a partnership with BMW which is keen to start deploying its silicon anodes in its EVs from 2023 with the expectation of obtaining a 10 to 15% increase in the amount of energy packed into its battery cells. "The conventional chemistry (graphite anodes, lithium metal oxide cathodes) which has been thoroughly optimized, is reaching a technological limit. Achieving dramatic performance improvements while ensuring high levels of safety requires moving to a new generation of materials chemistry," Sila said in a statement.

Sila followed this in April 2019 announcing Daimler—which owns the Mercedes-Benz brand—had acquired a minority stake in the



Sila Nanotechnologies is looking to first use its technology in smaller devices

company. “We are on our way to a carbon free future mobility. While our all-new EQC model enters the markets this year we are already preparing the way for the next generation of powerful battery electric vehicles,” said Sajjad Khan, EVP for connected, autonomous, shared & electric mobility at Daimler in a statement.

Berdichevsky expects Sila to begin supplying the EV market in the mid-2020s. “It will initially take a tiny portion of the market, then we see five years of massive growth. The beauty is that for any battery factory, using our materials immediately upgrades the factory capacity. A 5GWh factory will still make the same number of batteries but it will produce 6GWh and then 7GWh without adding any new equipment,” he said.

For Enovix, the auto industry still needs to provide guidance of where it wants to be and what it wants to achieve. “There is a lot of excitement about the EV market and it is going to be the biggest. But, unlike with mobile devices, the battery manufacturers and auto manufacturers have not yet worked out exactly where they want to be in terms of packaging, size, weight, cost, duration and other factors. This will need to be jointly determined and developed. There is a tipping point in 2024-2025 but what that is going to look like is still not clear to the industry,” said Enovix’s Pharr.

The target to drive mass-market adoption could be something like an average, compact SUV costing US\$28,000 which gets 350-400

miles on a charge and can fully recharge in 1-2 hours.

For Berdichevsky, car manufacturers are more focused on cost than on having more power. “Batteries can already achieve a 300-mile range. They want the same amount of energy in a smaller pack so they can use fewer cells and reduce the cost of the vehicle. They want to reduce the cost of the system; not by using cheaper materials but by making the performance of the device much better. Dollars per kWh is the key. We can get 20% more energy in a battery which means we need 20% fewer cells. We improve costs and make a cheaper battery even if the materials cost more because the power increases more than the cost,” he said.

