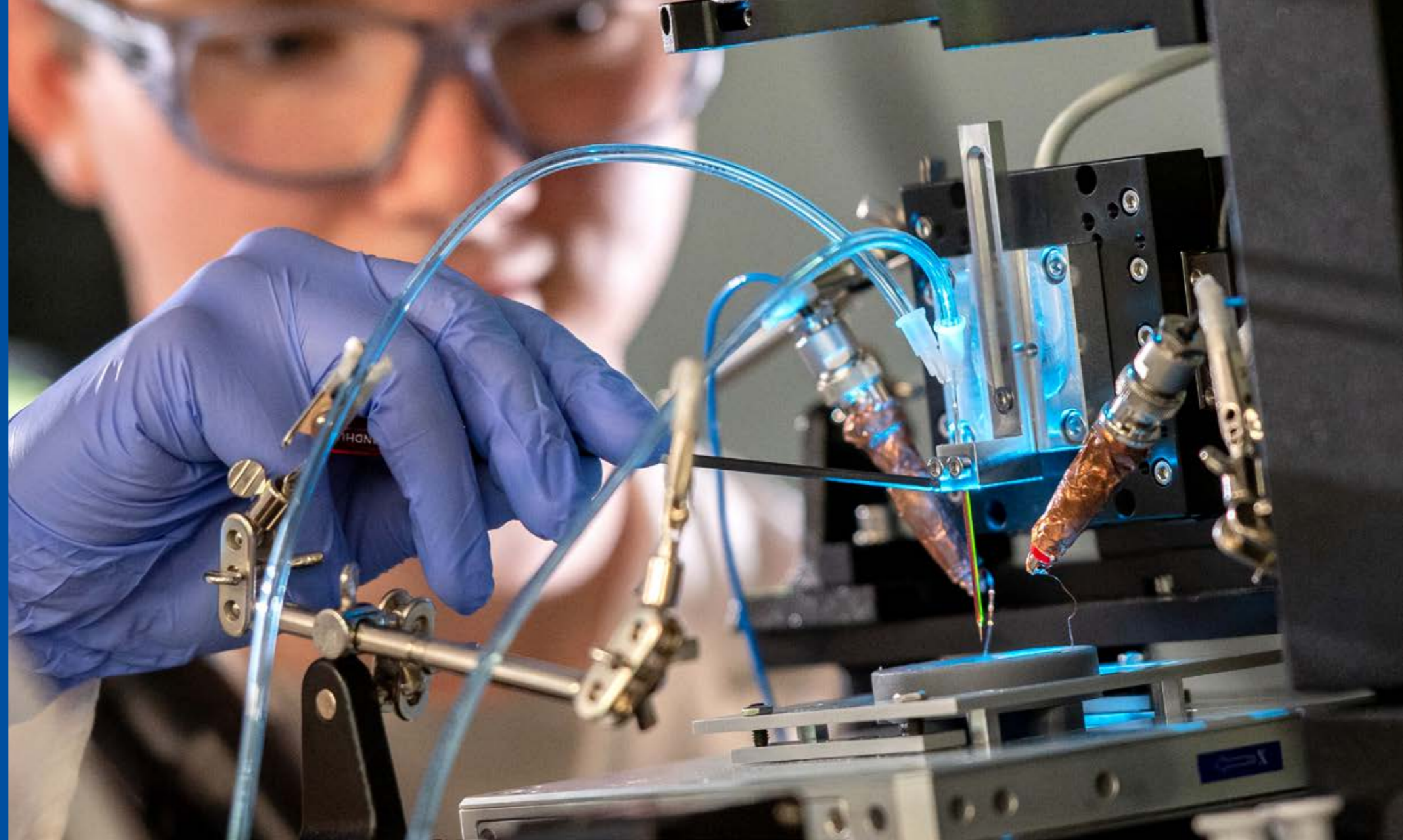


Printing atom by atom

A research team led by chemist Dmitry Momotenko has developed a new 3D printing technique for manufacturing ultrasmall metallic objects. Using this technique, the researchers aim to substantially increase the surface area of battery electrodes to drastically reduce charging times. A lab visit allows to take a look.



A very special kind of 3D printer: Masters student Simon Sprengel makes some final adjustments to allow two metal solutions to flow simultaneously through the tiny printing nozzle.

It takes chemist Liaisan Khasanova less than a minute to turn an ordinary silica glass tube into a printing nozzle for a very special 3D printer. The chemist inserts the capillary tube – which is just one millimetre thick – into a blue device, closes the flap and presses a button. After a few seconds there is a loud bang and the nozzle is ready for use. "A laser beam inside the device heats up the tube and pulls it apart. Then we suddenly increase the tensile force so that the glass breaks in the middle and a very sharp tip forms," explains Khasanova, who is working on her PhD in chemistry in the Elec-

trochemical Nanotechnology Group. Khasanova and her colleagues need the minuscule nozzles to print incredibly tiny three-dimensional metallic structures. This means the nozzles' openings must be equally tiny – in some cases so small that only a single molecule can squeeze through. "We are trying to take 3D printing to its technological limits," says Dr Dmitry Momotenko, who leads the junior research group at the Institute of Chemistry. His goal: "We want to assemble objects atom by atom."

Nanoscale 3D printing – in other words 3D printing of objects that are a just few billionths of a metre in size –

opens up amazing opportunities, the chemist explains. For metal objects in particular, he can envisage numerous applications in areas such as microelectronics, nanorobotics, sensor and battery technology: "Electroconductive materials are needed for all kinds of applications in these areas, so metals are the perfect solution."

While 3D printing of plastics has already advanced into these nanoscale dimensions, manufacturing tiny metal objects using 3D technology has proven more difficult. With some techniques the printed structures are still a thousand times too large for many advanced applications, while with others

it is impossible to fabricate the objects with the necessary degree of purity.

Momotenko specializes in electroplating, a branch of electrochemistry where metal ions suspended in a salt solution are brought into contact with a negatively charged electrode. The positively charged ions combine with electrons to form neutral metal atoms which are deposited on the electrode, forming a solid layer. "A liquid salt solution becomes a solid metal – a process which we electrochemists can control very effectively," says Momotenko. This same process is used for chrome-plating car parts and gold-plating jewellery on a larger scale.

However, transferring it to the nanoscopic scale requires considerable ingenuity, effort and care, as a visit to the group's small laboratory on the Wechloy campus confirms. The lab contains three printers – all built and programmed by the team itself, as Momotenko points out. Like other 3D printers they consist of a print nozzle, tubes for feeding in the print material, a control mechanism and the mechanical components for moving the nozzle – but in these printers everything is a little smaller than usual. A coloured saline solution flows through delicate tubes into the thin capillary tube, which in turn contains a hair-thin

piece of wire – the anode. It closes the circuit with the negatively polarized cathode, a gold-plated silicon flake smaller than a fingernail, which is also the surface on which the printing takes place. Micromotors and special crystals that morph instantaneously when an electrical voltage is applied rapidly move the nozzle by fractions of a millimetre in all three spatial directions.

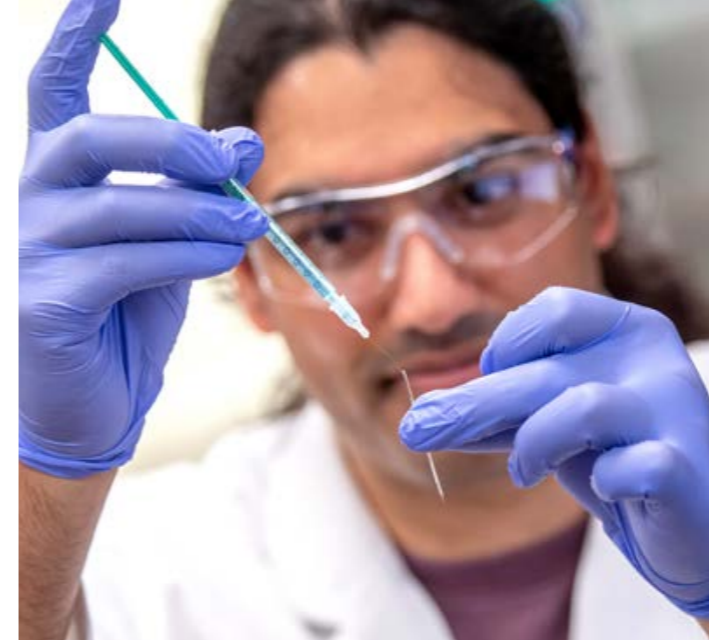
Since even the slightest vibrations can disrupt the printing process, two of the printers are housed in boxes covered in a thick layer of dark-coloured acoustic foam. Furthermore, they are resting on granite plates, each weighing 150 kilogrammes. Both measures



Dmitry Momotenko specializes in the 3D printing of metals. He wants to manufacture objects one atom at a time.



Liasan Khasanova uses a micropipette puller to prepare the tiny printing nozzles made of special glass.



To close the circuit with the negatively polarized cathode, Karuna Kanes positions a hair-thin wire – the anode – inside the printing nozzle.



Tiny gold-coated silicon plates smaller than a fingernail are used as a printing surface.

are aimed at preventing unwanted vibrations. The lamps in the lab are also battery-powered because the electromagnetic fields produced by alternating current from a socket would interfere with the tiny electrical currents and voltages needed to control the nanoprinting process.

Meanwhile, Liasan Khasanova has prepared everything for a test print: the print nozzle is in its starting position, the box is closed, a vial containing a light blue copper solution is connected to the tubes. She starts a programme which initiates the printing process. Measurement data appears on a screen as curves and dots. These show the variations in the current flow and register the nozzle briefly touching the substrate and then retracting again and again. What is the machine printing? "Just a few columns," she replies.

Columns are the simplest geometric forms generated in 3D printing, but the Oldenburg researchers can also print spirals, rings and all kinds of overhanging structures. The technique can currently be used to print with copper, silver and nickel, as well as nickel-manganese and nickel-cobalt alloys. In some of their experiments, they have already ventured deep into the nano-world. Momotenko and an international team of researchers reported in a study published in the journal *Nano Letters* in 2021 that they had produced copper columns with a diameter of

just 25 nanometres – taking 3D metal printing below the 100-nanometre limit for the first time.

One of the cornerstones for this success was a feedback mechanism that enables precision control of the print nozzle's movements. It was developed by Momotenko together with Julian Hengsteler, a PhD student he supervised at his previous place of work, ETH Zurich in Switzerland. "The continuous retraction of the print nozzle is enormously important, because otherwise it would quickly become clogged," explains the chemist.

"A liquid salt solution becomes a solid metal – a process which we electrochemists can control very effectively."

The team prints the tiny objects layer by layer at speeds of a few nanometres per second. Momotenko still finds it amazing that objects too small to be visible to the human eye are being created here. "You start with an object you can touch. Then a certain transformation takes place and you are able

to control these invisible things at an extremely small scale – it is almost unbelievable," says the chemist.

Momotenko's plans for his nanoprinting technique are also pretty mind-boggling: his goal is to lay the foundations for batteries that can be charged a thousand times faster than current models. "If that can be achieved, you could charge an e-car within seconds," he explains. The basic idea he is pursuing is already around 20 years old. The principle is to drastically shorten the pathways of the ions inside the battery during the charging process. To do this, the electrodes, which are currently flat, would have to have a three-dimensional surface structure. "With the current battery design, charging takes so long because the electrodes are relatively thick and far apart," Momotenko explains. The solution, he says, is to interlock the anodes and cathodes like fingers at the nanoscale and reduce the distance between them to just a few nanometres. This would allow the ions to move between anode and cathode at lightning speed. The problem: so far it has not been possible to produce battery structures with the required nano dimensions.

Momotenko has now taken on this challenge. In his NANO-3D-LION project, which is funded by a European Research Council Starting Grant awarded in March 2021, the goal is to develop and employ advanced nanoscale 3D printing techniques to fabricate ac-

tive battery materials with ultrasmall structural features. Having collaborated successfully with a research group led by Prof. Dr Gunther Wittstock at the Institute of Chemistry in an earlier project, Momotenko then decided to base the project at the University of Oldenburg. "The Department for Research and Transfer was very helpful with my grant application, so I moved here from Zurich at the beginning of 2021," he explains.

His research group now has four members: besides Khasanova, PhD student Karuna Kanes and Master's student Simon Sprengel have joined the team. Kanes focuses on a new method aimed at optimizing the precision of the print nozzle, while Sprengel investigates the possibility of printing combinations of two different metals – a process necessary to produce cathode and anode material simultaneously in one step.

Liasan Khasanova will soon focus on lithium compounds. Her mission will be to find out how the electrode materials currently used in lithium batteries can be structured using 3D printing. The team is planning to investigate compounds such as lithium-iron or lithium-tin, and then to test how large the nano "fingers" on the electrode surfaces need to be, what spacing is feasible, and how the electrodes should be aligned. One major hurdle here is that lithium compounds are highly reactive and

can only be handled under controlled conditions. For this reason, the team recently acquired an extra-large version of a laboratory glove box, a gas-tight sealed chamber that can be filled with an inert gas such as argon. It has handling gloves built into one side with which the researchers can manipulate the objects inside. The chamber, which is about three metres long and weighs half a tonne, is not yet in operation, but the team plans to set up another printer inside it. "The chemical conversion of the material and all other tests will also have to be carried out inside the chamber," Momotenko explains.

The team will run up against some major questions in the course of the project: How do tiny impurities within the argon atmosphere affect the printed lithium nanostructures? How to dissipate the heat that is inevitably generated when batteries are charged within seconds? How to print not just tiny battery cells but also large batteries for powering a mobile phone or even a car – within a reasonable time? "On the one hand, we are working on the chemistry needed to produce active electrode materials at the nanoscale; on the other, we are trying to adapt the printing technology to these materials," says Momotenko, outlining the current challenges.

The problem of energy storage is extremely complex, and his team can only play a small part in solving it, the

researcher emphasises. Nonetheless, he sees his group in a good starting position: in his opinion, electrochemical 3D printing of metals is currently the only viable option for manufacturing nanostructured electrodes and testing the concept.

In addition to battery technology, the chemist is also working on other bold concepts. He wants to use his printing technique to produce metal structures that allow for a more targeted control of chemical reactions than possible so far. Such plans play a role in a relatively young field of research known as spintronics, which focuses on the manipulation of "spin" – a quantum mechanical property of electrons.

Another idea he hopes to put into practice is to manufacture sensors that are able to detect individual molecules. "That would be helpful in medicine, for detecting tumour markers or biomarkers for Alzheimer's at extremely low concentrations, for example," says Momotenko.

All these ideas are still very new approaches in chemistry. "It is not yet clear how it would all work," he admits. But that's how it is in science: "Every meaningful research project requires long thinking and planning, and in the end most ideas fail," he concludes with a smile. But sometimes they don't – and he and his team have already taken the first successful steps on their journey. (uk)