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Charge masters

Anode materials suppliers are pouring resources into improving the performance of EV cells.

featuring Paraclete Energy

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Paraclete has developed a process for making silicon anodes using a polymer matrix rather than graphite (Courtesy of Paraclete Energy)

This is more scalable than the silane chemical vapour deposition process, and does not need an etching process using hydrogen fluoride at the end.

"Right now we are seeing 30% substitution of silicon as a drop-in material in graphite anodes, so that gives 1100 mA/g – the target is 1200 mAh/g for blended anodes," Zeitoun says.

"The issue is the cell expansion during charging, so 150 nm is the upper limit for the size of the smallest silicon particles to ensure they don't crack open and form an inhibiting layer, the solid electrolyte interphase [SEI], later. That's why silicon is limited to 10% in graphite anodes at the moment."

This can produce pure silicon anodes with an energy density of 3000 mA/g compared with the typical 350 mA/g of graphite, but there are issues with the electrolytes. "You can have 100% pure silicon, but as soon as you put that into a water-based binder – which is where the market is going – it will surface passivate with a thin oxide coating, and that is a problem," Zeitoun says.

"The trick is finding the right balance. For example, a 75% silicon anode performs better than one with 99% silicon."

The company has only explored 30 acres of the 650 acre mining site, and the silicon is accessible with surface mining across 160 acres, avoiding the higher costs of deep mining. It has developed anode materials and built battery cells in-house, and is testing them with graphite blends to 1100 mA/g and silicon anodes up to 3000 mA/g.

Polymer matrix

Paraclete Energy has also developed a process for silicon that uses a polymer matrix instead of a carbon matrix. Jeff Norris, founder, and CEO of Paraclete Energy, also reported that Argonne National Lab recently published a study on extreme fast charging that concluded that Paraclete Energy's silicon increases rate capability from 1C to 8C (7.5 minutes to fully charged). Improves capacity retention (cycle stability), energy density (driving distance per charge), and reduces the possibilities of lithium plating (safety).

Nearly all of Paraclete's competitors use a carbon matrix with over 80% inactive carbon-based material. This inactive carbon matrix creates porosity and mitigates some of the issues caused by silicon swelling that occurs during lithiation. However, this means that only 12% of the active silicon material per particle is used by Paraclete's competitors. Although this can make it 30 – 40% better than graphite, these carbon matrix-based silicon products with all the inactive materials are only an incremental improvement over SiOx.

Paraclete Energy's use of a polymer matrix enables over 70% active Si material per particle, producing over 2500 mAh/g active silicon material, which is the highest energy density material for lithium-ion batteries. With Paraclete Energy, there is no longer a limitation of 12% silicon, an incremental improvement over SiOx, but with Paraclete Energy's polymer matrix a nearly 8x improvement over graphite.

"We use a polymer matrix – we can

Lithium metal anodes

Lithium metal anodes are currently produced using a rolling process (left), which causes problems, so Li-Metal has switched to vacuum-based physical vapour deposition (Courtesy of Li-Metal)

Using lithium as the anode has even higher theoretical energy density than silicon, but there are major challenges.

One is a gap in the supply chain for next-generation batteries for high-performance anode materials, says Maciej Jastrzebski, co-founder and CEO of Li-Metal.

"On the one hand the technology is starting to get to the point of being taken seriously with testing for EVs, but on the other there is a gap in metal production and understanding the drawbacks, and coupling that with a production process for low-cost anodes," he says.

Between 7000 and 20,000 tonnes of battery-grade metal will be needed by 2030; the industry currently has a capacity of 7000 t of nominal capacity, with half of that used for batteries. The lithium is produced from lithium chloride via lithium carbonate from brine, or lithium sulphate from rocks, but the latter needs to be refined to lithium carbonate and then turned back into the chloride.

"This creates an upstream problem, so the challenge is to turn the carbonate feedstock into metal," Jastrzebski says. "We are therefore looking at taking lithium carbonate and turning it into the chloride as a precursor."

Current production uses a rolling process, extruding the lithium into a foil 200-300 microns thick. There is a problem, however, in that keeping the foil from breaking or splitting becomes harder as the foil gets thinner, and is harder still as the lithium metal itself is weak.

"You can cut it with a knife, so the problem of rolling the material is profound," Jastrzebski says. "It ends up much thicker than you want it to be, and you are forced to build the cells using thin strips of lithium."

One of the challenges is the need to minimise the inclusions in the metal, as they create splits in the foil. "That forces people into strange-size formats, and I see rolling as a dead-end technology," he says. "You are composing the anode to make the rolling as easy as possible, which constrains the anode's performance."

Li-Metal has therefore developed a process using vacuum-based physical vapour deposition (PVD), similar to that used for the thin metallic coatings on bags of potato crisps.

"What attracted us to this approach are the economics and commercial availability of the equipment as a manufacturing platform," Jastrzebski says. "The other, less appreciated

use any source of silicon, whether it's mined or solar grade," Norris said. This starts with millions of 150nm diameter silicon particles in a polymer sphere with a diameter of 5 to 7 µm.

"We put a polymer matrix around the silicon, which gives it elasticity with self-healing properties. The architecture manages the swelling within the porosity of the polymer and prevents the electrolyte from seeing the silicon while it remains highly ionically and electronically conductive as metal," he said. "Nonetheless, the silicon expands upon lithiation. The flexible, highly conductive, porous polymer matrix mitigates the typical issues when working with silicon. Then we place this in a silicon-free SILO™ shell, which is ionically and electronically conductive and surrounds the polymer matrix, allowing the electrolyte to form the SEI on the outer SILO™ shell, thereby the silicon never comes into contact with the electrolyte."

This is used for anodes with 25% and more silicon to give existing battery packs a range of up to 1000 km, says Norris.

"Our customers routinely achieve 1000 cycles due to the conductive polymer matrix and the fact that the electrolyte is not consumed," Norris said. "Although we have been in product development since 2012, we started testing with customers in late 2021 and some customers are in the third or fourth cycle of performance optimization. Each cathode has a different voltage range and traditionally you have to match that with the graphite and the silicon. The massive manufacturing infrastructure required to form a carbon matrix is not required with Paraclete Energy."

Using a polymer is a low-temperature, low-waste process. Paraclete Energy's manufacturing plant can be located at characteristic is that the cost of PVD versus foil rolling falls for thinner materials, which is exactly what you want.

"The costly part is the vacuum. Getting the material into a vacuum is the initial cost, but the cost of adding other materials is very low. You can modify the composition of the lithium with various alloys to suppress dendrite formation and create layered structures with a protective layer on the surface. Because you are laying the materials on a substrate you are no longer bound by the mechanical strength of the lithium, and the substrate becomes the current collector."

"The metallised films can be up to 2.5 m wide, and we have a substrate 200 mm wide that allows us to verify the process. In theory, to broaden that substrate is not too difficult, as it is a known process."

The process starts with a copper foil 6 μm thick, with varying thicknesses of lithium up to 25 μm thick deposited on top, although a thinner layer provides a lighter anode without reducing the performance. That reduces the cost, and speeds up the process compared with rolling,

"You end up with 40-60% of the cost being the metal, 20-30% the depreciated machine cost, and the rest as the processing cost," Jastrzebski says.

PVD can also be used to add other layers to the anode, such as protective coatings or changing the structure of the lithium in the anode to suppress dendrite formation. The technique can also be used for solid-state batteries.

Solid electrolytes have a higher affinity to the lithium, but with polymer electrolytes there's lower ion mobility so the cell cannot charge as fast. Oxides and sulphides have similar conductivity but are either difficult to process, allow dendrites to form or end up with a heavier cell, as the materials are very dense.

"We are looking to deposit high-performance materials using a low-cost process. It's definitely possible to deposit complex ceramics on surfaces using PVD," Jastrzebski says. "PVD allows the structure and chemistry of the anode to be modified in many ways, contingent on producing the material fast enough to offset the capital cost of the equipment.

"We are shipping these materials to battery developers now. Most are looking at pouch cells, but we produce rolls of materials by design, which works well with mass-production, and we are working with partners on a demo facility for the qualification of samples."

Sakuu's first printed batteries have demonstrated energy densities from 800 to 1000 Wh/litre (Courtesy of Sakuu)

3D printing

Battery start-up Sakuu has demonstrated a lithium metal battery cell with an energy density of 800 Wh/litre, and believes it can achieve 1200 Wh/litre. It uses a proprietary electrolyte that is non-flammable.

The batteries are printed as cells that contain patterned openings for thermal management, in a fully dry process, at Sakuu's Silicon Valley battery pilot line.

This is a key step for the planned commercial-scale production of next-generation batteries which Sakuu calls SwiftPrint, including a solid-state version, which will be printed on the company's Kavian 3D-printing platform.

"Our development shows that the Kavian platform can enable commercial-scale, sustainable production of a wide range of battery technologies, from lithium-ion to lithium metal and even solid-state batteries," says Karl Littau, CTO at Sakuu.

Sakuu uses a multi-material, multi-layer approach with a dry process instead of layer-on-layer printing or screen-printing. The first printed batteries have demonstrated successful cycling performance at C5 rates with energy densities from 800 to 1000 Wh/litre.

The patterned approach allows the integration of sensors and thermal transport pathways, as well as regulation through the patterned design, especially when thin sub-cell battery structures are stacked with identical patterned openings for thermal management in alignment.

the battery cell manufacturer or the electric vehicle plant. "97% of the chemicals used in the process are recovered and 3% are used in the product," he said. "We don't use carcinogens. We use commodity chemicals and equipment and Paraclete Energy's materials are air-stable and we only have 2% swelling at the cell level."

The low temperature is not a problem for the cell manufacturing process, says Norris. "Up to 400-500°C we have no problem with the battery, and beyond that, there are high-temperature polymers that we can use," he said.

The polymer can also be changed to work with the electrolytes used in solid-state batteries. "We can add a reactive group to have an affinity with any of the customer's proprietary additives."

The process is currently in qualification with battery cell makers with commercialization occurring thereafter.

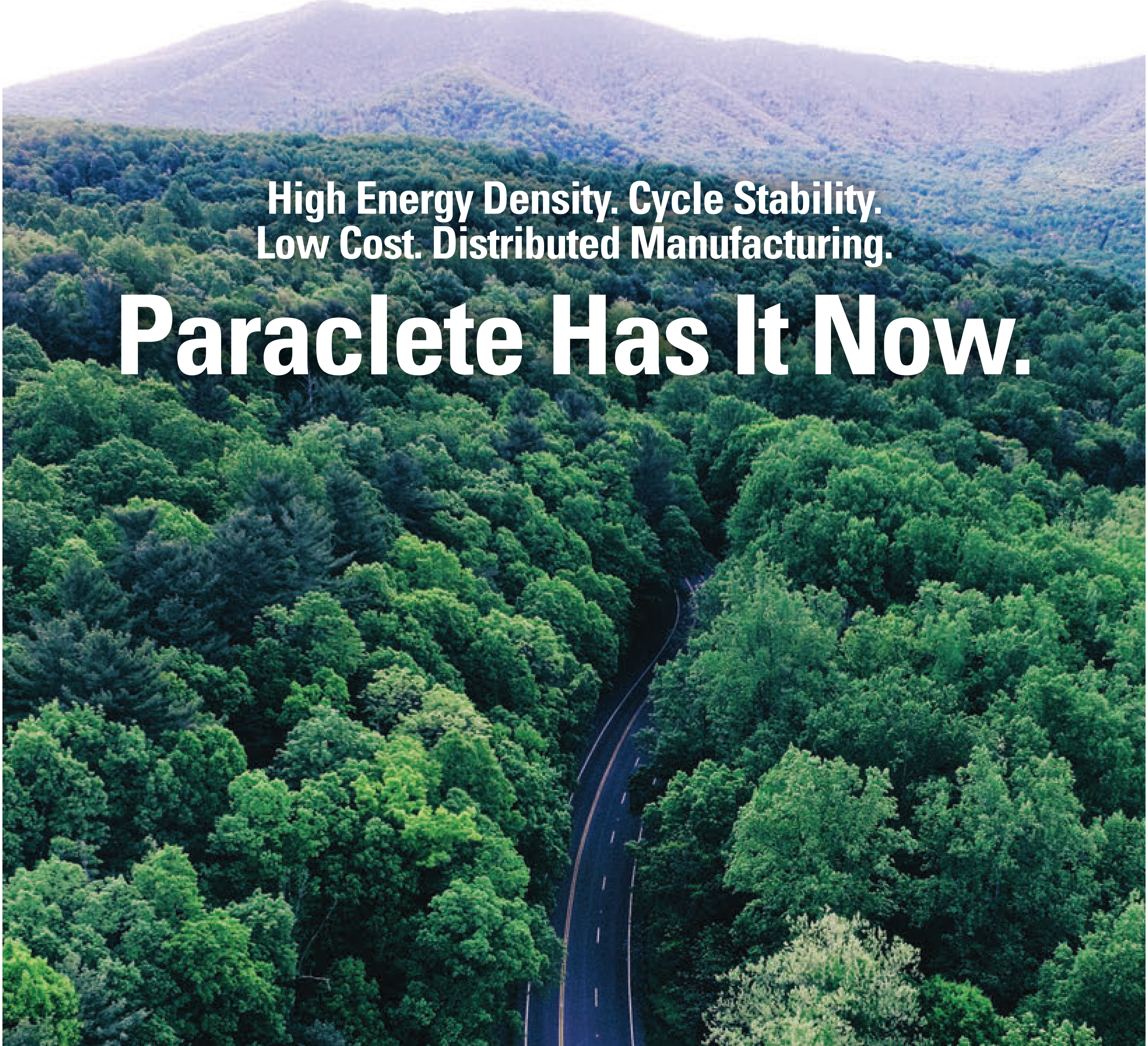
Conclusion

Making battery anodes can be an energy-intensive process with lots of nasty chemicals.

The ability to drop a material into the existing process of making an anode to boost the energy density is attractive. The current silicon oxide materials allow that, with modifications to sidestep the initial drop-in capacity that comes as a result.

New ways of producing composite particles without the high temperatures and corrosive chemicals are gaining traction and enabling a new class of anode materials with far higher energy densities and more cost-effective production.

In addition, existing PVD and 3D-printing technologies are improving the process of making high-capacity anodes without high temperatures or caustic materials.



Paraclete Energy surpasses all silicon competitors.

Silicon will be disruptive. **But which silicon?**

It must be silicon that substantially mitigates the expansion issues from lithiation while offering significantly higher energy density and good cycle stability. It must offer a **disruptive** bang for the buck. And it has to be something that can be made when and where customers need it.

Where others use a hard carbon matrix, Paraclete's competitive advantage derives from its flexible, highly conductive, porous **polymer matrix**, which enables over **four times** more silicon loading than its competitors.

The only silicon that checks any of those boxes – and the silicon that checks all of those boxes – is **Paraclete's SM-Silicon/3590™.**

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