Empa News

Magazine for Research and Innovation
Volume 11 / Issue 40 / May 2013

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EMPA
Materials Science & Technology

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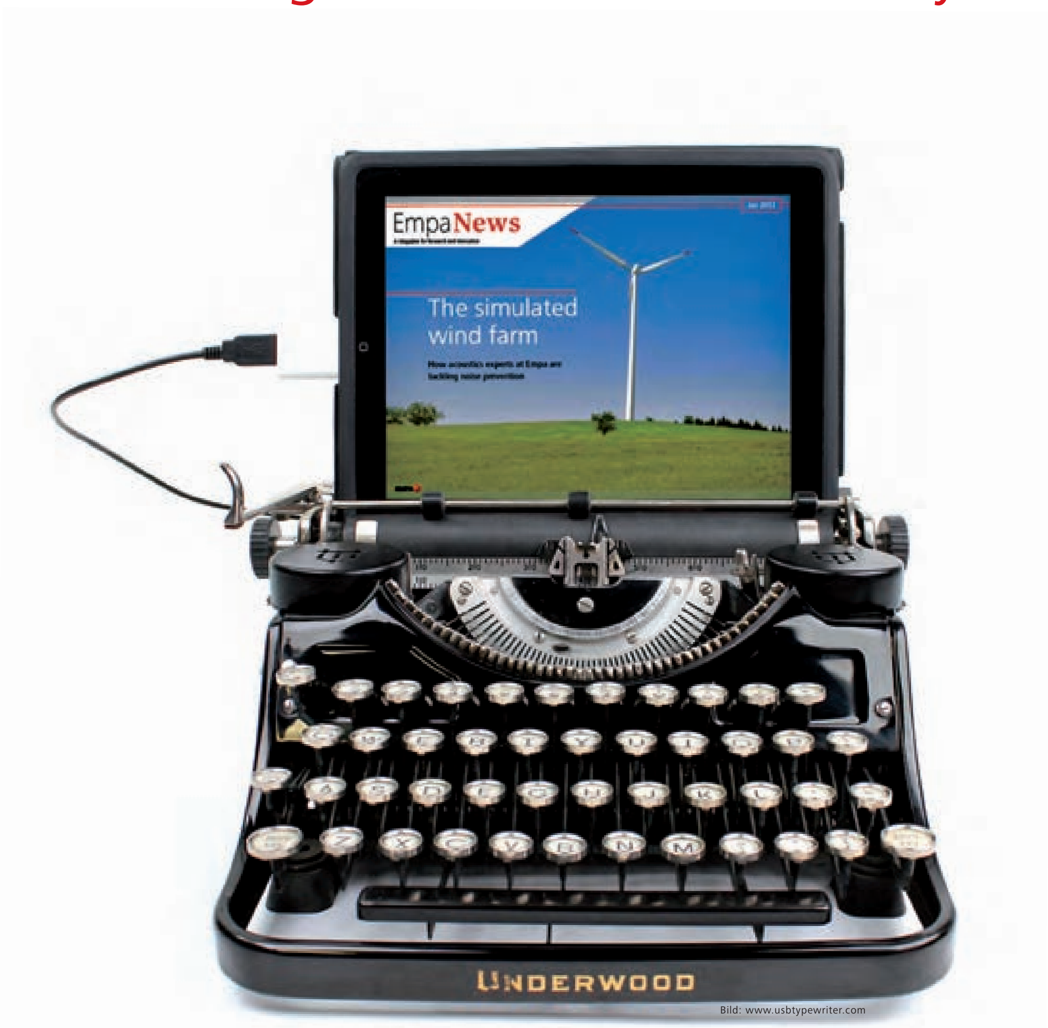

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EmpaNews

TOUCH THE SCIENCE

MICHAEL HAGMANN Head of Communications

It’s the interface, stupid!

Dear Reader,

Many chemical reactions and physical processes take place on surfaces or within boundary layers, such as (heterogeneous) chemical catalysis, i.e. the conversion of one substance into another, changes in state of matter such as the condensation of water vapor, or corrosion processes.

The boundary layers and interfaces in question are often very thin and, in extreme cases, only consist of monomolecular layers. In order to understand the processes at these layers (and ideally, control them in a specific manner), they must first be analyzed in as much detail as possible, both structurally AND chemically. Ideally, this is done down to the atomic level and, if possible, even beyond. Researchers at Empa are doing just that by developing new analytical tools and devices and pushing them to the max. The current edition of EmpaNews highlights some impressive examples of these “super-microscopes” and the like.

It is only by name, though, that these high-tech gadgets are related to the instrument, through which we once marveled at the stinging hairs on a nettle or the stone cells in the flesh of a pear in biology class.

With the same sense of discovery we want to encourage you, dear reader, to try out our new App taking EmpaNews to the next level: a multimedia-enriched reading experience for your iPad or Android tablet.

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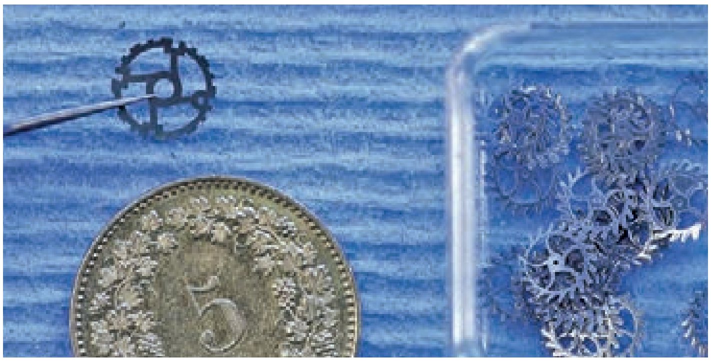
Cover
High-temperature joining test with 200 ultra-thin layers of aluminium-nitride and copper. Copper in extremely thin layers melts more quickly than usual. This protective manufacturing method could soon bring major advantages to the electronics industry.



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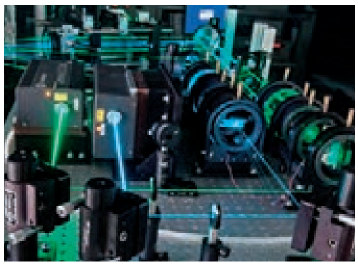

Laser-measurement in the exhaust-lab 26

ClimatePartner climate neutral
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Mercury in energy-saving bulbs – a sword of Damocles?

How much mercury is floating above our heads in energy-saving bulbs? Where does it "disappear" when the bulbs go out? And how dangerous is it if a bulb breaks, for instance in a child's bedroom? Empa is investigating the scope of the problem.

TEXT: Rainer Klose / PICTURES: Empa

Energy saving is something that is politically desirable. Lawmakers are encouraging the change to energy-saving bulbs by issuing bans. The 100 Watt light bulb disappeared in 2009, the 75 Watt variant went in 2010, the 60 Watt bulb disappeared in 2011, and in September last year the 40 Watt bulb was discontinued, too. But where are we heading with this? "Everything that we create also has to be recycled at some point", says Renato Figi, who examines the amount of mercury in light bulbs in Empa's laboratory for "Analytical Chemistry". According to the packing slip, each energy-saving bulb contains 1-2 milligrams of mercury, which makes it illuminate.

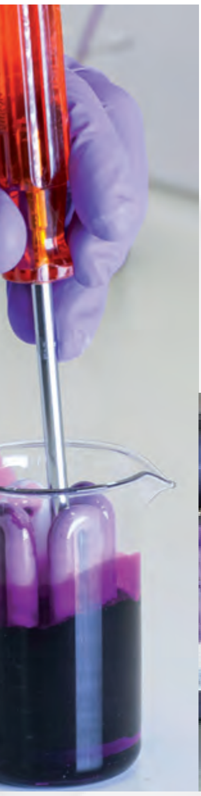
Illegal disposal?

However: the information isn't always right. "We had some real "Aha" results", reports Figi. Some bulbs that he analyzed illuminate with less than 1 mg of mercury, and others contain several times this amount. The mercury content differs considerably – even in bulbs of the same type.

Few people used to know how much mercury the bulbs contained. The Federal Office for the Environment (FOEN) brought this uncertainty into the arena. Empa was commissioned to look into the scope of the problem. Initially the intention was to find out the annual amount of mercury that was being used in energy-saving lamps and other types of light in Switzerland, i.e. where it originates and where it goes to. Another problem quickly emerged. The investigations had previously always been restricted to the mercury that was bound in the bulbs, i.e. the amounts that stick to the glass or other solid components. Nobody thought about gaseous mercury – which is considerably more hazardous to human health than liquid or solid mercury.

Analyzing the problem

Figi discovered a simple but effective way of quntifying all of the mercury in the lamp: the entire lamp is immersed in a violet solution of sodium permanganate, which acts as a strong oxidation agent. The glass bulb is then broken under water with a pair of pliers. The saline solution immediately shoots into the glass body, since it contains a vacuum. The gaseous mercury (chemical formula Hg^0) is therefore oxidized to Hg^{2+} ions and dissolves in the solution. The proportion of gaseous mercury can thus be determined.



How Empa measures the amount of mercury in energy-saving lamps: The lamp is submerged in a potassium permanganate solution and the glass bulb is broken. Because of the pressure difference, the solution shoots into the lamp and washes out the gaseous mercury. The glass is then ground into a powder and the attached amounts analyzed separately.

Figi then determines the amount of bound mercury in the same bulb by separately analyzing the remaining solids (amalgamated mercury, metal mercury and glass) after the bulb had been broken. The glass part is pulverized in a pebble mill cooled with liquid nitrogen at -196 degrees C. None of the mercury evaporates – the heavy metal that is stuck to the glass fragments is dissolved in concentrated nitric acid in a microwave oven under pressure and at a high temperature. From the solution Figi determines the remaining quantity of mercury, i.e. the mineral-bound mercury. If amalgamated or metal mercury is also present, this is dissolved in nitrohydrochloric acid at high temperatures and high pressure and the amount of mercury determined in the same way as with the glass fraction.

Until now, the FOEN estimated that up to 200 kg per year has been used in lamps throughout Switzerland. "At the end of the investigation we will know whether this assumption is correct", says Figi. "Various international committees have outlawed the use of heavy metals such as cadmium, lead, arsenic and mercury in the last few decades. Now, at the beginning of the 21st century, we are starting to tolerate mercury in our living rooms again".

Two-thirds end up in domestic waste

The tests with a total of 80 bulbs (five bulbs each from 16 different commercial bulb types) resulted in some interesting findings: brand new bulbs contain a considerable amount of bound mercury but little gaseous mercury. However, the longer they are used, the greater the amount of gaseous mercury. Mercury-containing bulbs that have reached the end of their service life after thousands of hours of use and are then replaced are, therefore, a serious disposal problem. "Unfortunately, all of the calls to hand in the bulbs to electrical shops have so far been in vain", says Figi. "According to statistics, only one third of all bulbs end up being recycled".

The case is clear to the Empa researcher: "Energy-saving bulbs can only be a temporary solution. We must change to low-pollution LED technology as soon as possible". Until then, he would like a deposit of five Swiss francs to be charged on every energy-saving bulb that is sold. He thinks that this is the only way to be sure that the majority of used light bulbs are being recycled. //

Anti-mercury laws

The first binding agreement for restricting the production and use of mercury was signed by 140 countries in Geneva on 18th January 2013. The convention regulates the production, use, and storage of mercury and the handling of waste containing mercury. No new mines may be set up and existing mines must be closed within the next 15 years, meaning that mercury will then only be available from recycling.

Mercury must be gradually removed from thermometers and blood pressure measuring devices by 2020. Bulbs with output of less than 30 watts may contain no more than 5 mg of mercury. The use of mercury as a preservative for vaccines is still permitted because of the lack of alternatives. The agreement text was presented for ratification in October 2013. If it is ratified by a minimum of 50 states, the agreement will come into force no later than 2018.

The export of mercury and mercury-containing items (with exceptions) has been banned in the EU since 2011. Since then, mercury has been considered to be hazardous waste, and must be disposed of in underground high-security areas (abandoned salt mines, for example). Europe used to be the global leader in mercury production. About one thousand tonnes of mercury are in use in Germany, mainly for chlor-alkali electrolysis.

Source: *Wikipedia/New Scientist Deutschland*

What should you do if an energy-saving bulb breaks?

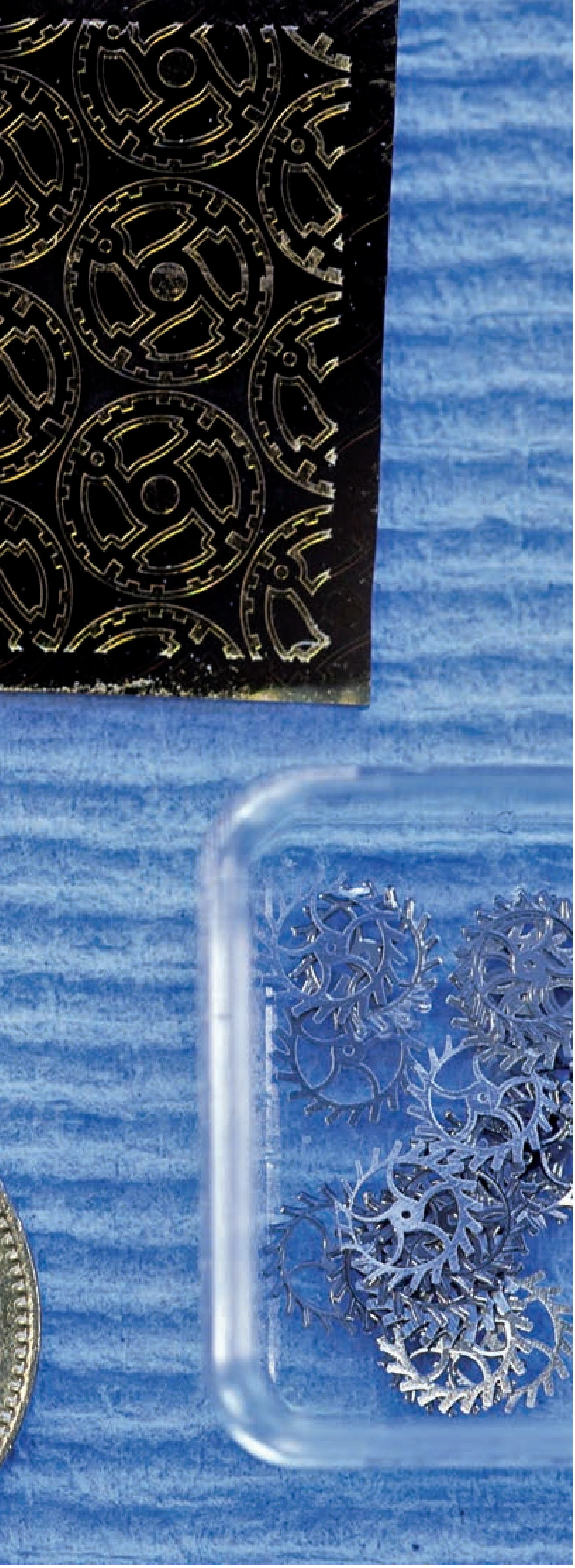
– Open the window and ventilate the room for 15 minutes
– Carefully sweep up the pieces of glass, picking up the glass using adhesive tape
– DO NOT vacuum up – because this will distribute mercury vapour and particles in the air
– Put the glass, the adhesive tape and the wiping cloth in a screw-top jar with a secure seal, then hand in for recycling.

Information: *http://www.bag.admin.ch/themen/chemikalien/00228/03912*

Stainless steel from cold water

The “Electroplating Centre of Excellence” has its headquarters at the Empa site in Thun. Johann Michler and his team work out solutions for problematic cases – and discover layers that previously did not exist. Stainless steel, for example, cold-deposited on any conductive metal from a saline solution.

TEXT: Rainer Klose / PICTURES: Empa



World first from the Empa laboratories: high-precision stainless steel components, manufactured using electroplating. This stainless alloy is not made in a furnace, but in a basin with cold water at low cost.

The laboratories of the Empa "Mechanics of Materials and Nanostructures" laboratory extend over four floors of the General Herzog house in Thun. This is probably the most important centre for electroplating research in the whole of Switzerland. It is also a place where industrial problems are solved. This is done for medium-sized companies, for example, who want to make their production more efficient, and also for large companies who are looking for a new range of products.

"When we are working on new materials, we always look at three important core areas at the same time: the manufacturing process, the microstructure of the materials and the characteristics of the materials", says Johann Michler, who studied material science in his home town of Erlangen and has been working at Empa for 13 years. During this time, he and his teammates have built up a sizeable pool of analysis equipment (some of which they developed themselves), with which the structure and technical properties of new materials can be characterized. This is because systematic optimizations can only be made to processes and materials if a detailed analysis is carried out – anything else would just be "trial and error".

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Hannes Michler operates a FIB-SIMS – one of the hightech inststruments used to characterize new materials.

2
Electroplating engineer Mario Wick bridges the gap between research and industry: the proof of whether or not a laboratory test also works on a large scale can be seen in this electroplating bath.

3
Marks for surgery: small steel plates coated with titanium oxide. The harmless oxide produces interference colours that indicate exactly what the workpiece is intended for. For example, the surgeon knows which coloured screw to secure the implant with.

His team therefore consists of material scientists, chemists, physicians, mechanical engineers and electroplating engineers in order to cover the entire process chain all the way up to the properties of the final products.

Analytic equipment makes the difference

Michler's team can crack all kinds of technical problems with system and persistence: they coat conductive surfaces with metal, mark medical implants using thin, coloured interference markers and are galvano-forming experts. Using this method it is possible to manufacture micro-mechanical components with extreme precision in small quantities and at low cost, which is extremely useful for the watch industry, for example.

Another procedure is used in medical engineering. Surgeons have to work fast – and they don't like instruction leaflets. Medical implants, therefore, have colour marks. This means that it is clear to the surgeon at a glance which screw has to be fixed with which screwdriver, and which components fit together and which don't. Of course, the coloured marking has to be harmless and must not come off inside the body.

Previously it was possible to mark titanium implants by applying a thin coating of titanium oxide. This coating, which has a blue or red metallic colour, is harmless – titanium oxide is used as the white pigment in toothpaste and sun cream, for example. However, there are also implants made from other metals that also need to be

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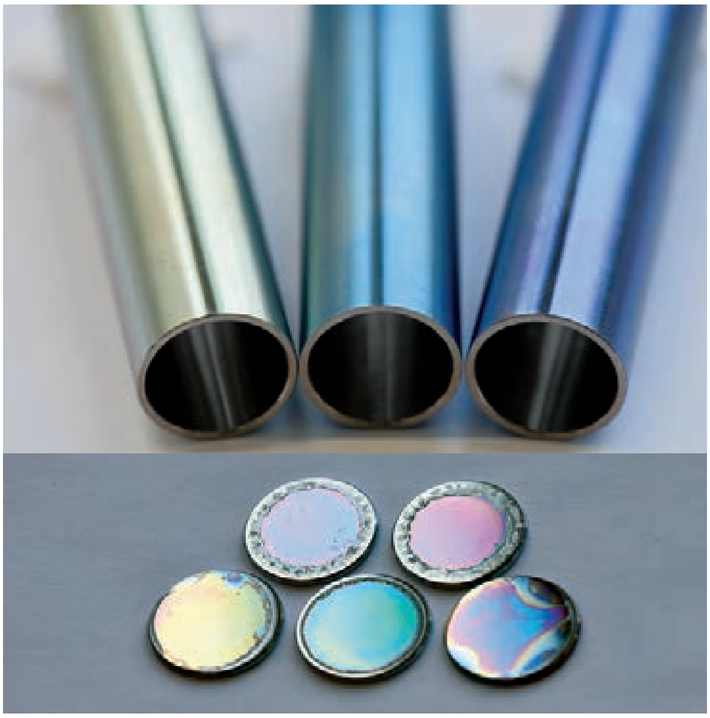


marked. Michler's team succeeded in applying the harmless titanium oxide coatings to stainless steel screws as well. The medtech company DePuy Synthes is already marketing the screws. Advantage for the manufacturer: the electroplated marking of the screws is about 50-times cheaper than a coloured marking produced by the previous sputtering method.

Aluminum – a hard nut to crack

In the case of aluminum, electroplating is extremely tricky because in air, a thin oxide coating that prevents other reactions forms on the lightweight metal. Empa researcher Laetitia Philippe succeeded in circumventing this problem. Here too, it was a case of systematic analysis and fine tuning, not stabbing in the dark until it worked. The nanostructures of the adhesive coating were analysed using scanning electron microscopes (SEM), five of which are available in Thun. Laetitia Philippe now has sufficient data to be able to assess the quality of the coating on the basis of the current density alone.

Stainless steel without the furnace

Christoph Niederberger, who is also an electroplating expert, has recently started his own business. His company Eleoss is in the same building as Empa, and provides small, high-precision stainless steel components manufactured by electroplating. The stainless steel, which is an alloy consisting of iron, chromium and nickel, was separated from a saline solution. A special combination of complex-forming agents in the solution forces the metal ions to arrange themselves as though the metal originated from a molten mass.

Here too, the analysis technology at Empa was crucial for success. The researchers used Glow Discharge Optical Emission Spectroscopy (GDOES) to check the chemical composition of the electroplated stainless steel coatings. Pictures taken under the transmission electron microscope (TEM) and in the SEM have provided information about the grain size. X-ray diffraction (XRD) provided information about the crystal structure of the steel, and also about the density and any defects. The micro-gears produced in this way are now going to be used in the Swiss watch industry.

Basic solar cell research

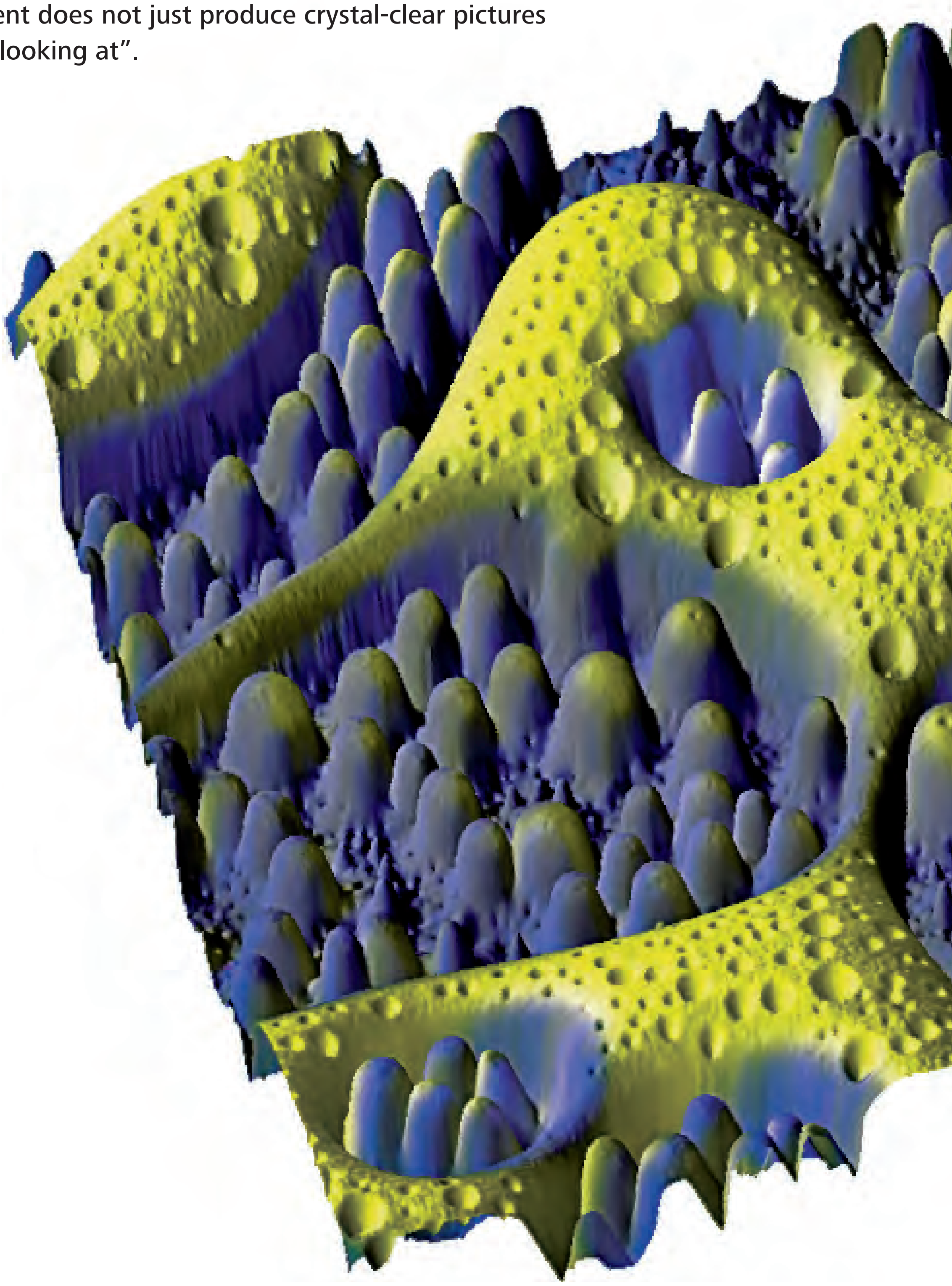
Although Empa's know-how is already being applied to practical production matters, basic research projects also abound. These deal with the problems of tomorrow, such as providing energy from renewable sources.

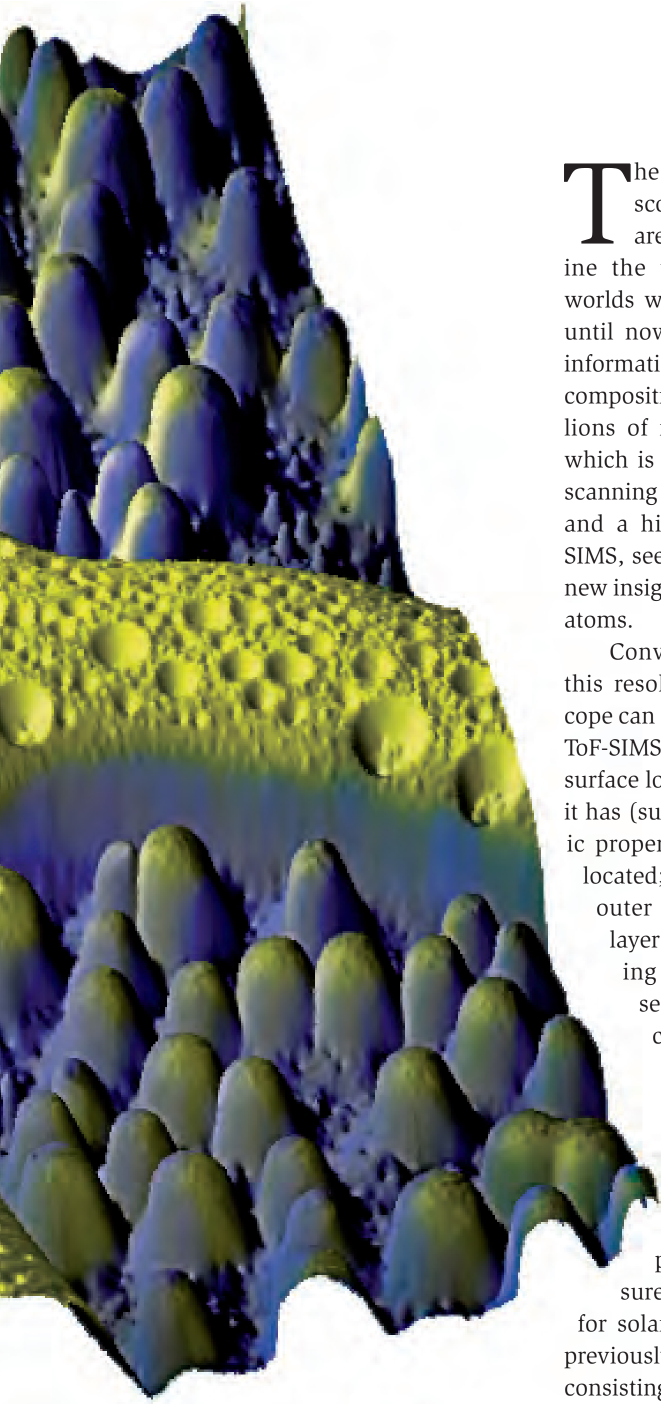
Laetitia Philippe's team is investigating the galvanic separation of semiconductor materials such as silicon or zinc oxide on metal foil. This could make the manufacture of solar cells much cheaper in future, because much cheaper electroplating methods could be used to manufacture the cells rather than the expensive vacuum-based sputtering method. High-tech materials are hence manufactured using a procedure that is hundreds of years old and that can be deployed by any medium-sized company. //

The not-so-odd couple

The 3-D NanoChemiscope is a posterchild for modern-day analytical technology. As an ingenious combination of known microscopy techniques, it depicts material surfaces with nanometer precision, i.e. down to the level of individual molecules and atoms. But it doesn't stop there: it also examines the chemical composition of the sample. The one-of-a-kind instrument does not just produce crystal-clear pictures but also knows what it is "looking at".

TEXT: Martina Peter / PICTURES: Empa





A typical image from the 3-D NanoChemiscope showing the atomic structure of a surface: the instrument provides information about the chemical composition of the upper layers.

The newly-developed 3-D NanoChemiscope and the "Curiosity" Mars rover are similar in many ways. Both examine the topography and composition of worlds we knew very little about - at least until now. Whereas "Curiosity" transmits information about the surface condition and composition of the rocks on Mars over millions of miles, the 3-D NanoChemiscope, which is the world's first combination of a scanning force microscope (SFM, see box), and a high-end mass spectrometer (ToF-SIMS, see box) provides us with completely new insights into the world of molecules and atoms.

Conventional SFMs can also achieve this resolution, but the 3-D NanoChemiscope can do much more thanks to its built-in ToF-SIMS. Not only does it show what the surface looks like, which physical properties it has (such as special magnetic or electronic properties) and where exactly they are located; it also shows which molecules the outer layer consists of. And since one layer after another can be removed using the high-energy ion beam, researchers can create a kind of chemical depth profile of the sample. This results in a three-dimensional representation of the sample at molecular level.

Among other things, this knowledge allows the researchers to anticipate chemical processes and design made-to-measure surfaces and interfaces, such as for solar cells. Whereas developers could previously only detect a multi-layer system consisting of many different polymers on a surface, with the 3-D NanoChemiscope they can now locate each single molecule, one at a time, and identify which polymers are lying on top of each other and how they are arranged (flat or in droplet form).

Collaboration – from idea to product

It is no coincidence that a significant proportion of the device was built at Empa. The driving force behind the development of the 3-D NanoChemiscope has been Hans Josef Hug, the head of the "Nanoscale Materials Science" laboratory and professor of physics at the University of Basel. Together with his co-workers, he has already developed countless scanning force microscopes and introduced many of them to the market. He finds combining different analytical methods particularly appealing: For example, in collaboration with the Paul Scherrer Institute (PSI) he developed "NanoXAS", a microscope, with which samples can be analyzed using X-ray absorption and scanning probe microscopy simultaneously.

Hug's colleague, physicist Laetitia Bernard, took over the job of managing the 3-D NanoChemiscope project at Empa in 2008. The project, which was funded by the 7th EU framework programme, was coordinated by German industry partner ION-TOF GmbH, which also provided the know-how for the mass spectrometer.

"If you wanted to examine both the chemical and physical properties of surfaces, there was no other way but to carry the sample across the corridor from one instrument to the other", explains Laetitia Bernard. Firstly, the SFM scans the topography of the sample using a fine tip, then it has to be taken to the ToF-SIMS, which determines the chemical composition of the solid surface's uppermost monomolecular layer. "We were faced with two types of problems", says the physicist. "On the one hand, the sample could oxidize or be contaminated. On the other hand, it was practically impossible to find the exact spot that had been examined by the SFM."

It was obvious that the two devices needed to be combined. However: "At first

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glance this seemed impossible. Many colleagues had their doubts", recalls Laetitia Bernard. There were too many differences between the SFM and the ToF-SIMS. With the SFM the sample and the scanning tip are in a chamber with dampers that suppress any unwanted vibration. In the ToF-SIMS, however, everything is arranged around the sample (the cannons for the ion beams, the cameras etc.). "From a geometrical point of view, we quickly reached our limits. It was simply impossible to measure the sample using both methods simultaneously."

The scientists then tried another approach: it should be possible to position the two devices as close as possible to each other in an ultra-high vacuum chamber and equip them with a reliable transport system that carefully moves the sample between SFM and ToF-SIMS.

Plans for countless parts

Just the job for Sasa Vrankovic. The experienced mechanical engineer who had already constructed numerous microscopes for the nanoworld in Hug's team collaborated with the ToF-SIMS specialists to produce geometrically feasible designs on the computer using a joystick and a CAD program. He assembled thousands of parts on screen and specified how component after component was to be manufactured in the Empa workshop and then assembled in the laboratory.

On several occasions, Vrankovic and Bernard were confronted by major difficulties. The current method of transport, whereby the sample is transported using an electric motor, proved to be unsuitable. In a system that rests on ball bearings, there is always sufficient play for the sample to move by a tiny amount on its 23 cm route between the SFM and the ToF-SIMS.

For this reason, the scientists decided on a piezo-electric motor developed by ION-TOF. "It pushes the sample holder forwards jerkily like a carriage on rails", explains Vrankovic, "but without jerking the sample, which is the special feature". In order to do this, a voltage is applied to a piezo-electric material that expands. If the current is turned off, the material contracts again. The movement is leisurely, and the sample holder glides gently as though it were on skids. Until the sample reaches its destination.

Tool change in vacuum

The high-vacuum was a particular challenge - pressure of just 10^{-10} mbar, in which the 3-D NanoChemiscope is operated. The water film on the rails that acts as lubricant simply evaporates in vacuum. According to Vrankovic, it can also be tricky if the scanning tip is damaged during a measurement and has to be replaced. The team therefore quickly built a moving gripper into the SFM. The spare tips can now easily be replaced without having to ventilate the vacuum system.

With regard to the mobility of the sample in the ToF-SIMS flexibility was also a top-requirement. The sample had to be accessible from all sides: move to and fro, up and down, rotate and tilt, i.e. move along five axes. How could a scanning image with a molecular resolution and with with as little interference as possible be generated with so much freedom of movement? "We turned everything on its head", says Laetitia Bernard. They did not move the sample underneath the tip in the customary way, but moved the tip past the sample, which had now been fixed. With this highly complex solution the Empa team went far beyond the original approach. The team did not just develop and deliver a proof of concept, but a complete prototype.

Gliding on diamond layers

At the same time, the scientists kept an eye on the costs and looked for solutions that were as cost-effective as possible. In order to avoid using well-proven, but expensive aluminum oxide sapphire rails, they developed their own new type of rail with a coating made from diamond-like carbon (DLC). This has just the right friction coefficient for making the sample glide gently from one measuring point to the other in 40 seconds. The ToF-SIMS itself was also improved considerably by ION-TOF during the project, namely the focus of the ion beam. The ToF-SIMS was equipped with a pair of glasses, so to speak, with which it still sees less clearly than the SFM, but way better than before.

In January 2013, the four-year project came to an end. The prototype of the 3-D NanoChemiscope, a chromium steel monstrosity 1 meter in length, 70 centimeters wide and 1 meter 70 high, has since been in use at ION-TOF in Münster, Germany, for industrial customers and research partners. The construction of extra devices is in the pipeline: customers are extremely interested, and are prepared to pay a seven-digit amount in Swiss francs for the privilege. //

How a Scanning Force Microscope works...

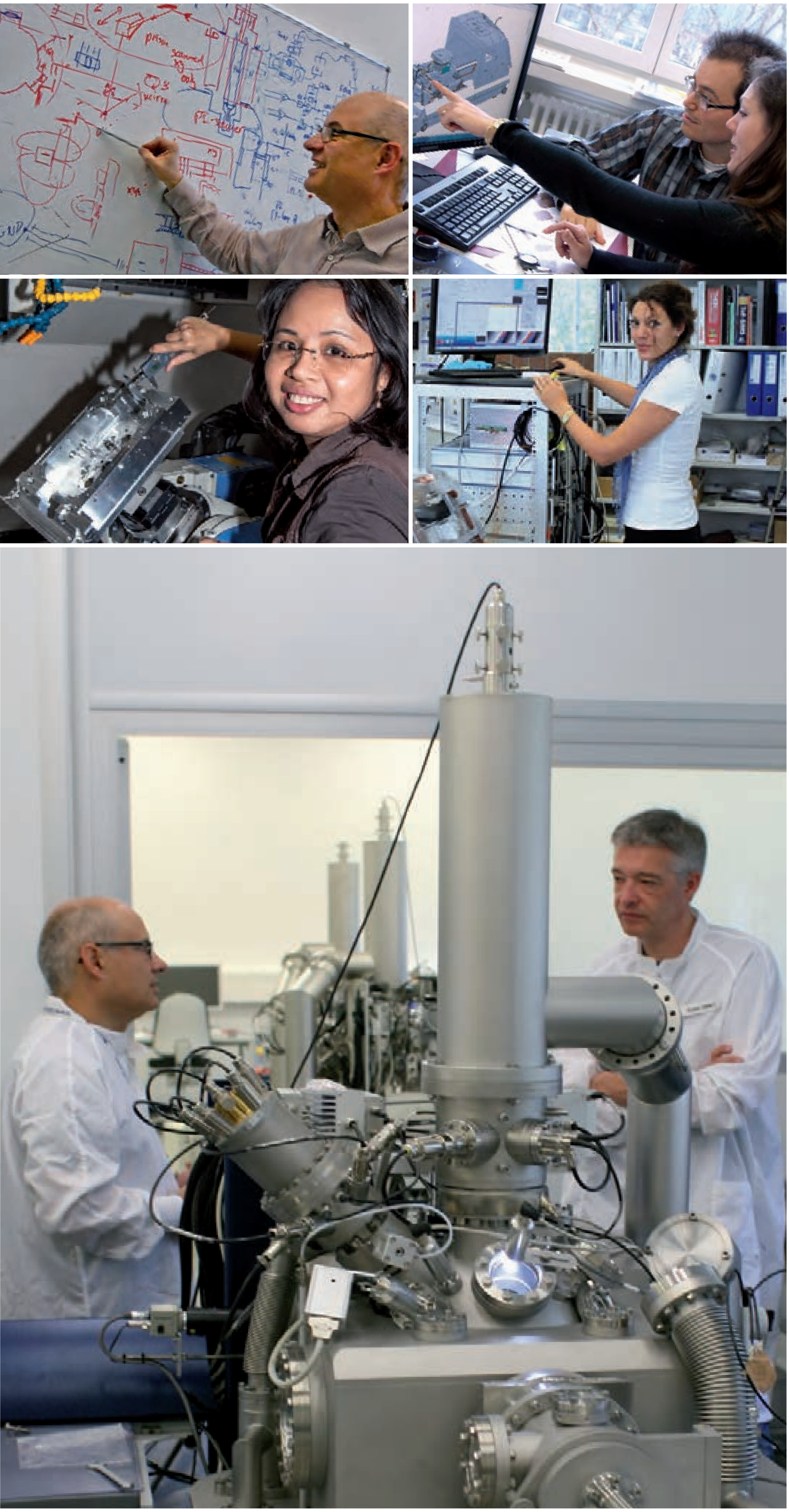
The Scanning Force Microscope (SFM, also known as the Atomic Force Microscope AFM) is not a classical microscope with an optical lens. The surface structures down to the sub-nanometer range are depicted by scanning the topography using a tiny cantilever The force that occurs between the tip at the end of the cantilever, which is only several atoms thick, and the sample that is being examined can be measured and recorded. Depending on the setting of the SFM, statements can be made about many different physical characteristics of the sample. Not only can the topography thereof be measured, the measurements also provide information about the hardness, elasticity and friction characteristics of the material and determine the electrostatic, magnetic and (piezo-)electrical force that is characteristic of the material.

... and a ToF-SIMS

So-called "Time-of-Flight Secondary Ion Mass Spectrometry" (ToF-SIMS) provides information about the molecular or elementary composition of the outer layer of a solid surface. Molecules and other fragments are "sputtered" from the outer layer and ionised by bombarding the surface with an high-energy ion beam. The chemical constituents can be analyzed in the form of ionised gases in a mass spectrometer.

The 3-D NanoChemiscope

The project was under the leadership of German company ION-TOF GmbH in collaboration with Empa, NanoScan, the Université Catholique de Louvain (UCL), Belgium, the University of Namur (FUNDP), Belgium, the Institute of Scientific Instruments (ISI), Czech Republic, the Holst Centre, Netherlands, and the Technical University of Vienna, Austria. More information under *www.3dnanochemiscope.eu*



The development of the 3-D NanoChemiscope at Empa – from initial sketch (top left) to CAD phase to completion. Hans Josef Hug, head of the "Nanoscale Materials Science" laboratory at Empa and Rudolf Möllers, project leader from industrial partner ION-TOF, in discussions during system integration of the instrument in Münster.

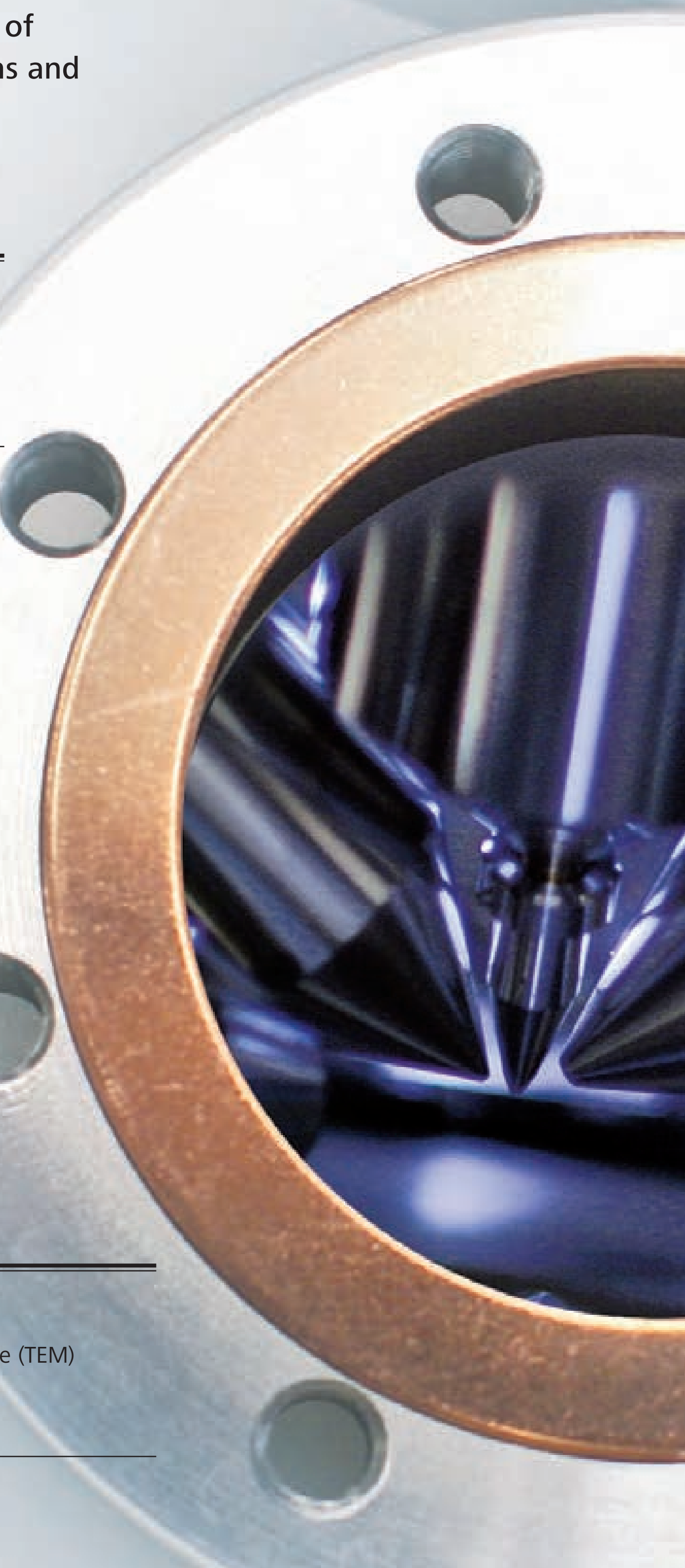
Empa's workshop

All individual components of the 3-D NanoChemiscope were manufactured in the Empa workshop – from millimeter-long screws to the 4-kilogram guide carriage. Many of the components have a lot to offer: micrometer-accurate machining of tough, hard materials and some extremely complex parts was a real challenge, even for the workshop professionals. All manufacturing had to be painstakingly prepared and every design plan checked before the components could be milled, eroded, hardened, ground and polished.

The Empa workshop has access to a comprehensive machine pool. A wire eroding machine was recently added. This can be used to machine extremely hard, tough metal to an accuracy of 3-5 micrometers.

Materials in the crosshairs

Empa researchers analyse surfaces and chemical structure of their creations using a variety of analytical methods. Atoms and their molecular surroundings have nothing else to hide.



Scanning Tunneling Microscopy STM

A fine, conducting tip is held above the surface to be examined. The electric current between top and surface is measured.

Individual atoms and electronic structure

Atomic Force Microscope AFM

A thin tip scans the sample. The attractive or repulsive force between tip and surface is measured. (This method works on insulators, too.)

Individual toms and material properties of the surface

Electron microscope

The sample is "illuminated" with an electron beam. Similar to an optical microscope, the beam shines through thin layers (Transmission Electron Microscopy, TEM); thicker samples are illuminated at the surface. (Scanning Electron Microscopy, SEM)

Structure of the material down to individual atoms

Electron tomography

Up to 150 single pictures of a transmission electron microscope (TEM) are matched via computer and form a 3-d-picture.

3-D-information on the material structure (p. 16)

3-D-Nanochemiscope

An AFM connected to a secondary ion mass spectrometer (SIMS) in a single unit

Topography of the surface combined with info on the chemistry – localized down to 100 nm

Photoemission spectroscopy XPS

The sample is treated with X-rays of different wavelength. The energy of the electrons, which are emitted, provides information

Chemistry of the surface

Glow Discharge Optical Emission Spectroscopy GDOES

The sample is bombarded with argon ions and removed in layers. The colour spectrum of the plasma, which is generated, provides information. Removed layers are subsequently analysed in a mass spectrometer

Chemistry in individual surface layers

Scanning Helium Ion Microscope SHIM

A new imaging technology based on a scanning helium ion beam. Better resolution than traditional SEM's.

High res images with topographic, material, crystallographic, and electrical properties of the sample

Nano-Indenter

A fine tip punches a hole in the material or scratches it

Hardness and strength at different temperatures

AFM + SEM

A thin tip scans the sample (Atomic Force Microscopy, AFM); in the same device the sample is illuminated with an elecron beam (SEM)

Topography of the surface and structure of the material

FIB-SIMS

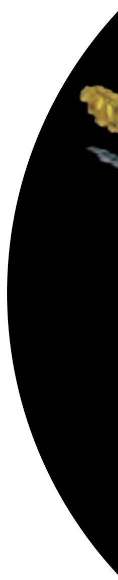
A beam of ions planes off atomic layers of the sample (Focused Ion Beam, FIB): The ions are analysed in the secondary ion mass spectrometer (SIMS)

Chemical information about surface and deeper layers in 3-D

Nanoparticles in 3-D

What do nanoparticles look like? It's not about aesthetics: special properties often depend on the spatial structure of a particle. Using a new method Empa scientists can take 3-D snapshots of tiny particles.

TEXT: Anna Ettlin / PICTURES: Empa



Nanoparticles are playing an increasingly important role in research and industry. Be it cosmetics or medicine, food or modern electronics – nanoparticles have huge potential. However, their small size, which gives the particles their amazing properties, is also the biggest challenge when they are being investigated. Nanostructures can be made visible with high-resolution electron microscopes; however, this results in a two-dimensional projection of the object. Such a flat representation is not particularly informative for nanoparticles, whose properties depend on their three-dimensional structure. This is why Rolf Erni, head of Empa's "Centre for Electron Microscopy", and his team have have been using a new method for the last year and a half: electron tomography.

Nanoparticles "X-rayed"

Similar to conventional X-ray tomography, electron tomography creates a 3-D image of the scanned object – within the nano range. In order to do this, the sample is scanned and X-rayed in a scanning transmission electron microscope (STEM) using an electron beam. Detectors beneath the sample register the number of electrons that have been scattered. This data produces a so-called darkfield image, an image in which the areas with the highest density look brighter – similarly to an X-ray image. In order to produce a 3-D representation, the sample is gradually rotated by one or two degrees around a total angle range of about 150 degrees in order to produce several darkfield images of the sample. This results in up to 150 images, which are combined to produce the spatial structure of the object using complex computer algorithms.

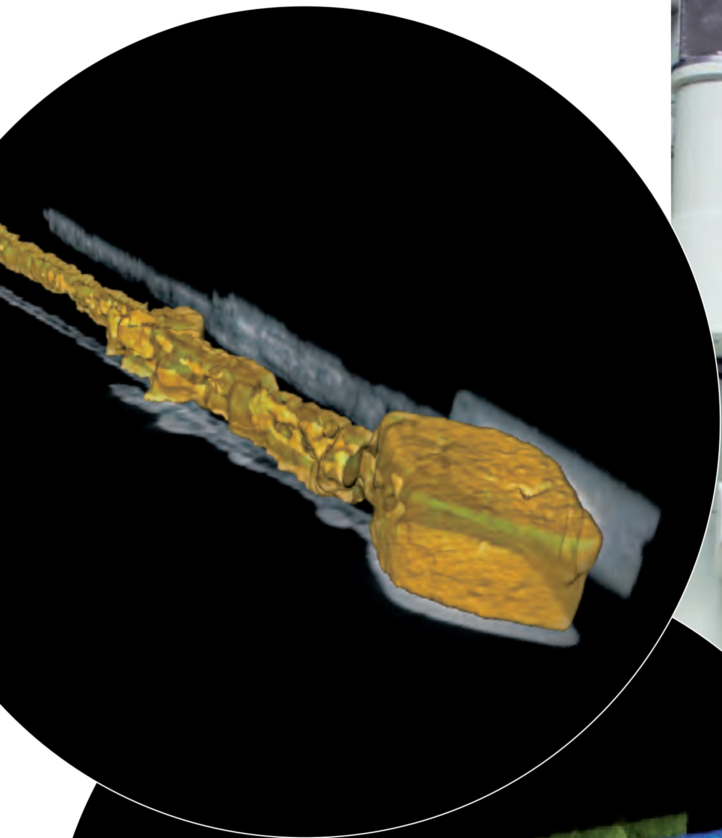
Although the technology has been available for several years, its implementation at Empa was anything but "plug-and-play". The hardware requirements were fulfilled; all that Empa had to do was equip the large STEM with a special sample holder. The software, however, was a different story: on the one hand, the program had to process tremendous amounts of data and combine 150 individual images into a realistic spatial image. And in order to be able to correctly interpret the tomogram, the researchers need a tremendous amount of know-how and experience.

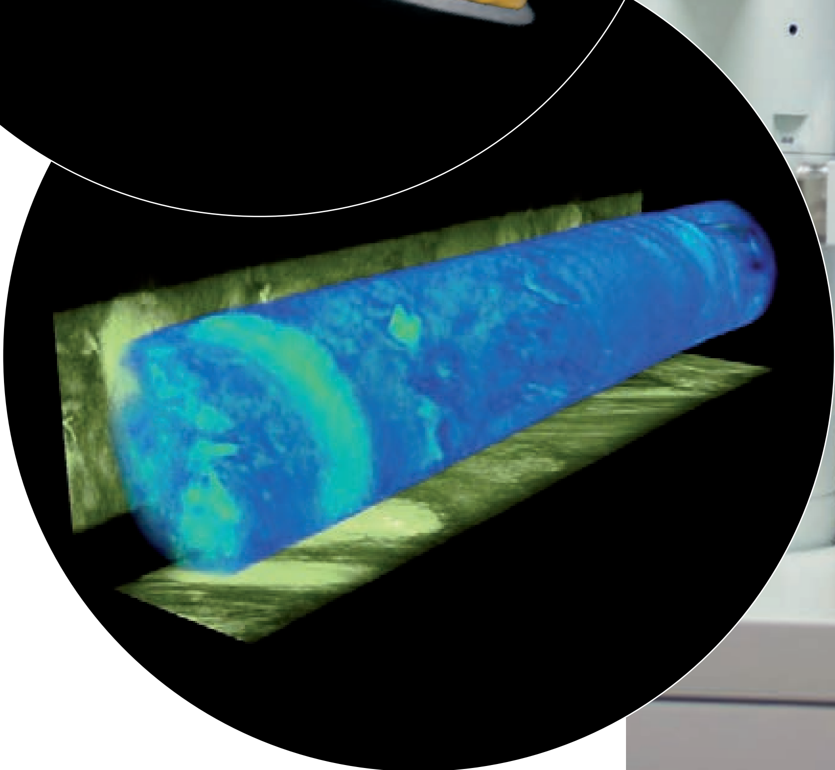
What holds the world together at its core

The preparation of man and machine has taken two years. But the obstacles have now been overcome. For the past year, Erni's team has been able to create cross sections and 3-D structures of individual nanoparticles and therefore throw some light on the inner workings of the minute particles.

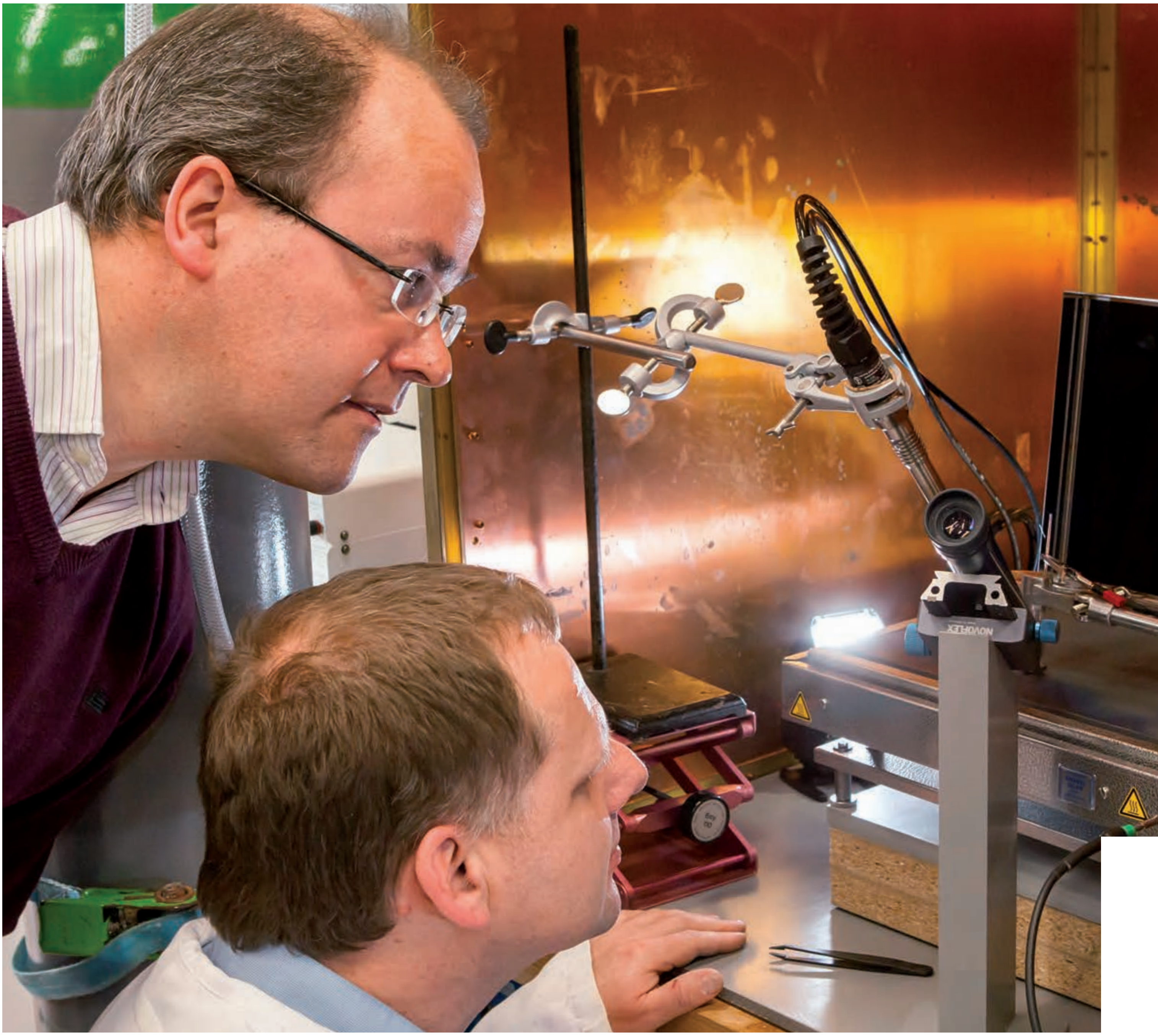
However, electron tomography is not perfect. It is not possible to X-ray the sample from every angle, and the high-energy electron beam damages radiosensitive materials. Nevertheless, the benefits of the method are undisputed. Researchers can now see whether the interior of a certain nanoparticle has a different chemical composition from its surface. This knowledge could help to design future batteries for hybrid vehicles, for example.

Electron tomography also plays a role in the disposal of radioactive waste from nuclear power plants that are still in operation: in collaboration with the University of Zurich for Applied Sciences (ZHAW) Empa scientists investigated the ultra-fine pore structure of the Opalinus clay, a candidate for the barrier layer in nuclear waste repositories. //





Rolf Erni working with the scanning transmission electron microscope: the individual images are put together electronically. Top: 3-D view of the type of lithium iron phosphate particle that occurs in lithium-ion batteries. Bottom: Opalinus clay, a potential barrier material for nuclear waste.

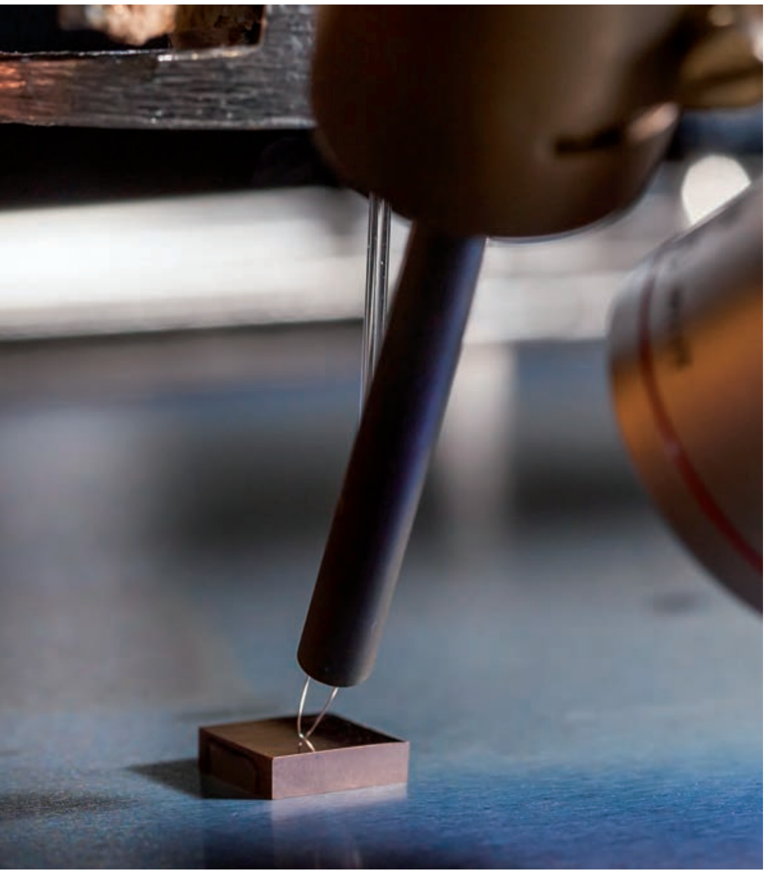


Understanding boundaries

Lars Jeurgens has been the head of the new "Joining Technology and Corrosion" laboratory since February 2012. Among other things, his team deals with solder connections, corrosion, local electrochemistry and the design of functional alloys, surfaces and boundary layers. Jeurgens originally became involved in this science because of his fascination with rocks.

TEXT: Marco Peter / PICTURES: Empa

Lars Jeurgens and his colleague Thomas Suter check a new test set-up: A sample with 200 overlaid nanolayers is heated to 700 degrees. As soon as molten copper penetrates through the barrier layers, an extremely weak current flows. In order to rule out electrical interference, the entire test set-up is shielded with sheets of copper.



As a teenager, Lars Jeurgens was fascinated with minerals and fossils. He looked after and cared for his collection with enthusiasm. It was this passion that influenced him to make the decision to study geology in Utrecht. He quickly noticed that geologists (at the time) were also concerned with matters concerning materials science. For example, one goal was to discover how heavy metals got into the atmosphere and what effect they had there. This topic caught Jeurgens's interest. He focused his attention on how chromium and tungsten could be filtered out of the environment, rivers, for instance, and experimented with porous oxides for binding the dissolved metals in water, therefore making an initial excursion into the chemistry of boundary layers.

From drill holes to turbine blades

After completing his master's degree, the 23-years-old changed track and applied his knowledge in physics and chemistry to his job working for mineral oil company Shell. During his work in the laboratory, he had used nuclear magnetic resonance spectroscopy (NMR) to investigate pore fluids in oil-bearing rocks. The method can also be used to analyze the oil content of undersea rock layers. This kind of research was "extremely interesting" in Jeurgens's words, though, without a doctorate, he could not continue to pursue it as project leader.

After working for Shell for a year he therefore enrolled at Delft Technical University. During his doctorate he studied the initial stages of metal oxidation and, as a postdoc, he looked into heat-resistant coatings for the blades of airplane turbines. Jeurgens was involved

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in the development of a surface treatment that would extend the service life of such a protective coating. Among other things, the scientists collaborated with a Dutch company that was taken over by the Swiss Sulzer Group shortly afterwards. “The partners from the aircraft industry patented our procedure, although it remains a closely-guarded secret as to whether it is actually being used in the field”, explains Jeurgens with his soft Dutch accent, which the Swiss find so agreeable.

In his current position at Empa, Jeurgens is still working with surface treatments and coating technologies. Among other things, his team is now investigating how the implant surfaces can be made more corrosion-resistant and biocompatible using an oxidative pretreatment. Because if an implant made from a material such as stainless steel starts to corrode within the human body it can release iron, chromium or nickel, which, in turn, can lead to complications such as inflammation.

«We published our scientific results, but we scarcely got feedback about what industry was finally doing with that.»

Basic research at the Max Planck Institute

Before Jeurgens joined Empa, he had worked at the Max Planck Institute for Metals Research in Stuttgart for almost ten years. His family – by then, Jeurgens had got married to a Swiss lady whom he had met on the train during a pre-university Interrail trip – moved from Holland to Germany, and the young father of two took on several responsibilities at once. On the one hand, he was responsible for services in the surface analysis area, and on the other hand he led his own research group, which was involved in the analysis of the chemical processes and phenomena on surfaces and in boundary layers. And they were successful: The Deutsche Gesellschaft für Materialkunde (German Society for Materials Science) awarded Jeurgens’s work the Masing Memorial Prize in 2008. He also taught at the University of Stuttgart and the “Max Planck International School for Advanced Materials”.

But the wind of change was starting to blow: Jeurgens wanted to use his knowledge in basic research – as is carried out at the Max Planck Institute – for more practical uses in industry. Because: “We published our results but never really found out what industry really did with it.”

It’s the team that counts

The timing of the job opening at Empa, which was looking for a new laboratory head, was just about perfect. And the job looked extremely interesting, too: The objective was to merge the “Joining Technology” and “Corrosion” laboratories. To Jeurgens, it was an extremely sensible idea: “In both cases, it’s all about reactions in boundary layers.”

The work with boundary layers does not just keep him busy in the lab but also when his leadership capabilities are in demand: “Team mentality is what counts as far as I’m concerned. There are people here in the lab with an unbelievable amount of experience. I am bringing in my own experiences, so now it is a case of combining our accumulated knowledge.” He and his team now frequently work with industry partners and develop innovative solutions for practical use – i.e. in exactly the way he had imagined it during his time at the Max Planck Institute. In cooperation with companies from the medical engineering area they are developing surface treatments for magnesium-based materials for use in biodegradable implants, for example. The keyword here is biocompatibility.

Nano enters joining technology

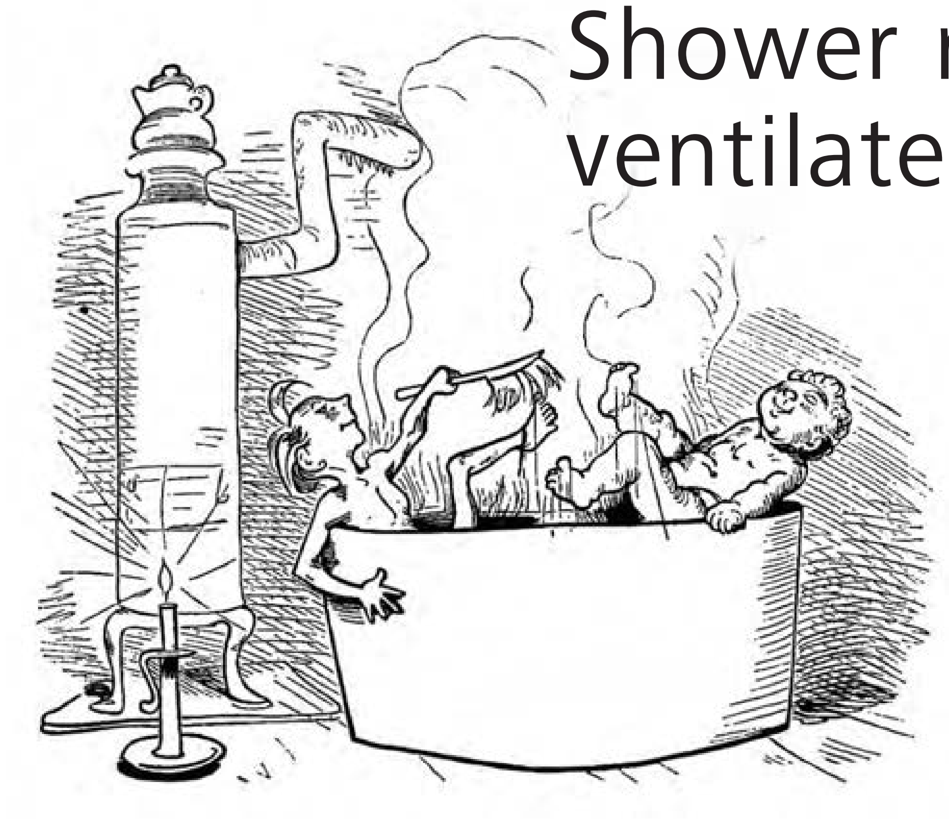
In his work with nanostructured soldering foil for use in joining technology Lars Jeurgens is faced with a major challenge. He wants to develop methods and procedures for soldering nanomaterials or electronic components at low temperatures, among other things.

Materials as heat-sensitive as these do not join well using conventional methods because their microstructures would change at the high process temperatures and they would, therefore, lose some of their advantageous mechanical or physical properties. The trick: Jeurgens coats the heat-sensitive materials with a nanostructured, metallic soldering material. For example, nanocrystalline titanium is provided with a coating system consisting of nanoscale copper and ultra-thin aluminum nitride barriers. The copper layers that are enclosed by aluminum nitride are so thin that they melt at a temperature of about 550 degrees C (rather than the usual 1083 degrees) and join the titanium materials to each other.

The melting behavior is determined by the sensitive equilibrium of the energy contributions of volume and boundary layers in the nanoscale system. This sensitive energy balance and therefore the melting behavior can be adjusted by means of specific changes to the boundary layers and the thickness of the copper coating. This might sound easy, but in practice it is quite challenging. It must also be ensured that the copper maneuvers itself through the thin barrier coatings as required when melting occurs, and does not react with the basic materials. This procedure could soon be used in innovative process technologies for the manufacture of heat-sensitive components and nanomaterials.

Jeurgens is entering new territory with his research in the nanorange. Only a few of the laws that apply when working with nanomaterials are known. The Empa researcher wants to do his part in conquering this unknown terrain of materials science for industry. //

Shower now, ventilate later



Old buildings with new insulated windows often have a problem: too much humidity. The moisture from the kitchen, the bathroom and the bedroom cannot escape; it accumulates at cold walls and mould starts to form. A new moisture buffering plaster developed by Empa and industrial partner Sto can help to solve this problem.

TEXT: Rainer Klose / PICTURES: Empa / DIAGRAM: Wilhelm Busch

The amount of water vapor that is generated in a house or apartment is something that our grandparents were well aware of: the moisture that was produced by boiling potatoes and roasting meat was deposited on the single glazing of grandma's kitchen windows. And when the bathtub was filled, you could hardly see a thing in the bathroom. The window was steamed up, and your privacy was protected.

Nowadays it is difficult to know how damp a house or apartment really is. Efficient, triple-glazed insulated windows hardly ever steam up – therefore giving the impression that all is well. However, the moisture is still there. It comes out of the spaghetti pan, evaporates from your wet winter coat in the wardrobe, billows out of the recently-used shower and spreads out from the bedroom. The married couple has just been sleeping peacefully in there for the last eight hours – but nobody has given a thought to ventilation.

Now the moisture is on the walls, where it can condense. Particularly in locations where a thermal bridge to the outside allows the wall to cool down, local air humidity can increase to more than 80 percent. Such a climate allows fungi and microbes to thrive, and is anything but desirable for living areas.

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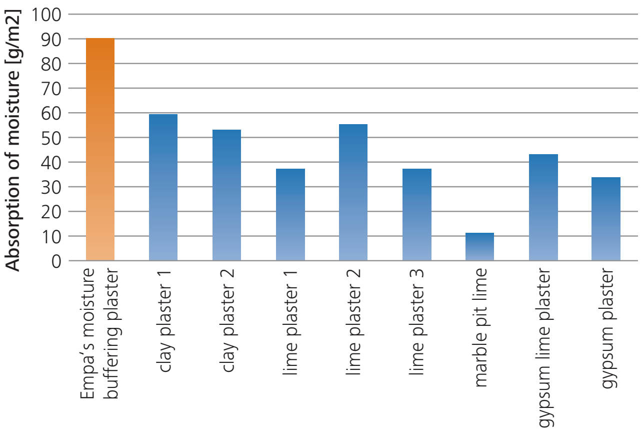
Moisture buffering measurement ("Nordtest")

The Nordtest method was developed by the Technical University of Denmark (DTU) and other universities in order to define a meaningful and uniform value for the moisture buffering behaviour of interior materials. The materials are stored for eight hours at a relative humidity of 75 percent and 23 degrees C. Then the relative humidity is reduced to 33 percent for 16 hours. Subsequently it is increased to 75 percent for eight hours. A scale records how much moisture the material absorbs or gives off. Values such as the "Moisture Buffer Value" (MBV) are measured – an important application-oriented variable. The value is a direct measured variable of the amount of moisture absorbed or given off by a material with the specified load, and is essentially a material property.



Example calculation: Buffering capacity of room air vs. absorptive active material

Room with dimensions of 5 m × 5 m × 2.5 m = 62.5 m^3

- Wall and ceiling areas (4 × (5 m × 2.5 m)) + (5 m × 5 m) = 75 m^2 minus door (2 m^2) and windows (3 m^2) Wall and ceiling areas = 70 m^2
- Material with moisture absorption of 30 g/m^2
- Moisture increase in room air from 40% to 80% relative humidity
- Constant temperature 21 °C

Moisture content of room air at 21 °C and 40% relative humidity = 7.3 g/m^3
Moisture content of room air at 21 °C and 80% relative humidity = 14.7 g/m^3
Difference = 7.4 g/m^3 × 62.5 m^3 = 463 g
Moisture absorption of material is 30 g/m^2 × 70 m^2 = 2100 g
This simplified calculation shows the enormous potential that a planned additional improvement to the moisture absorption characteristics would provide.

Moisture buffering plaster

In many new buildings, and even more renovated buildings, it would help if the humidity could somehow be regulated. If some intelligent material on the wall absorbed the moisture and gave it off again when the room was ventilated... This was the requirement with which Sto AG, a thermal insulation and plaster specialist from Germany, approached Empa. Empa building physicist Thomas Stahl went to work. Then the decision was made not to use special storage panels that would have to be exactly cut to size, but develop a plaster that could also be applied to angled sections of wall without problems. This moisture buffering plaster was developed within the scope of the SuRHiB (Sustainable Renovation of Historical Buildings) research project – an indication that renovated old buildings would particularly benefit from this technology.

Compare and mix

Stahl first obtained various commercial products that were claimed to be particularly good at buffering moisture These were clay plaster, lime plaster, slaked lime plaster and gypsum plaster. All of these reference samples were prepared in accordance with the manufacturer's instructions and tested in the Empa climate chamber and the Sto laboratory. Then Stahl and his partners at Sto started to develop their own mixtures. A plaster with extremely high water absorption capacity and extremely high diffusion openness was required. It needed to be be moisture-regulating, mineral-bound and also easy to process manually or using machinery. And last but not least, the ingredients should not make the plaster overly expensive. Because property developers look after their money.

Building physicist Thomas Stahl with moisture buffering plaster: humidity occurs wherever people sleep, cook and shower, and it can condense on cold sections of the wall. The Empa invention can prevent this.

Eventually, Stahl and the Sto laboratory found a hydraulic bonding material and lime hydrate-based mixture that they optimised in several series of tests. The results of the final testing were surprising. The newly-developed moisture buffering plaster system exceeded the original requirements by far, and had moisture absorption that was one-third better than even the best clay plaster. The storage effect and the moisture that is given off when the humidity in the room drops is three times better than that of normal lime plaster. It was even nine times better than the worst comparison product.

The moisture buffering plaster system consists of several products with brand names such as StoLevell Calce RP, StoLevell Calce FS and Calcelith, and will gradually come onto the market from the 3rd quarter of 2013. An application thickness of one to two centimeters is required for the desired effect, since the exchange of moisture takes place most efficiently in the uppermost layers. The finishing plasters that have been specially developed and coordinated for the system ensure that the moisture absorption capacity of the base plater is not adversely affected. According to Thomas Stahl it is very important for the plaster to be painted over with a suitable, moisture-permeable paint. "Using oil-based paint negates the effect".

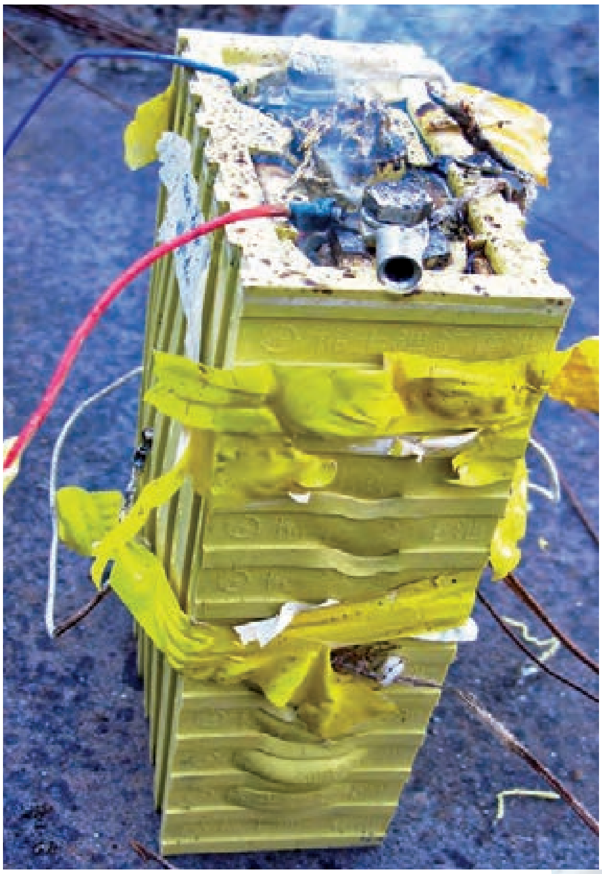
Feel good and save energy

As well as what is probably the most important financial advantage – mould prevention – the use of moisture buffering plaster also improves the well-being of the inhabitants. Lower humidity fluctuations are easier on human beings and furnishings, and have also been proven to improve intellectual performance. Dryer air also requires less heating to bring it to a comfortable temperature. This saves energy in the long term. The moisture buffering plaster can collect humidity to a certain extent, and reduces the risk of condensation forming on cool sections of the wall. Large humidity fluctuations can also affect cultural objects in museums and churches. "Just think about the way a church is generally used", says Stahl. "From Monday to Saturday it is cold and empty. On Saturday evening it is heated for the Sunday service – the humidity drops. On Sunday a hundred people in wet winter coats and snow on their shoes gather in the church. Moisture builds up. A few hours later the church has cooled down again." Fluctuations like these are ta nightmare for wooden altars, statues and pictures, and works of art age prematurely.

High-performance moisture-buffering plasters could be of help in these cases. The moisture buffering plaster developed by Empa and Sto absorbs 90 grams of water vapor per square meter in the "Nordtest" (see box). A plastered section of wall in the church 100 square meters in size could therefore absorb nine liters of water vapor and therefore effectively put increasing room humidity into intermediate storage.

Regeneration required

Since the plaster will eventually become completely saturated like a sponge, it must be given the opportunity to regenerate itself. Ventilation with drier fresh air will do the job. It is also possible to fill the room with fresh air and heat it up. The moisture buffering plaster would regenerate itself and be ready for the next moisture onslaught. //



This is what a lithium iron phosphate battery looks like after is has been pierced by a nail. The internal short-circuit makes the battery heat up. Gas escapes from the top; the casing becomes soft and bulges in several places. But the battery does not burn.

"Super-storage" or fire hazard?

Lithium-ion batteries are becoming increasingly popular due to their compact design and high energy density. But are they also reliable and safe? Do they last long enough, and are they worth the money? Empa researchers put individual cells to the test, and analyze the effects of failure and ageing. A unique protective container has been installed for large batteries.

TEXT: Rainer Klose / PICTURES: Empa

Quiz question: what do a Boeing Dreamliner and a Kyburz DXP (the electric three-wheeler used by the Swiss post) have in common? Answer: lithium-ion batteries beneath the seat. These two very different forms of transport therefore also have a common problem: the batteries can catch fire.

This begs the question of how dangerous our everyday life threatens to become if the rapid spread of powerful energy storage continues – in cars, laptops, mobile phones, airliners weighing several tons and childrens' toys. What happens if these batteries are incorrectly charged or physically damaged? And how long will they last?

Mysterious spontaneous combustions

Marcel Held looks after the newly established battery testing station at Empa, and systematically devotes himself to these matters - either within the scope of research projects or on behalf of customers from industry. Boeing hasn't called yet, but Swiss vehicle manufacturer Kyburz did. They had a serious problem: one of the DXP post three-wheelers caught fire overnight. Almost 2000 were in use in Switzerland at the time of the accident, and 1000 more were on order. The post in Germany, France, Norway, Liechtenstein and Luxembourg use the DXP, and evaluations are in progress in Belgium, Sweden, Denmark and Slovenia. If the DXP were to go up in flames at night, the entire vehicle fleet would be at risk. If this kind of risk existed, major clients would bail out and the business would collapse in one fell swoop.

As you can imagine, a certain amount of pressure was on to succeed with this investigation. Held and his colleagues started to examine the lithium-ion batteries installed in the Kyburz DXP and carried out several tests. A cell was fully charged, then charged for an additional five hours with a 10 ampère current; a cell was charged, then pierced with a nail to provoke an internal short circuit; and an entire battery pack (8 cells connected in series) in the DXP was charged and one of the cells was pierced with a nail.

Pierced battery did not start the fire

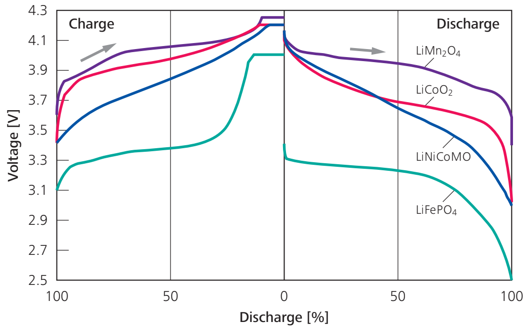
The reaction of the batteries to the first two tests was relatively harmless. The lithium-ion battery heated up to about 85 degrees C when it was overcharged at 10A, but remained externally intact. The "thermal runaway" did not occur until charging continued at 20A: the internals of the battery melted and hot, potentially hazardous gas at a temperature of 300 degrees came out of a hole in the casing. However, neither a fire nor an explosion occurred. The cells reacted in exactly the same way when they were pierced with a nail, causing an internal short circuit. Heating started immediately, and gas was emitted. But the battery still refused to ignite.

However, a fire did eventually start in the vehicle itself, a Kyburz DXP that was sacrificed for the testing. Even after an attempt to extinguish it, the fire re-ignited. Held discovered that the battery management system was to blame. These electronics are installed in the form of open printed circuit boards between the cells and are protected by a plastic cover. When one of the battery cells experiences a "thermal runaway", the hot gas cannot escape. The electronics beneath the cover, which are still live, start to smoulder. Sparks are generated; the escaping gas ignites, and after about 12 minutes the three-wheeler was up in flames.

The solution: silicon "implants"

The Empa team suggested encapsulating the electronics in silicone as a way of preventing sparking. An additional test confirmed the effectiveness of the idea. As a result, Kyburz converted almost 2000 vehicles within one month. Since then, there have been no more fires. What's more, the postmen no longer need to worry about the consequences of battery damage in the event of traffic accidents. //

Battery testing in the container



Comparison of the charging cycles of different lithium-ion batteries.

Extreme testing that destroys the battery can be carried out, but remains the exception during investigations. The output and cycle stability of lithium-ion batteries is far more interesting for industry and research. Improved charging algorithms that are adapted to the intended purpose of use, the age and the ambient conditions are important for making better use the potential of the storage technology and also being on the safe side.

Cell tester

Empa's "Electronics / Metrology / Reliability" laboratory has been working with a 6-channel cell tester made by Maccor since August 2012. This can be used to test and measure individual cells with a voltage of up to 5 V and an amperage of 300 A. The cells are in explosion-proof chambers the size of an oven during this testing. The testing takes place in a nitrogen atmosphere, if necessary. Temperature profiles of -40 to +180 degrees C can be used.

Empa scientist Marcel Held surveys the battery tester.

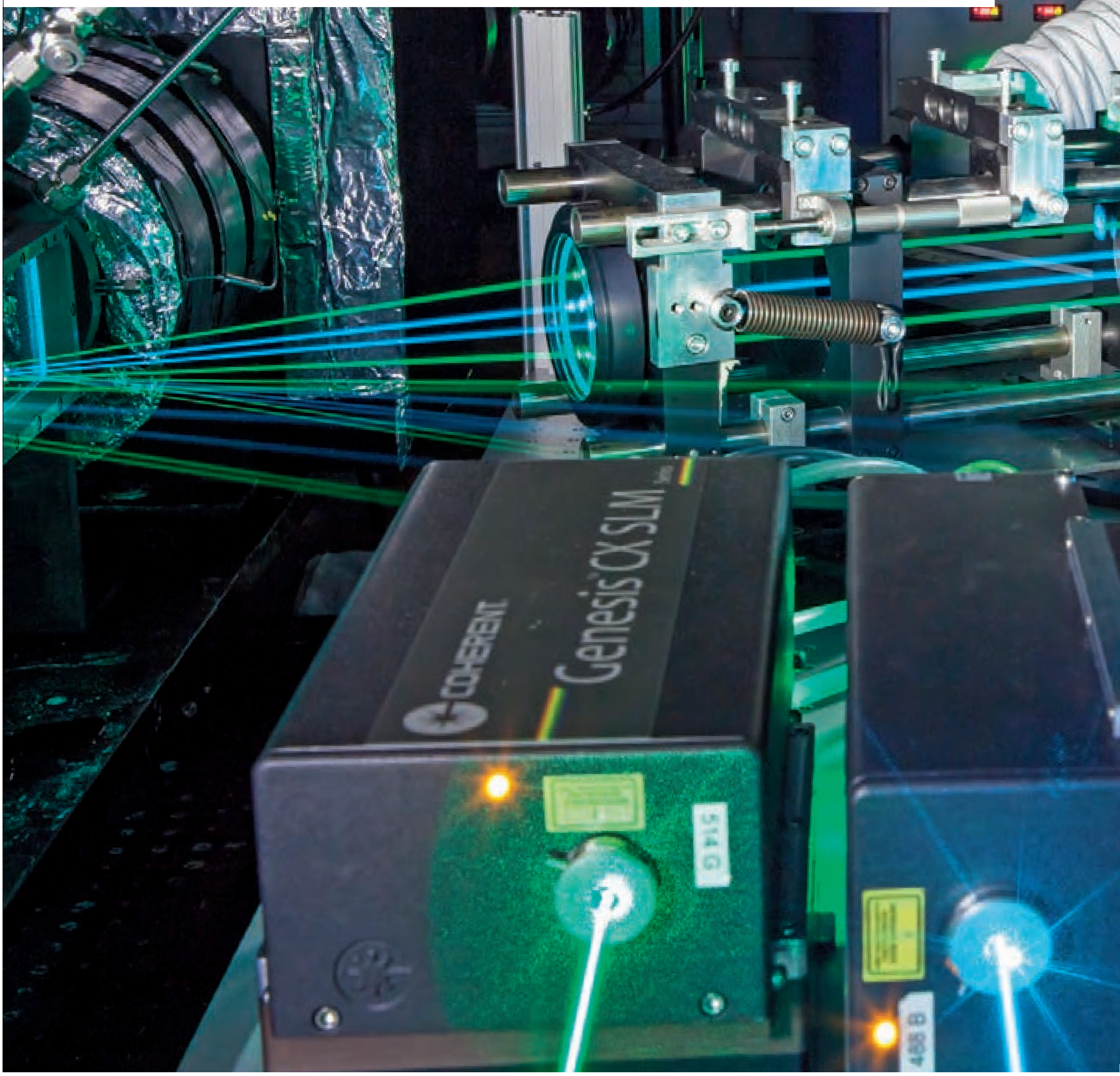
Battery tester

The battery tester is the "Big Brother" of the cell tester, and is unique in Switzerland. This is where interconnected battery blocks (such as the ones from electric cars) with voltage of up to 500 V and amperage of up to 1000 A can be characterized and tested. This tester is placed in a refrigerated container in an outdoor area at Empa because of the increased safety risk. A nitrogen atmosphere provides protection from fires if necessary; the battery can also be buried in quartz sand by an automatic sand tipper. The test is monitored by cameras and gas, temperature and flame detectors.

2,500 drops per second – each one measured individually

Alexander Spiteri is measuring a liquid spray in the Empa emissions laboratory using a phase Doppler anemometer. The measurement is part of a research project on a simulated exhaust system in a diesel truck or city bus (see EmpaNews No. 36, p. 6). Urea solution (commercial name: Adblue) is injected into the exhaust in order to eliminate carcinogenic nitrous oxide. Empa researcher Spiteri studies how the amount of nitrous oxide can be optimized in relation to the relevant engine load and exhaust temperature. Because: if insufficient Adblue is sprayed in, nitrous oxide will remain in the exhaust. If too much is added the exhaust will contain ammonia, resulting in a pungent smell emanating from the rear of the vehicle.

The phase Doppler anemometer splits each beam of a pair of diode lasers into two beam paths. These four laser beams are then focused on a point, where they form an interference pattern. Spiteri can measure 10,000 spray droplets passing through the measuring zone within four seconds using this pattern. The phase Doppler anemometer detects the speed, size and direction of each individual droplet – with a 99 percent hit ratio. It is hard to imagine how a spraying procedure could be analysed with greater precision.

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10. Juni 2013

Wissenschaftsapéro
Blasinstrumente – Auf der Suche nach den Klängen des 19. Jahrhunderts
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17. Juni 2013

Intelligente Materialien – Unsere neuen Helfer im Alltag
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20. Juni 2013

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