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ZEST for glass

Dr Mike Thomas of Morgan Advanced Materials and
Dr Pier Sazio of the University of Southampton, UK,
reveal how glass fibres put the zest in solid-state batteries.

Solid-state batteries (SSBs) have so far been limited to use in micro-scale devices like pacemakers. However, scaling them for electric vehicles (EVs) and aerospace could revolutionise energy density, charging times and safety – far surpassing today's lithium-ion batteries.

All-solid-state batteries stand out for their lack of a flammable liquid electrolyte, offering improved safety characteristics and superior stability, opening the way for more energy-dense anodes, such as lithium metal (rather than graphite). This delivers a transformative boost in volumetric and gravimetric energy densities (the energy density for a given volume or weight). A step change in energy density could extend EV driving ranges significantly, accelerating adoption.

In contrast to research into lithium-ion batteries, which offer incremental improvements towards theoretical limits, research into SSBs is high-risk, high reward.

The market opportunity is huge. Fortune Business Insights forecast growth from US$99mln in 2024 to more than US$1.3bln in 2032.

Many battery and automotive manufacturers are taking note. Toyota and Honda have both laid out plans to develop and manufacture their own SSB technology, while BMW and Volkswagen have invested in solid-state start-ups Solid Power and QuantumScape, respectively. Battery companies, including Samsung and CATL, are also investing heavily in the technology.

While SSBs are not expected to hold an extensive market share until the 2040s, the technology is already being deployed in some car models in China, albeit in a semi-solid-state form.

Other transport sectors, such as aerospace, could benefit from SSBs, where their high-energy density and safety characteristics would be particularly attractive. Global SSB demand in 2040 is expected to reach 300GWh and 1,600GWh per annum in the consumer electronics and EV market, respectively.

Like many areas of technological disruption, the adoption of SSBs will likely first centre around smaller niche applications where their performance or safety advantages are most pronounced. SSBs will need to achieve a step-change in cost, performance and manufacturability if they are to achieve their potential.

The solid-state battery market was worth **US$99mln** in **2024** and is expected to be more than **US$1.3bln** in **2032**

Source: Fortune Business Insights

Charging up

But achieving large-scale production of SSBs is one of the battery industry's most critical and complex challenges.

Central to this challenge is replacing the liquid electrolyte, which transports lithium ions between the anode and cathode, with a solid alternative. To meet the demands of high-performance EVs, a cost-effective method for producing vast quantities of solid-state electrolyte is essential.

One major class of materials being investigated as SSB electrolytes are sulphides, such as lithium superionic conductors and argyodites. These materials show promise due to high-ionic conductivities at room temperature, which are comparable to liquid electrolytes. But their use brings many challenges.

Sulphides are highly reactive in air, requiring manufacture under an inert atmosphere – a costly hurdle for scaling up to meet EV demands and high-volume sectors.

Additionally, sulphides lack stability at high voltages, causing battery performance to degrade after only a few cycles. There are also challenges with processability – sulphides behave as a paste during processing, but form brittle ceramics after heating and compression, which cannot be reworked once cast.

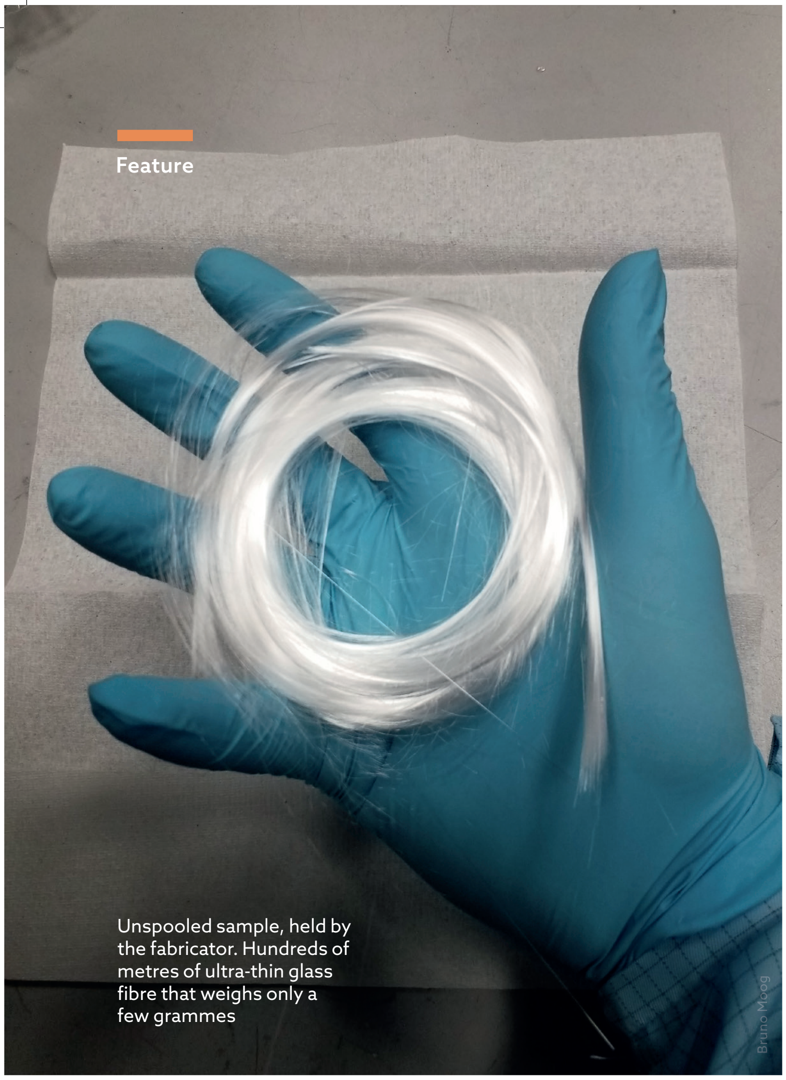
Conductive lithium-based glasses are also being widely investigated as solid-state electrolytes, particularly lithium lanthanum zirconium oxide (LLZO). These materials can be processed in air, making this class of materials potentially more scalable and cost effective. However, like sulphides, bulk glasses face processability limitations.

Enter two unlikely collaborators – the Novel Glass Group at the University of Southampton, UK, with experts in manufacturing advanced photonic fibres used in fibre optics, and Thermal Ceramics UK Ltd, a subsidiary of Morgan Advanced Materials.

Through the Faraday Institution Industry Sprint project, ZEST, they have investigated whether glass fibres of lithium aluminium titanium phosphate (LATP) could form the basis for a composite electolyte for SSBs.

But why use glass in batteries? And why in fibre form?

Several of Morgan's battery materials customers have requested LATP in a fibre form.



Unspooled sample, held by the fabricator. Hundreds of metres of ultra-thin glass fibre that weighs only a few grammes

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LATP has a similar ionic conductivity as LLZO (at $\sim 10^{-4}$ Siemens cm^{-1}), but is unreactive with water. Processing and use of these materials is less expensive and easier, which is important for any SSB electrolyte.

Fibre-based electrolytes show promise as they could increase conductivity by providing better conduction pathways, so promoting ion migration. Use of glass fibres could also help prevent dendrite growth – one of the main challenges of all types of SSBs. The mechanical flexibility of thin fibres also makes them less prone to cracking than other types of solid electrolytes.

The problem? LATP fibres are not commercially available. Developing a scalable, cost-effective method to fabricate fibres with an exact composition and set of properties was critical.

Functional fibre

Standard photonic manufacturing involves heating glass to form a melt, then 'drawing down' fibres by pulling a thin strand through a hole at the bottom of the vessel and wrapping it around a spool while still flexible.

The fibre's diameter is controlled by the speed of draw down, the system's temperature and glass viscosity. Too slow and the fibre is too thick. Too fast for the glass properties and the fibre breaks.

However, these conventional techniques are not suitable for producing LATP fibres for use in SSBs. A new production method was needed to ensure an extremely uniform fibre diameter to make sure resistance (and therefore current flow) is homogeneous across the electrolyte. Additionally, standard processes typically draw only one fibre at a time, making it impractical to scale up to the tonnage needed for automotive applications.

"A new production method was needed to ensure an extremely uniform fibre diameter to make sure resistance (and therefore current flow) is homogeneous across the electrolyte."

In response to this challenge, researchers at the Novel Glass Group, including Bruno Moog and Chris Craig, led by Principal Research Fellow, Pier Sazio, completely reimagined the process for drawing fibres.

They developed, built and trialled a proprietary, continuous, very low waste, single-step fabrication process to manufacture ultrafine specialist fibres to a tight tolerance in the fibre diameter, with high speed and very high yield.

Typically, when you start drawing down fibres you get a big blob of glass before you get the thin fibre, which has to be thrown away. The new technique is 'zero shot' i.e. this blob doesn't form, making it very low waste also.

Hundreds of kilometres of fibre have been successfully fabricated. The patent-pending process is fundamentally scalable and shows great promise to meet the demands of high-volume industries.

Manufacturability is a discipline in and of itself and operates in a very different way to academia. The various constraints that are imposed at the start of a project look restrictive, but in fact force you to come up with creative solutions.

Testing connections

Many glasses lack the ability to be drawn into a fibre without breaking so need to be modified or doped with certain amounts of other elements. For LATP glass, no fibre drawing process previously existed, so researchers had to develop a fundamental understanding of LATP glass behaviour alongside the new processing method.

Optimum fibre composition is judged based on a combination of cost, maximum ionic conductivity and ease of which the material can be drawn into thin structures such as fibres or plates.

More than 10 different LATP compositions were trialled, changing the amount of various dopants – i.e. silica and germanium – to enhance glass-forming stability while having minimal impact on ionic performance and cost.

By understanding ionic conductivity across a wide composition range, the team identified the optimal fibre composition.

Lithium is volatile and can be lost from molten glass. Materials testing of the fibres is therefore critical. X-ray diffraction determined the material phases; X-ray fluorescence spectroscopy and inductively coupled plasma analysis checked chemical composition; electrochemical impedance spectroscopy assessed lithium-ion conductivity; and optical microscopy measured the variability in fibre diameter.

The group successfully manufactured LATP fibres with ionic conductivities comparable to other solid-state electrolytes. Process modifications were discovered that led to increased ionic conductivity and further research will be carried out to understand and optimise process-related performance enhancements.

End of the road?

But kilometres of fibre does not a battery make.

After manufacture, the conductive LATP fibres are broken into shorter rods and aligned to create electrolyte membranes with the fibres held together by a non-conductive binder. This process could be tailored to the specific battery application requirements and specifications from the battery manufacturer.

This method of composite manufacture is used in LLZO, and in electrospun and nanofibres. However, the new process developed is far more manufacturable and lends itself to making other forms of LATP, such as plate, flakes or particles, and so can address the needs of all battery designs.

LATP has a significant advantage over LLZO, in that it can be made and processed in ambient conditions. This differs from LLZO, which is sensitive and reacts with water and needs to be manufactured in 'dry room' conditions.

In the next testing stage, the compositive electrolyte will be incorporated into battery cells to validate properties and materials performance in various configurations. This will be carried out by global customers of Morgan Advanced Materials.

Initial tests show that the fibres have properties that meet customer needs, but full battery testing will validate electrochemical performance during cycling and the extent to which the materials degrade over time.

This is not the end of the road for this fruitful academic-industry collaboration. The Sprint helped Southampton win an Engineering & Physical Sciences Research Council grant of £1.25mln to undertake a follow-up project. This will involve fabricating glass sheets to be used as the electrolyte/separator in SSBs, by forming flat ribbon-type fibres.

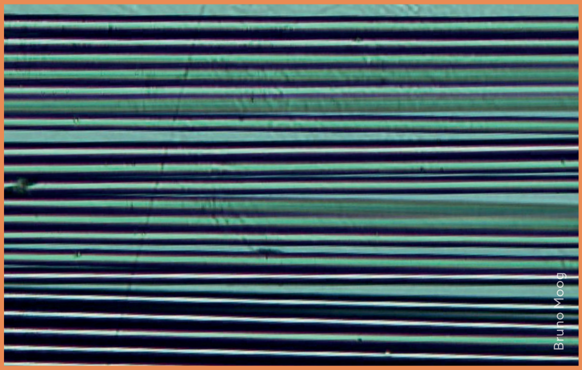
The Roll-2-Roll Manufacture of Multilayer Solid-state Batteries project will run until January 2027 and brings in expertise from the electrochemistry group at Southampton.

And the secret of the collaboration's success? In a word, responsiveness, with constant and regular communication. ZEST is an interesting example of how researchers with deep expertise in one discipline can bring insight to challenges being experienced in a completely unrelated sector – in this case, batteries. It is also a prime example of how the close involvement of an industry partner, with an active and current demand for a commercial product, can ensure academic research retains a laser focus on meeting customer requirements.

The project has accelerated early-stage commercial scale-up of LATP fibre production for the battery market and enabled significant technology transfer.

Whether high-end automotive or aerospace, ZEST showcased the potential of a novel fibre-production process that battery manufacturers can tailor to the requirements of high-volume SSB production.

Below: Micrographs of the precisely aligned fibres with a very narrow range of diameters along the entire length



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Below: The novel glass fabrication method that spools the glass fibre onto the steel drum at the base of the tower

University of Southampton