A Look Inside **the Black Box**

What happens inside lithium-ion batteries when they are being charged and discharged? Anatoliy Senyshyn and his team are taking a close look – with the help of neutrons

Blick in die Blackbox

Neutronen sind ein geeignetes Werkzeug, um zu beobachten, was im Inneren von Lithium-Ionen-Batterien beim Laden und Entladen geschieht. Dies beweisen Arbeiten von Dr. Anatoliy Senyshyn und seinen Mitarbeitern an der Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) der TU München. Die Wissenschaftler positionierten handelsübliche Li-Zellen der Bauart 18650 in einem Neutronenstrahl. Die ungeladenen Elementarteilchen werden am Elektrodenmaterial der Zellen abgelenkt. Die Winkel, unter denen dies geschieht, lassen Rückschlüsse auf den Aufbau und die Zusammensetzung der Batteriekomponenten zu. Mit anderen Methoden war es bisher nicht möglich, den Zustand während des Betriebs zu untersuchen. Denn öffnet man die Zelle, kann das Auswirkungen auf ihr elektrochemisches Gleichgewicht haben und die Ergebnisse verfälschen.

Neue Mechanismen bei der Einlagerung von Lithium-Ionen
Bei der Untersuchung des Ermüdungsverhaltens konnten die Forscher zeigen, dass sich bei fortschreitendem Betrieb der Zellen einige Lithium-Ionen irreversibel auf der Anode ablagern und dann nicht mehr zur Verfügung stehen, was die Kapazität der Batterie verringert. In weiteren Analysen beobachteten die Wissenschaftler Beugungsmuster, die auf einen bis dahin unbekannten Mechanismus bei der Einlagerung von Lithium-Ionen in die Grafitanode hindeuten. Bei ihren neuesten Messungen fanden sie heraus, dass sich die Menge des Elektrolyten in den Zellen nach vielen Ladungszyklen verringert, gleichzeitig mit der Menge der aktiven Lithium-Ionen. Künftige Analysen sollen die Ursache dafür finden.

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Link

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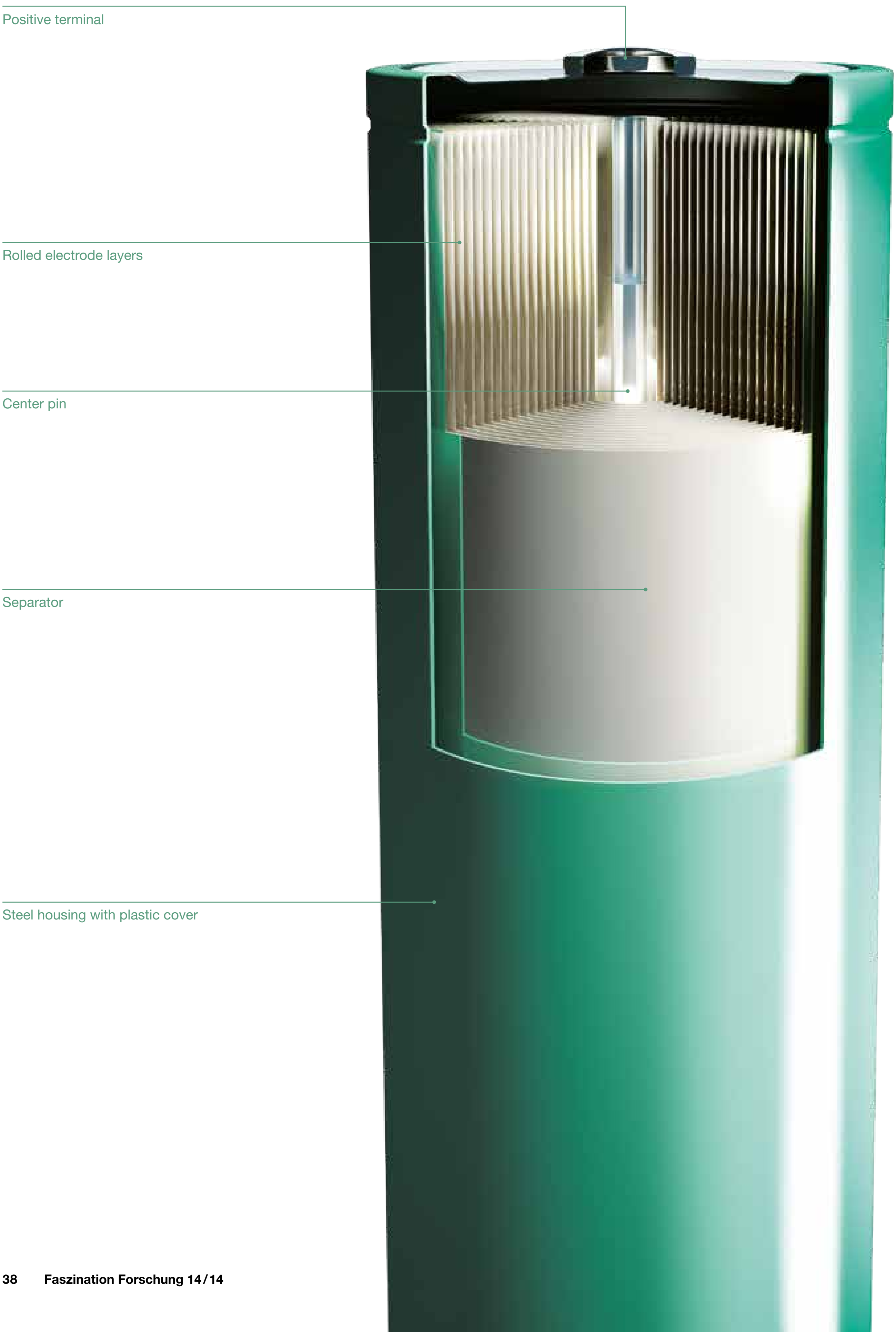
Technology has become pervasive in many facets of our modern lifestyle. But many of the gadgets we have come to rely on – laptops and smartphones included – would not be possible without lithium (Li)-ion batteries. These rechargeable batteries are designed to undergo thousands of charging and discharging cycles – which they do with no problem most of the time. Sometimes, though, we hear reports of the tiny power packs suddenly bursting into flames. Such incidents are very rare, however, considering that billions of batteries are in use worldwide. They usually occur as a result of cell damage or misuse followed by a thermal runaway. Which is why lithium-ion batteries are typically protected against short-circuits, overcharging and deep discharge.
High capacity – at a comparatively low price – makes Li-ion batteries the energy storage solution of choice for today's electric cars. They are even used in modern aircraft. ▷

Picture credit: Heddergott



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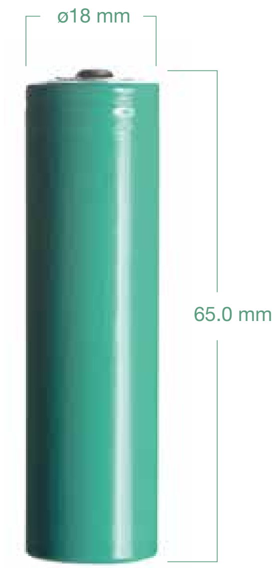


Left: Commercially available 18650 Li-ion cells are used in most laptop battery packs. Recently they have also been making their way into electric cars
Below: Martin Mühlbauer mounts a Li-ion cell on the sample table of the high-resolution powder diffractometer SPODI

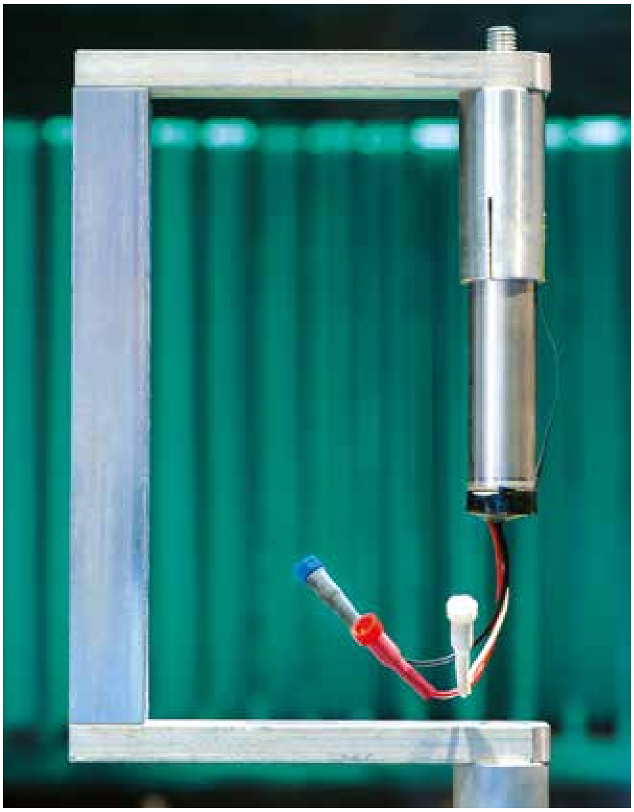
For these applications, however, the batteries are of course scaled up and the internal stress is much higher. Particularly when it comes to mobility, safety – besides weight and energy density – is one main concern. So understandably, the public was hugely disturbed when the battery of a Dreamliner passenger plane burned in early 2013, and when a Tesla electric car caught fire because of battery damage. "Despite the fact that there have been many advances in this technology, Li-ion cells still have some drawbacks, which require careful and systematic research," admits Dr. Anatoliy Senyshyn. "That is why we decided to undertake a study on safety issues, the stability of the electrode material and ways to increase capacity."

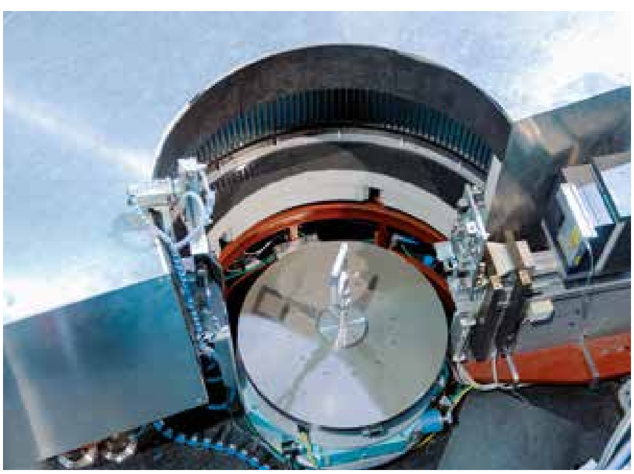
Using neutrons to look inside batteries

The physicist works at the Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) of TU München (TUM). Along with colleagues from the Institute for Applied Materials – Energy Storage Systems (IAM-ESS) at Karlsruhe Institute of Technology (KIT) and the Materials Science Department at TU Darmstadt, he uses neutrons to look inside Li-ion batteries – more closely than it was ever possible before. "We have the great advantage of being able to see what is happening inside the battery while it is being charged and discharged," he explains. "With other methods, it is usually only possible to examine the battery beforehand and afterwards. During the actual charging process, the cell is a black box. If it is opened for examination, this can disturb the equilibrium of its chemical components in some cases and thus impact the validity of the study findings."

For their investigations, the researchers focus on commercially available 18650 Li-ion cells with a diameter of 18 mm and a length of 65 mm. These cylindrical cells are found in the majority of laptop batteries, and recently they have also been making their way into flashlights and increasingly into electric cars. Their anode is made of carbon – graphite to be exact – and the cathode consists of a lithium metal oxide, often lithium cobalt dioxide. For each electrode, the powder based materials are mixed with a binder to form a solid paste. A film is inserted to separate the two layers. This separator electrically isolates the two electrodes. ▷

Picture credit: Heddergott





Looking inside batteries with the powder diffractometer SPODI (bottom): Mounted 18650 cell (top, with removed plastic cover) as seen by the neutron beam. Elastically scattered neutrons have to pass neutron collimators (green background) installed in front of the neutron multi-detectors

It is permeable for the lithium ions, however, and these then create the current flow. During charging, they move inside the graphite, and to the metal oxide while discharging. On both sides they are intercalated into the respective crystal lattice. The electrode material is coated on electrically conductive foils made of aluminum or copper, which act as a supply line or contact to the outside. The stacked layers comprising electrodes and separator are rolled up and fitted inside the cylindrical housing. This is filled with a liquid electrolyte, which acts as a medium for lithium transport.

Thermal neutrons are a good way to gain insight into a rechargeable battery during operation as they have very little energy and therefore do not effect changes in the cell. The uncharged elementary particles move through many materials almost unhindered, but they are diffracted by ordered systems like the crystalline electrode material. The angles at which this happens allow conclusions to be drawn on the structure and the elemental composition of the battery components. The researchers made use of this effect and placed the cells in a thermal neutron beam. At the same time, detectors arranged in a semicircle around the sample recorded the distribution of the neutrons scattered at the corresponding angle. The resulting graphs show peaks of varying heights at various scattering angles depending on the charge status of the cells.

At the same time, the researchers generated radiographs using a procedure similar to medical X-ray tomograms. “We measured the intensity of the neutrons penetrating the sample at various angles and then generated tomograms of the interior of the cells,” explains KIT researcher Dr. Martin Mühlbauer. The images obtained can be compared with the X-ray tomograms of the batteries previously recorded at a nearby chair at TUM. “With X-rays, the spatial resolution is actually better than with neutrons,” points out Mühlbauer, “but only neutrons enable us to trace the distribution of the lithium ions.”

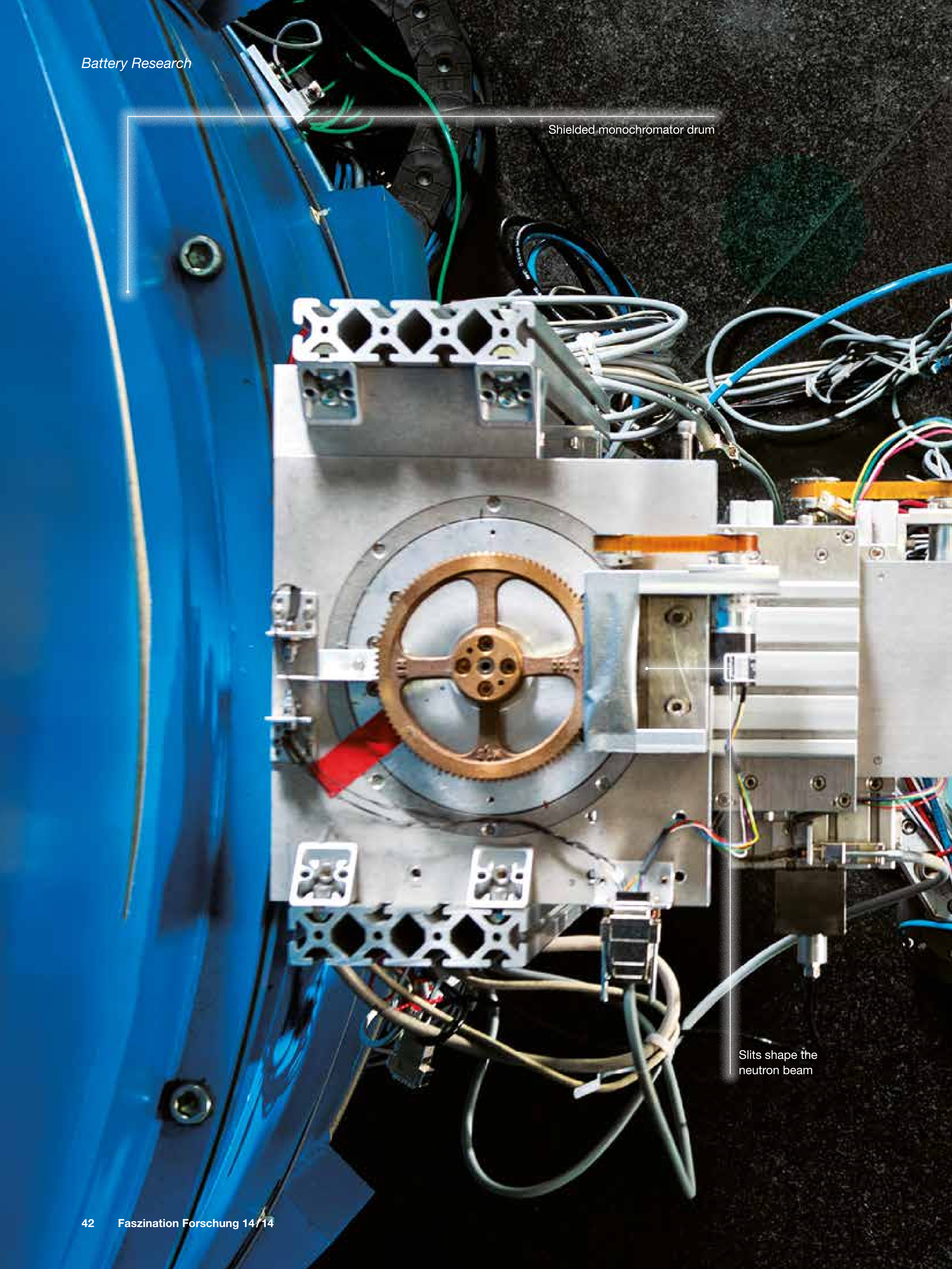
Lithium ions stick to the anode

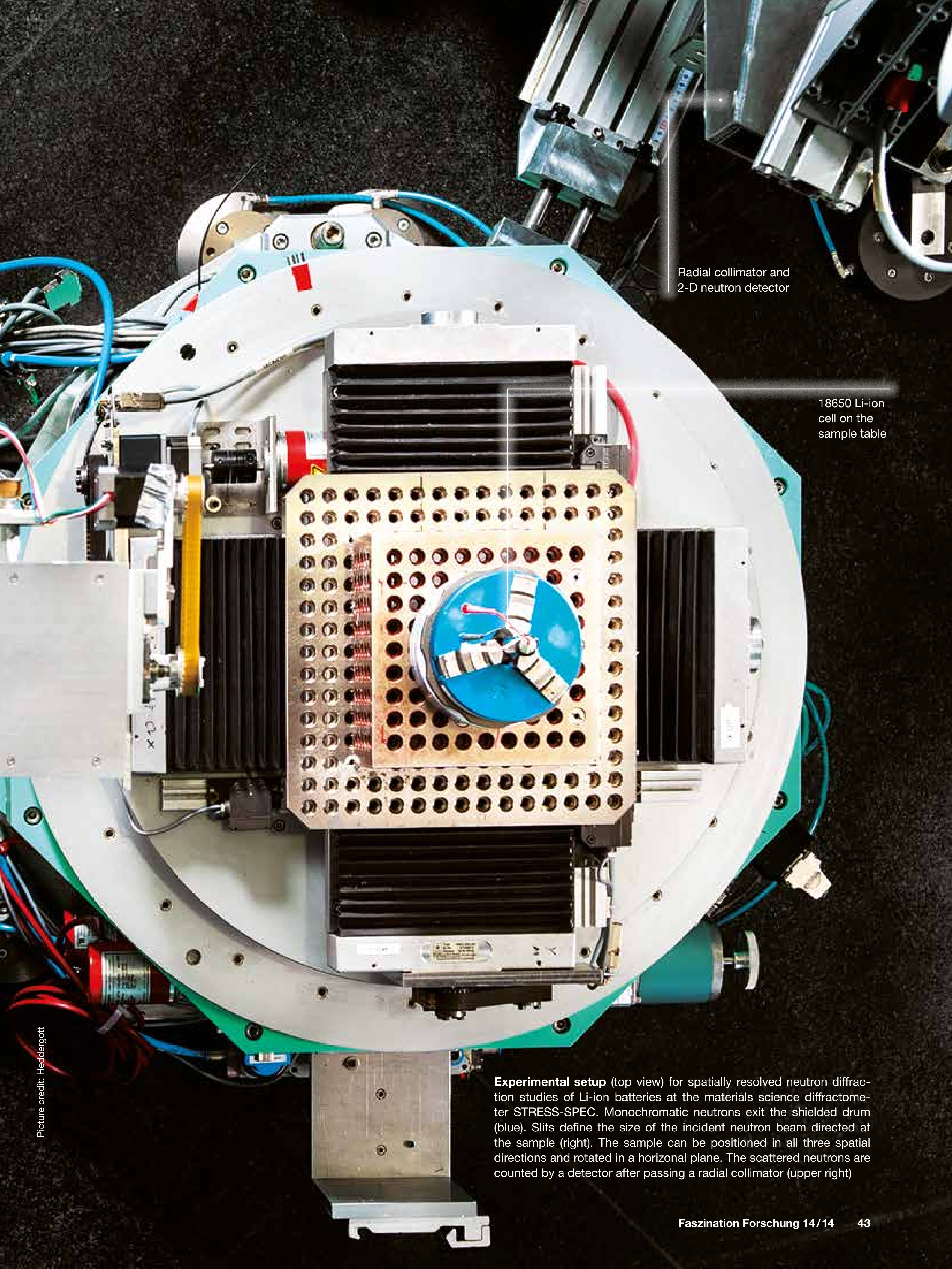
During evaluation of the measurement graphs, numerous geometric, physical and metrological factors have to be taken into account. Based on a model representation of the material, individual parameters are adjusted by the computer until – in an ideal case – the measured values fully correspond with the calculated values. If this does not happen, the researchers modify the model until they achieve the best possible match.

Already two years ago the researchers made a discovery, showing that when the cells are used continuously, some of the lithium ions are irreversibly deposited at the anode and are therefore lost for subsequent cycles, which reduces the battery’s capacity. “This enabled us to prove that there are processes at the anode, which affect the performance of the storage system. These are not yet fully understood, however,” comments Senyshyn. One thing is clear at this stage: the process is temperature-dependent. Electrochemical analysis allowed for monitoring a decrease of the battery capacity down to only about 80 percent of the original capacity after 1000 cycles. Neutron measurements confirmed a corresponding decrease in the number of lithium ions exchanged between the two electrodes. At 25 degrees Celsius, the effect was much more pronounced ▷

Picture credits: Heddergott

The materials science diffractometer STRESS-SPEC is one of the instruments used by Anatoliy Senyshyn (right) and Martin Mühlbauer to analyze the charge and discharge processes inside batteries

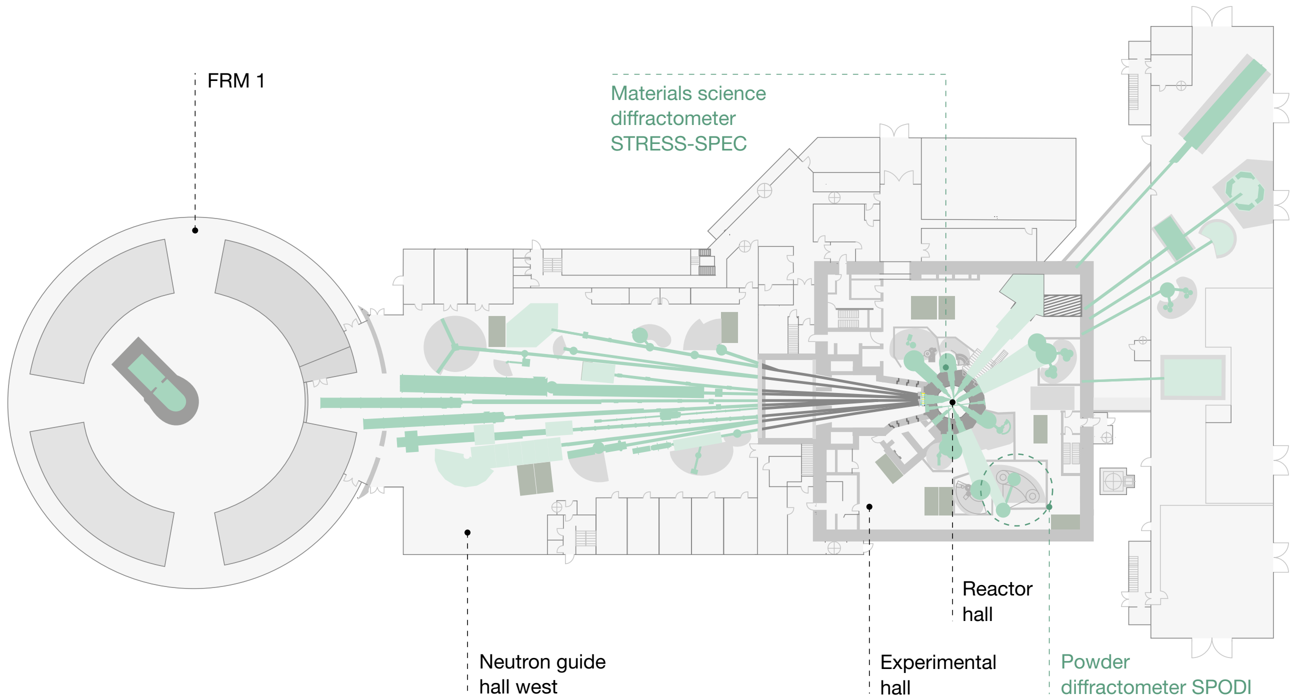

Shielded monochromator drum
Slits shape the neutron beam



Picture credit: Heddergott

Experimental setup (top view) for spatially resolved neutron diffraction studies of Li-ion batteries at the materials science diffractometer STRESS-SPEC. Monochromatic neutrons exit the shielded drum (blue). Slits define the size of the incident neutron beam directed at the sample (right). The sample can be positioned in all three spatial directions and rotated in a horizonal plane. The scattered neutrons are counted by a detector after passing a radial collimator (upper right)

Right: The FRM II reactor building. The neutron guide hall occupies the space between the new and the old reactor, the so-called Atomic Egg. Soon a new neutron guide hall east will start its operation. The high-resolution powder diffractometer SPODI and the materials science diffractometer STRESS-SPEC are located in the experimental hall
Bottom: Side view of the setup for spatially resolved powder diffraction studies of 18650 Li-ion batteries at the instrumtent STRESS-SPEC. The red laser beam marks the center of the neutron beam for sample alignment



than at 50 degrees Celsius. Batteries operated at the higher temperature only showed about two thirds of the capacity loss observed at room temperature after 1000 cycles. Apparently the Li-ions retain greater mobility at elevated temperatures and can overcome transport barriers built up due to fatigue more easily.

Neutron measurements indicate unknown mechanisms

Meanwhile, more detailed measurements revealed that the process of charging and discharging lithium-ion batteries is different to previous assumptions. The researchers observed an intensity distribution inside the diffraction pattern, indicating a previously unknown mechanism occurring during the intercalation of lithium ions into the graphite anode. Contrary to the accepted opinion that this intercalation only takes place in well-defined stages, they only found two of these states forming defined stages at high lithium concentrations, where each lithium ion is coordinated with either six or twelve carbon atoms. These stages are known as LiC_6 and LiC_{12}. At lower lithium concentrations, the transformation from graphite to LiC_{12} is a quasi-continuous process, whereby intercalated lithium forms "islands" in every second layer of graphite. These gradually grow as lithium concentrations rise until a stage corresponding to LiC_{12} is reached.
"These findings force us to reconsider the intercalation of the lithium ions into the anode's graphite layers close to the discharged state," says Senyshyn. "The deviations we have observed may have considerable influence on critical battery properties like quick-charge behavior, low-temperature performance or depth of discharge." All of this information could be extremely valuable to battery manufacturers and users – if it is incorporated into the design and testing of new products. "Beyond an academic environment, industry undoubtedly faces financial constraints in funding research projects such as these," reckons Mühlbauer, "or the persons in charge are simply unaware of these possibilities."
Money could be saved, however, by developing optimized battery concepts. The researchers in Garching have discovered in their latest measurements, for instance, that the amount of electrolyte in the cells decreases after numerous charging/discharging cycles, simultaneously with the number of active lithium ions. "Opinions are divided on what actually happens to the electrolyte," relates Senyshyn. "We cannot say with certainty, however, which theory is the valid one." The geometric structure of the cells is another area that could be optimized: "In some types of rechargeable batteries, we have found areas where a comparatively small amount of lithium is intercalated. That is a waste of material," states Mühlbauer. "One might be able to prevent this by improving the structure, at the same time increasing cell capacity without using additional material." So the researchers still have a lot of work to do. They are currently investigating different cell types and materials. "The electrolyte in particular is an extremely critical component," Senyshyn points out. "So analyzing its temperature behavior will be a top priority. Battery cells have many parameters allowing for changes. They look like simple structures, but are extremely complicated in terms of how they work. We assume there are many opportunities for optimization."

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Picture credit: Heddergott, Graphics: ediundsepp (Source TUM)