EmpaQuarterly

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Exhaust gas – a closer look

Optoelectronics made from dye droplets

Portait: Eco scientist Patrick Wäger

Textile membranes for heart pumps

Empa
Materials Science and Technology

MICHAEL HAGMANN Head of Communications

Dear readers

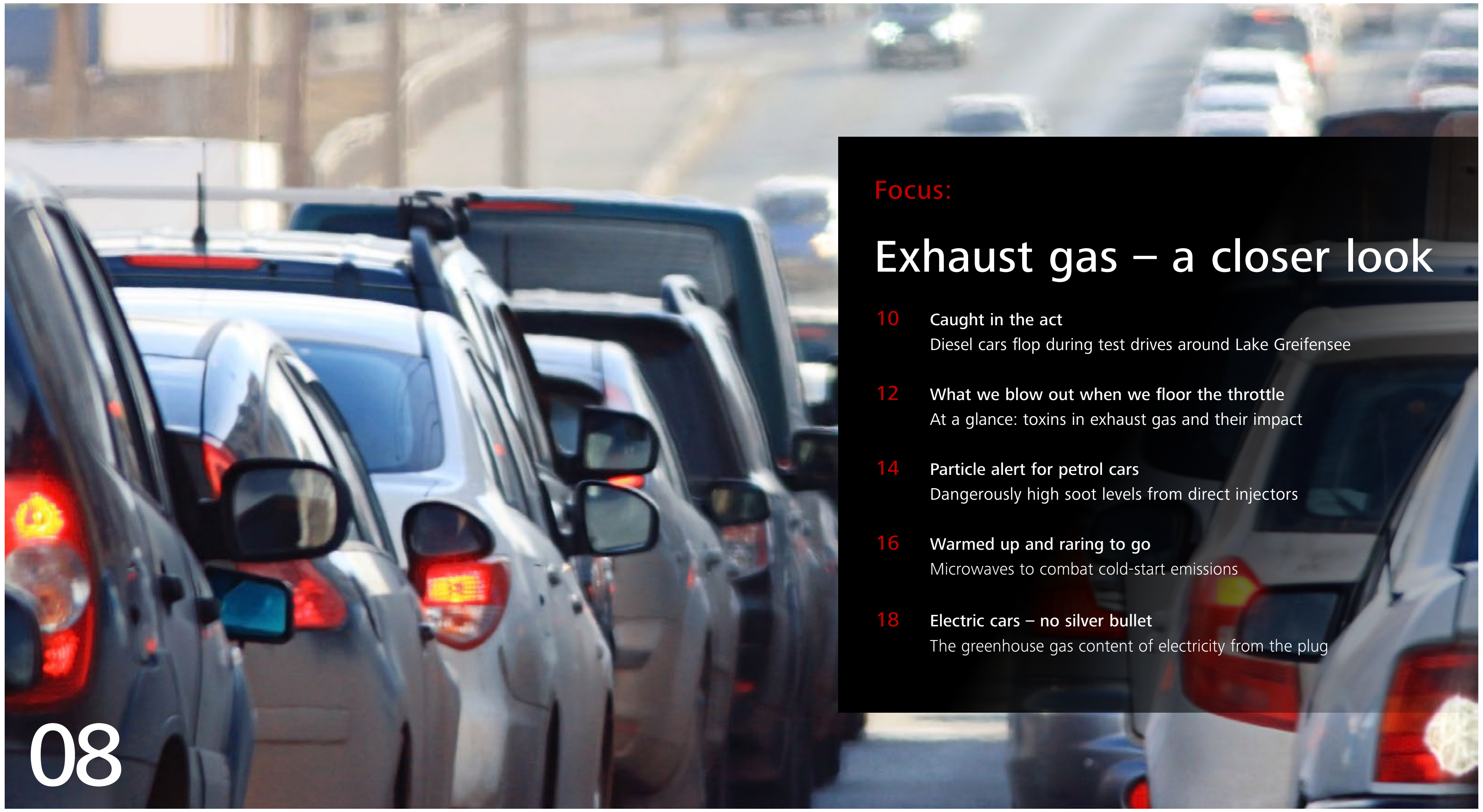
The 64,000-dollar question: why is the air in a highway tunnel cleaner than in town? Engine researchers know the answer: in a tunnel, cars have warm engines, drive at a constant speed (100 km/h) and hardly anybody steps on the gas. In other words, prime conditions for the catalytic converters, particle filters and AdBlue injection systems. It's a very different story in inner cities. Drivers start their cars from the cold and really floor the throttle to overtake. It's the same at traffic lights, where almost everyone tries to make up for lost time. And others look to flaunt the expensive horsepower they've splashed out on as they roar past sidewalk bars and cafes. Welcome to reality!

> «The crucial thing is what comes out at the end.»
>
> Helmut Kohl, German Chancellor 1982–1998)

This driving behavior is stretching the exhaust gas cleaning in diesel and gasoline cars to its limits. Until now, the law has turned a blind eye precisely here and relied on unrealistic tests on test rigs to set limits and classify cars. As a result, some pollutants slip through the net (virtually) unbridled while others are only produced in the hot catalytic converter from the chemically reactive ingredients that the engine provides. The result: urban traffic in European cities is already fraught with fine particle alerts, driving bans and pollution badges. But what really comes out the rear end? Empa has been on the case (see pages 08–20).

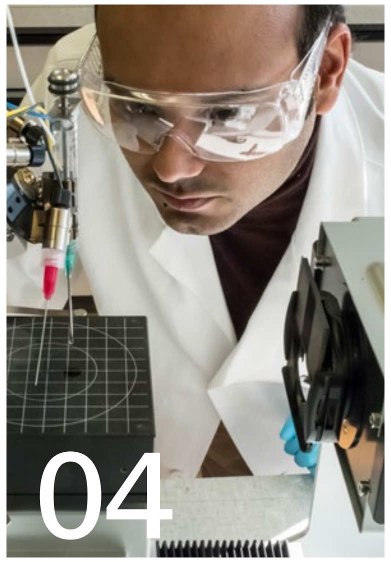
With all the talk about nitric oxides and fine particles, however, we shouldn't forget one thing: combustion engines do exactly what they are supposed to – they burn carbonic fuels, together with all their numerous pollutants. And unfortunately, it isn't just water vapor and carbon dioxide that are generated – the end products of every complete combustion process. As we are unwilling to compromise on the comfort of our own (or rented) cars, we will have to live with a certain amount of environmental pollution from traffic for the foreseeable future.

Despite this sobering topic, I wish you enlightening insights and a riveting read!



Focus:

Exhaust gas – a closer look



Cover
*Car designers like using souped-up exhaust pipes to draw attention to a car's engine power. Read what actually comes out when drivers step on the gas from **page 8.***
Photo: BMW AG.

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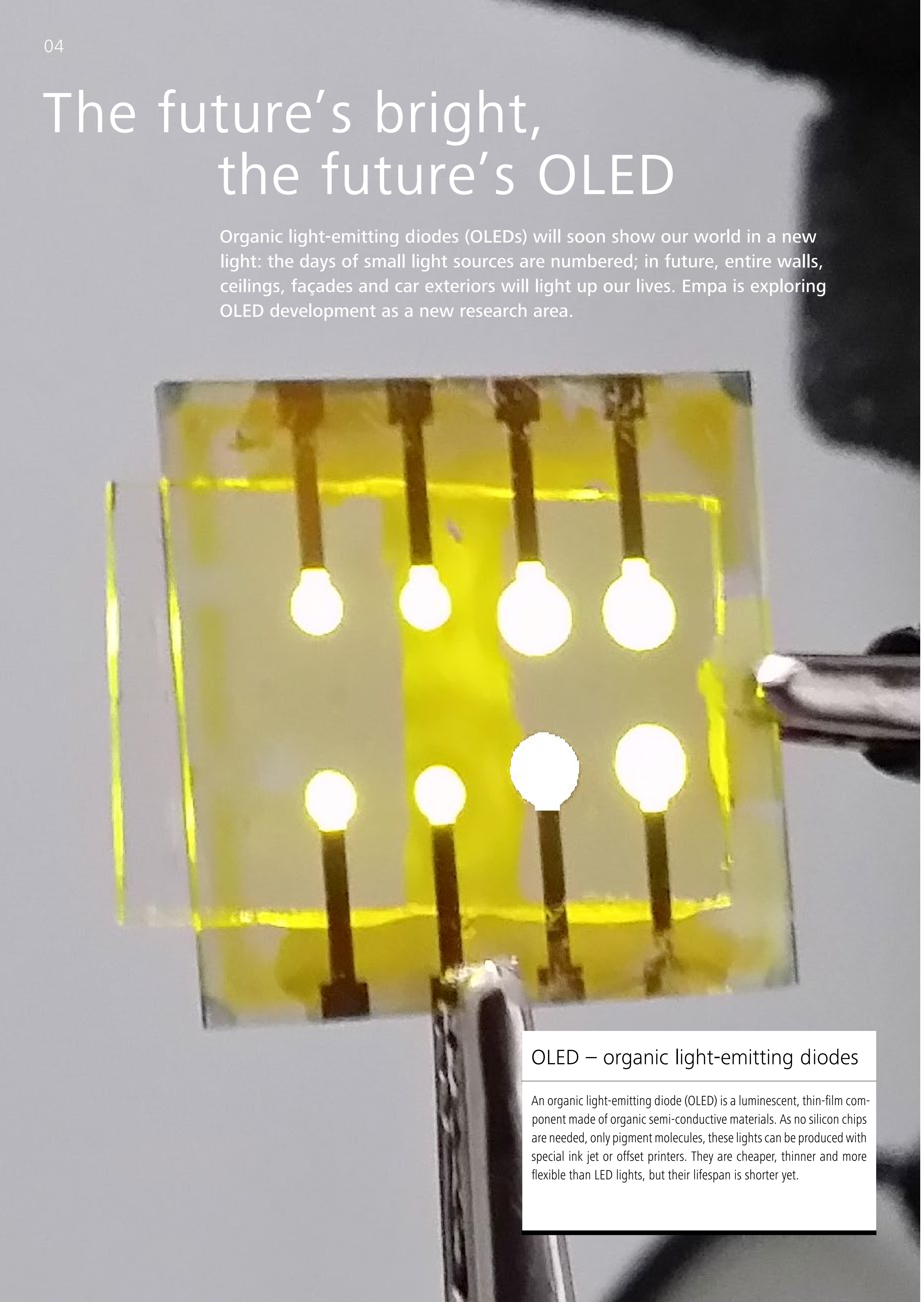


The future's bright, the future's OLED

Organic light-emitting diodes (OLEDs) will soon show our world in a new light: the days of small light sources are numbered; in future, entire walls, ceilings, façades and car exteriors will light up our lives. Empa is exploring OLED development as a new research area.

OLED – organic light-emitting diodes

An organic light-emitting diode (OLED) is a luminescent, thin-film component made of organic semi-conductive materials. As no silicon chips are needed, only pigment molecules, these lights can be produced with special ink jet or offset printers. They are cheaper, thinner and more flexible than LED lights, but their lifespan is shorter yet.

TEXT: Ramona Ronner / PICTURES: Empa

Organic light-emitting diodes (OLEDs) are the light sources of the future. Luminescent paintwork on cars, colorful living room walls and kitchen ceilings that light up, billboards of a very different kind – all this will now be conceivable. Last year the EU project TREASORES, coordinated by Empa, created flexible, transparent electrodes, the basis for supple, rollable OLEDs. Acquiring the experience to fabricate and functionalize the multi-layered structures of OLEDs light sources is the next step forward. After all, manufacturing a homogenously lit wallpaper is anything but trivial. Thus, expertise from the industry is urgently called for.

Anand Verma brings these expertise and know-how to the table. He started his career as a professional conventional printer at India Today after obtaining a Bachelor of Engineering in printing and media technology from Manipal Insititute of Technology. He extended his knowledge to the developing field of printed electronics by gaining a Master's degree at Chemnitz University of Technology (Germany). With his extensive research work on OLEDs in cooperation with Holst Center in Eindhoven (Netherlands), Novaled (Germany) and Cynora GmbH (Germany), he gained expertise to develop inks and new printing processes for OLED fabrication.

At Empa, as a coating / printing expert his area of research involves developing wet coating and printing for the Coating Competence Center (CCC). At CCC, he works on printing perovskite solar cells, actuators, and the like. Besides, he continues to explore the printing of flexible OLEDs on various substrates. "I can estimate optimal layer architectures, which will function in OLEDs depending on the substrates being investigated," says Verma. "So I also know the process parameters that need to optimized besides ink composition."

Ultrathin layers

Most of the light sources we are familiar with are point light sources or neon tubes. OLEDs, on the other hand, are surface lights. "If you look at OLED structure," explains the Empa researcher, "they consist of multiple nanometer-thin layers." The positively charged anode usually consists of transparent indium tin oxide (ITO), which can be used to produce electrically conductive windows or films. This is followed by an organic semiconductor layer (poly 3, 4-ethylenedioxythiophene polystyrenesulfonate, PEDOT:PSS), a light emitting layer (Super Yellow, fluorescent color), calcium for work function and a cathode, usually made of aluminum.

It takes up to three days to produce a batch of OLEDs. First of all, it is important to clean the ITO substrate carefully as even tiny specks will show up on the finished product later on – especially because the layers are only a few nanometers thin. Electronically and morphologically stable layer architecture differentiates between a good and bad performing OLED: "Generally, the thinner the layers, the higher the risk of inhomogeneity during wet coating. On the other hand: if the layers are thicker, a higher turn-on voltage is needed to achieve the same luminosity," says Verma.

Plasma makes for a smooth color

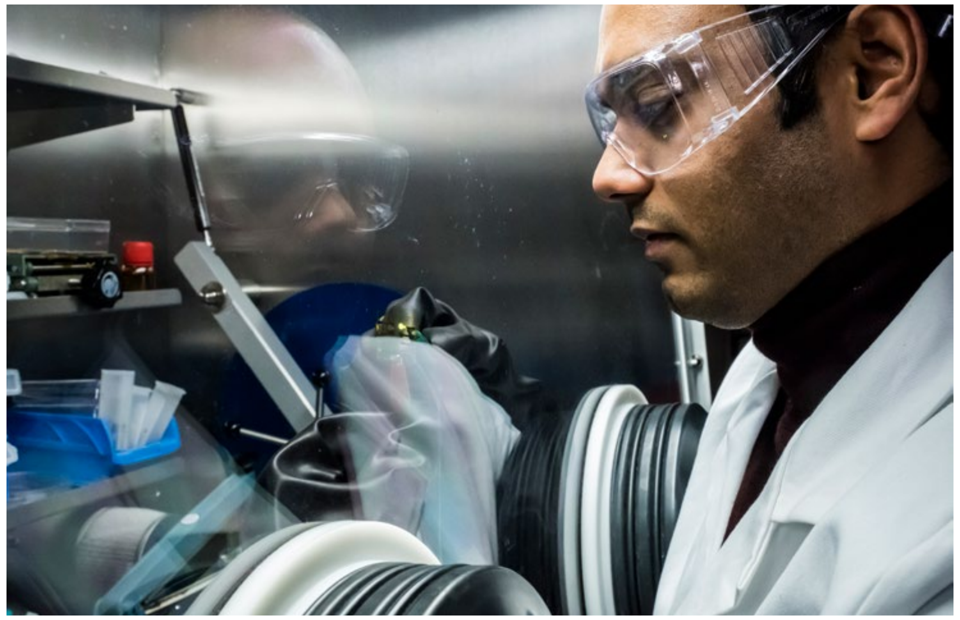
After the cleaning phase, the substrate is treated with an oxygen plasma: it is bombarded with ions to increase the surface energy, which facilitates wetting behavior of inks thus obtaining a homogeneous layer. It is important for the substrate's surface energy to be higher than that of the ink being coated. "Depending on the surface energy of the material and surface tension of the ink, it either wets the surface or it de-wets it.

However, in some cases treating the substrate is not enough. When producing the ink – for the next layer of material – Verma first has to work out the right solvent in the ideal concentration to achieve the desired surface energy level, required thickness and morphology.

Moreover, the solvent should be as environmentally friendly as possible. "If we chose chloroform, for instance," says Verma, "this would have a harmful impact on health during the production phase because rather high quantities of it are required."

left
Successful experiment: the OLED test fixtures light up. The power stems from a small, 9V battery.

right
Large portions of the work on OLEDs have to take place under protective gas. Anand Verma needs a healthy dose of patience and a delicate touch in the glove box.



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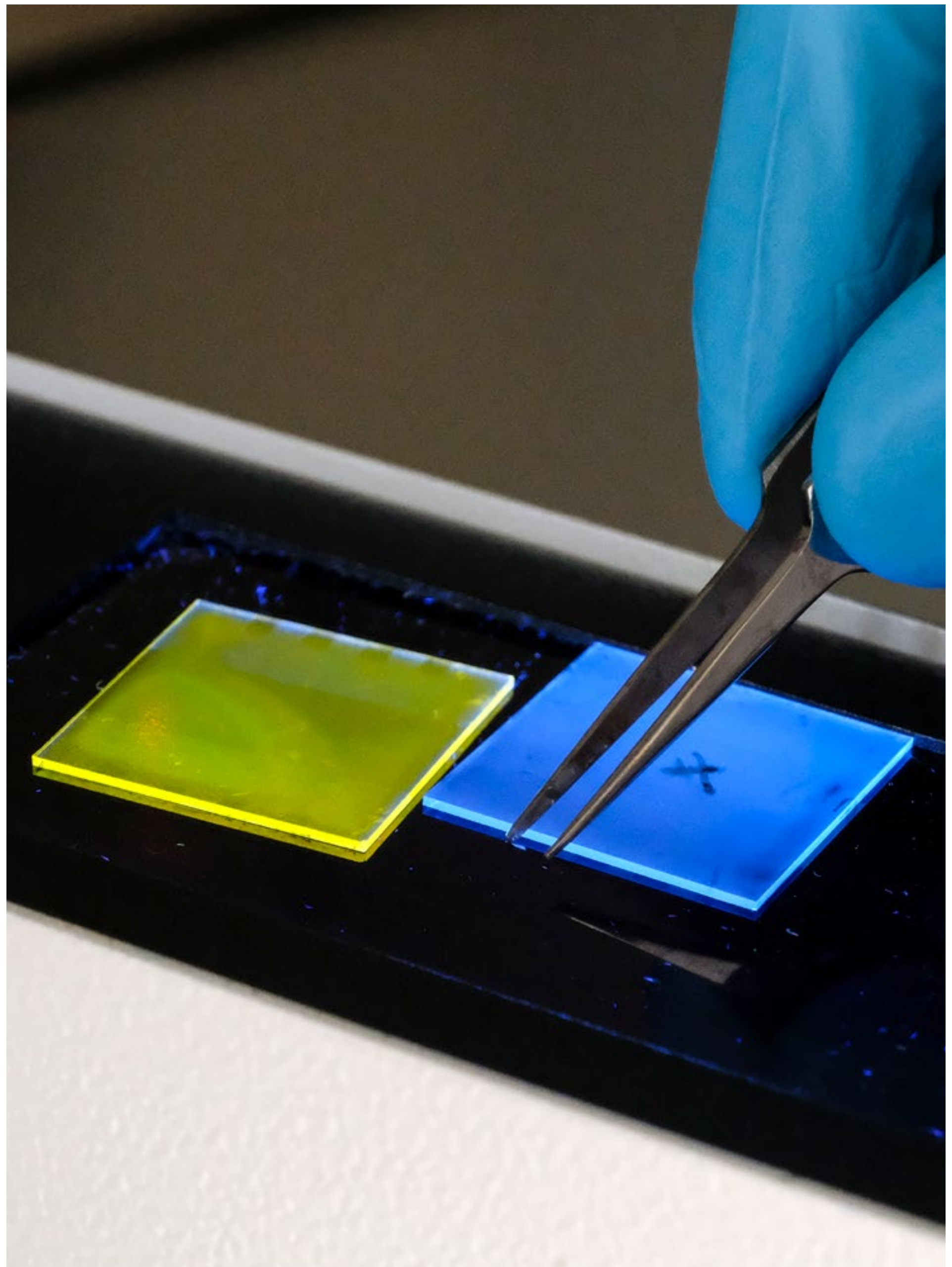
For the color to be distributed perfectly, the dye droplet needs to have a lower surface energy than the area to be coated.

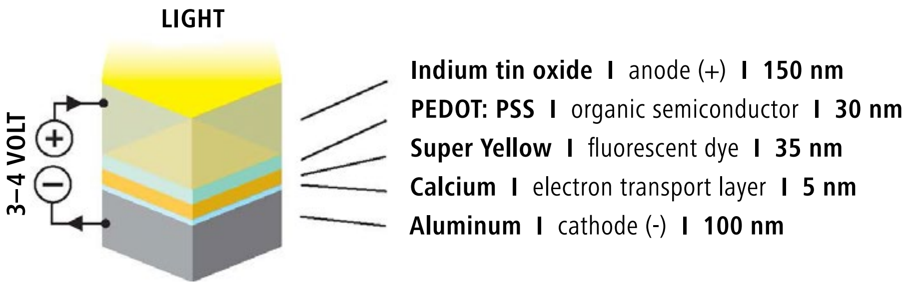


One of the used inks is Super Yellow. The most important layer is the light-emitting one. It is crucial for the researcher to already make this ink 24 hours beforehand as it takes that long for the solvent to dissolve in the dye. In contrast to the previous layers, calcium and subsequently aluminum is vacuum evaporated. To do so, the printing specialist has to use a glove box including a vacuum chamber to prevent the oxidation of calcium. Why opt for such a sensitive metal? "You could also use a different one. But all those that make suitable candidates are in the same group in the periodic table; they all oxidize."

Protected from oxygen and moisture

To use the fabricated devices in ambient conditions, Verma has to encapsulate the finished OLED to protect it from oxidation and moisture. This requires another layer made of transparent film or glass and special glue, which hardens under influence of UV light.

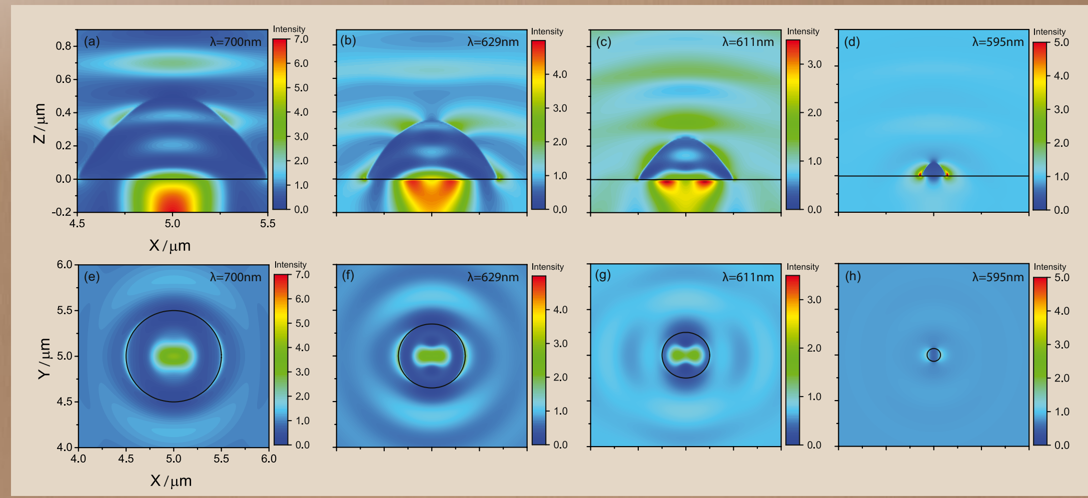
The tests involving the different substrates and the carriers for these flexible OLEDs will run until Empa's demonstrators light up reliably. Anand Verma is already thinking of the next step: "Printing and coating devices at Empa's new Coating Competence Center would already be capable of producing OLED patterns or surfaces on a larger scale." The lighting from the lab is within reach. //



Graphic: Typical layer structure of an organic light-emitting diode (OLED)

Light switches from a spray can

Researchers are on the lookout for rapid, reliable and affordable switches for the opto-electronics of the future. The solution: dye droplets measuring just a few submicrometers in diameter.



Physicist Jakob Heier discovered the special optical properties of dye droplets.

TEXT: Rainer Klose / PICTURES: Empa, Wiley-VCH

Scientists from Empa's Laboratory for Functional Polymers are on the lookout for liquids that spread as evenly as possible on a surface for the production of OLEDs (see page 04). However, the very same lab is also working on precisely the opposite: a liquid that is supposed to break up into as many droplets as possible when applied to a surface. Each of these droplets forms a microlens when it dries. A whole field of these microlenses can influence beams of light in a specific way, which makes them extremely interesting for optic signal processing in computers and fiber optic networks.

Cheap to produce

"We take advantage of the fact that the droplets organize themselves," says Jakob Heier, who is studying the optic properties of these microlenses. "This has a major economic advantage: we don't need any machines to make the microlenses; a spray nozzle does the trick." In the lab, however, the dye is not yet sprayed on; Heier and his colleagues produce the microlenses using spin-coating. The dye is placed in the center of a turntable and spreads across the entire area thanks to the centrifugal force.

Anyone who would like to understand exactly how these fields of microlenses behave in the light needs to delve deep into math. Heier talks about Fourier transforms and Kramers-Kronig relations, which help describe the properties of thousands of droplets in a single mathematical formula. "The mathematics behind it all might be 100 years old, but the insights we gain are up to the minute."

Components made of cyanine dye

Heier and his colleagues succeeded in demonstrating that a whole series of optic switch elements can be constructed from droplets of cyanine dye. The study was published in the journal Advanced Optical Materials in February 2017. The switch elements can specifically block or let through certain wavelengths. Heier uses the change in the dye's refraction index. What makes it all so exciting: by selecting different dyes and varying the size of the droplets, the properties of the switch can be tailored to the desired application.

For instance, phase gratings can be constructed from these microlenses – a popular tool in optoelectronics. This is able to divide beams of light into individual frequencies, without compromising the light's intensity. Hence, the signal losses remain low, less light energy is required and the components don't heat up as much. "With our observations and calculations, we've physically paved the way for these switches," says Heier. "Now I'm excited to see who uses this knowhow for the first real applications."//

Exhaust gas – a closer look

At the end of 2016, 4,524,029 cars were registered in Switzerland – that's more than one for every two citizens. Every year, the car stock increases by around two percent. Switzerland's car fleet, therefore, increased by a total of 56 percent between 1990 and 2015. Among the four and a half million registered cars at the end of 2016, precisely 10,727 were electric – a mere 0.2 percent. All the other vehicles, i.e. 99.8 percent, emitted exhaust fumes to some extent.

PICTURE: Alfa Romeo

Caught in the act

As of October 2017, newly launched car models will have to pass more stringent exhaust gas tests in the EU and in Switzerland. The new test method includes measuring drives in actual traffic. Empa already tested currently available cars with the new method – with alarming results.

TEXT: Rainer Klose / PICTURES: Empa

By now, it's no secret: the certification requirements for cars in the EU and in Switzerland have precious little to do with the cars' actual exhaust emissions on the roads. The "real" exhaust emissions are, therefore, determined in separate studies, including at Empa. Air pollution control experts from the Federal Office for the Environment (FOEN) draw upon this kind of data if they want to estimate road traffic emissions. On behalf of the Swiss government, Empa measures about a dozen vehicles a year, which are supplied by randomly selected individuals for a small fee. The data is fed into the European HBEFA database (Handbook Emission Factors for Road Transport) and is used, amongst other things, by international research institutes and authorities as a basis for expert reports.

High nitric oxide emissions

Last January was a prime example of what can happen during such measurements: the test candidate, a 2016 diesel Renault Mégane, already displayed high nitric oxide emissions at Empa's test rig. This is because the Empa researchers focused on the vehicle's actual values – as intended in the new WLTP method – and not the outdated standards of the previous approval procedure. For instance, the vehicle was measured as being almost 300 kilograms heavier than the type test regulations allow for – not out of spite, but because the car drives around the streets at this weight. Later, during the so-called RDE test (Real Driving Emissions), up to 1,300 milligrams of nitric oxides per kilometer were measured in the exhaust. In other words, this current Euro 6 vehicle emits about as much nitric oxides as a ten or 15-year-old diesel car. As of October 2017, however, new models will only be allowed to emit 170 milligrams per kilometer!

Acclaimed by motor journalists

A year earlier, the very same model had been crowned "Car of the Year" by European car journalists. How is it possible for a modern diesel vehicle to display such high emissions on the roads? One problem is the previous exhaust gas regulations, which failed to keep up with the rapid developments in powertrain systems. These regulations are fraught with unrealistic dead-weight and driving resistance requirements, and predefined, high-speed gearshift points that have nothing to do with reality. This realization is nothing new: already back in 2010, a decision was made to develop a new, more realistic exhaust gas measuring technique. But why has it taken so long? The topic is complicated and processed by an international working group, which had to make do with many, sometimes even divergent demands.

In the case of the Renault Mégane, the exhaust gas recirculation evidently turned itself off during the test drive – perhaps because the outside temperature was below the minimum temperature in the lab. Other manufacturers also switch off the exhaust gas treatment to go easy on the engine, when it is used outside the test rig – which is perfectly legal according to EU emissions regulation 715/2007/EG.

In Audis and Fiats, for instance, it is turned off after 22 minutes, as the German newspaper *Handelsblatt* reported (the NEDC dynamometer test lasts 20 minutes); in Mercedes cars below 10 degrees and in Opels even below 17 degrees Celsius, as *Handelsblatt* also stated (the NEDC dynamometer test requires temperatures above 20 degrees). Opel also switches to another cycle at an air pressure below 915 millibars, as the magazine *Der Spiegel* reported. The deactivation, therefore, occurs at an altitude of over 850 meters above sea level (the highest testing lab for car certifications in Europe is situated in Madrid, at an altitude of 700 meters).

In February 2017, Opel, Daimler and VW expressed their willingness to voluntarily recall around 500,000 vehicles across Europe to correct their exhaust gas treatment software, which was not illegal so far. On top of this, VW has to correct 2.4 million cars containing an illegal software.

Empa´s public research

If we also want to use exhaust gas treatment systems continuously at low temperatures and in other adverse conditions, they need to be understood in technical detail, designed correctly and operated under optimal conditions. As the current scandal reveals: there is a still a lot of catching up to do in this respect. Empa makes significant contributions in this sector with a high-temperature flow lab by studying in detail the injection behavior of AdBlue, an aqueous urea solution that is injected into the exhaust gas in new diesel vehicles. Researchers measure the spray cone right down to single droplets using laser measuring devices, study the formation and evaporation of liquid AdBlue films on the walls of the exhaust pipe, and gage the AdBlue breakdown all the way until the formation of the reduction agent for the nitric oxides in the adjacent catalytic converter. These results are channeled back into the refinement of exhaust gas treatment systems.

During Empa's exhaust gas tests, the experts from the Automotive Powertrain Technologies lab drive along a defined route southeastwards from Dübendorf, around Lake Greifensee, then back on the highway from Uster via Brüttiseller Kreuz (see map). During the journey, the NO_x emissions are meticulously recorded by a so-called PEMS (Portable Emission-measuring System).

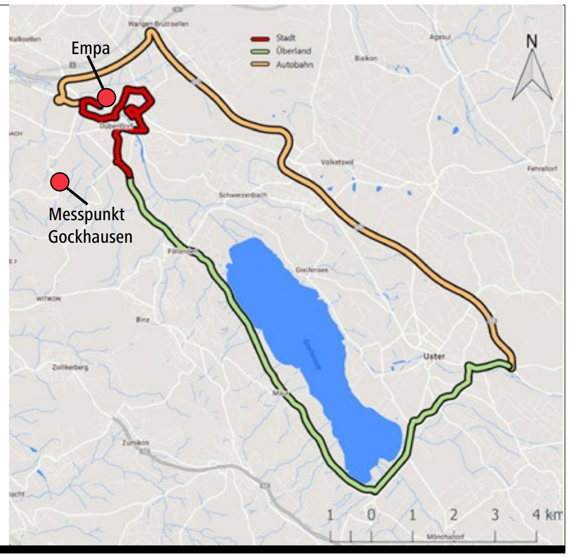
The Mégane is not alone

Empa has already tested three new lower mid-range diesel vehicles with the current exhaust gas standard Euro 6 using the new RDE procedure. In all of them, NO_x emissions during every phase of the trip lay between 600 and 1,400 milligrams per kilometer; exhaust gas tests by other labs reveal a similar picture. In other words, the Renault Mégane is not alone. These vehicles can continue to be sold until the fall 2019; however, upcoming model series must pass the stricter WLTP and RDE tests to be approved.

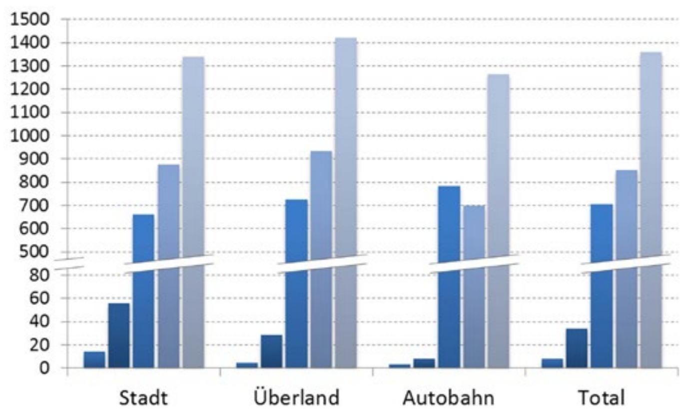
Anyone who would like to drive a cleaner car than the law requires today does have an alternative, though: with NO_x emissions way below 10 milligrams per kilometer, the natural / biogas vehicle that was also included in the measurements fared around 60 to 140 times better than the diesel cars. //

Checking exhaust gas plumes in Gockhausen

Another team of researchers confirmed that diesel cars display considerably higher NO_x emissions than on the test rig when driven under real-world conditions – using a completely different measuring technique very near the Empa test route. Jens Borken-Kleefeld from the IIASA Institute in Austria and Yuche Chen from the University of California, Davis, evaluated exhaust gas measurements from passing cars on Bergstrasse from Dübendorf to Gockhausen by sending a beam of infrared light through their exhaust gas plume. At the same time, the researchers take the license plate numbers and retrieve the vehicle data for all cars registered in the Canton of Zurich from a database: model year, fuel type, engine output, emission class, weight. In the course of the 13 year-long measuring campaign, 110,000 gasoline cars and 18,000 diesel cars drove through the measurement barrier and left their "exhaust gas fingerprint". As the researchers write: "NO_x emissions from diesel cars are about 20 times higher than those of gasoline cars from the same model year." The conclusion: "Under real-world conditions, the NO_x limits for diesel vehicles don't have the effect that the legislators intended."



An Opel Astra 1.6 CDTI on Empa's dynamometer test rig: the tubes connect the exhaust tract to a mobile PEMS device (portable emission measuring system) inside the car. Thus equipped it then heads off around Lake Greifensee.

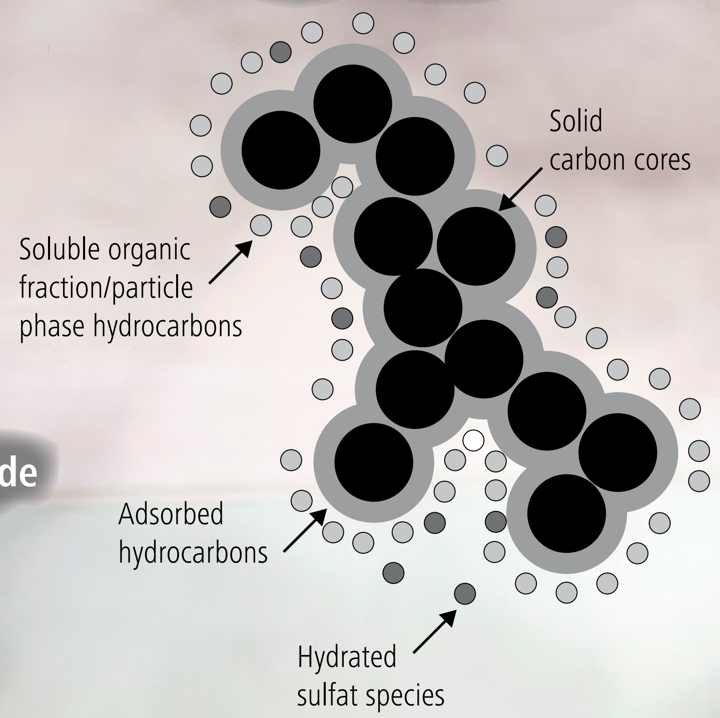


A comparison of the NO_x emissions during the test drive around Lake Greifensee: on the left, a natural gas vehicle (CNG) and a gasoline car; on the right, three current Euro 6 diesel cars (Opel Astra, Ford S-MAX, Renault Mégane).

What we blow out when we floor the throttle

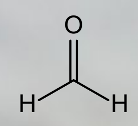
Empa researchers studied exhaust emissions from seven gasoline cars and one diesel, six of which were built between 2012 and 2016. Alarming substances came to light in the gas chromatograph, a fine, analytical instrument. As the dynamometer revealed, most of these substances are produced when the vehicle accelerates.

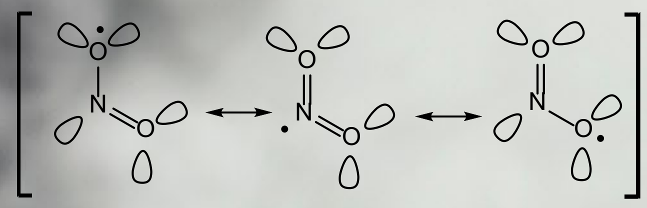
Soot particles



Carbon monoxide

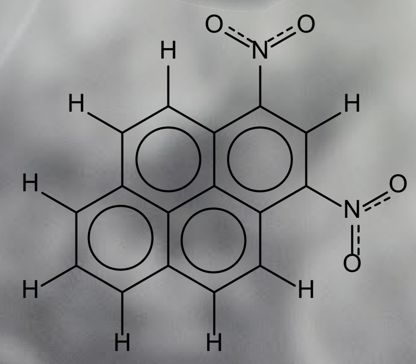
Formaldehyde



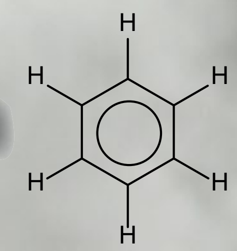


Nitric oxides

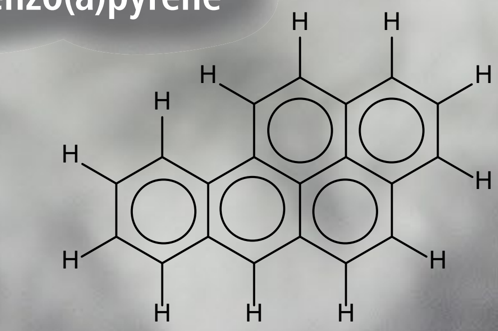
Dinitropyrene



Benzene



Benzo(a)pyrene



Soot particles

The nanoparticles, which initially have a diameter of 15 to 20 nanometers (millionths of a millimeter), congregate to form larger particles measuring 80 to 100 nanometers, and penetrate the alveoli of the lung (The lungs can only remove particles that are larger than 200 nanometers). Chemical pollutants accumulate on the surface of the soot particles, which transport them into the lungs and thus into the bloodstream – like a Trojan horse.

➡ *Euro 6 permits 6 trillion particles / km for direct-injection gasoline cars and 600 billion particles / km for diesel vehicles. For gasoline cars with intake manifold injection, there are no emission limits at all.*

Carbon monoxide (CO)

The gas is poisonous as it binds to hemoglobin and thus interferes with oxygen transport in the blood. CO poisoning is fatal within a short period of time. In January, six teenagers died in Germany using a gasoline power generator in a summerhouse.

➡ *Euro 6 permits 1,000 mg CO / km for gasoline cars and 500 mg / km for diesel.*

Nitric oxides (NO und NO_2)

In air NO rapidly oxidizes to form NO_2, a poisonous gas with a pungent odor that irritates the throat and dissolves readily in water to form nitric acid. Above 21 degrees Celsius, it transforms into N_2O_4, a corrosive and highly oxidizing gas.

➡ *Euro 6 permits 60 mg NO + NO_2 / km for gasoline cars and 80 mg / km for diesel.*

Formaldehyde (CH_2O)

Formaldehyde can cause allergies and skin, respiratory tract or eye irritations. In concentrations of 30ml/m³ and above, it can be life-threatening. In case of chronic exposure, it is carcinogenic and affects the memory, ability to concentrate and sleep.

➡ *Euro 6 does not specify any limits.*

Benzene (C_6H_6)

Its breakdown in the body produces toxins that can trigger cell mutations (cancer). Its long-term intake can harm the inner organs and bone marrow, which causes anemia. In humans and animals, benzene accumulates in the brain, bone marrow and fatty tissue.

➡ *Euro 6 does not specify any limits.*

Dinitropyrene ($C_{16}H_{18}N_2O_{64}$)

Dinitropyrene is produced in the hot exhaust tract in diesel engines through the reaction between pyrene and NO_2. 1,3-, 1,6- and 1,8-dinitropyrenes are particularly mutagenic and trigger malignant tumors in many organs in various lab animals.

➡ *Euro 6 does not specify any limits.*

Benzo(a)pyrene ($C_{20}H_{12}$)

Benzo(a)pyren is one of the longest known carcinogenic substances. It is found in cigarette smoke and causes lung cancer. Benzo(a)pyrene is converted chemically in the body. The metabolic product reacts with DNA, which can prevent cell division or cause mutations.

➡ *Euro 6 does not specify any limits.*

Particle alert for petrol cars

First, diesel vehicles tainted their reputation with soot particles, then high nitric oxide emissions. So are owners of new gasoline cars environmentally friendly? Not always, says a new study led by Empa scientists: some direct-injection gasoline engines emit just as many soot particles as unfiltered diesel cars did in the past. Particle filters can remedy this.

TEXT: Rainer Klose / PICTURES: Empa

Worldwide, three new cars roll off the line every second – that's 73 cars and 18 million utility vehicles per year. Most run on gasoline. In industrialized nations, the trend is moving towards so-called downsizing engines: smaller but with direct gasoline injection and turbocharging. This technology is kind to the environment and saves fuel, the manufacturers say. Experts estimate that by 2020, 50 million of these direct-injection gasoline engines will be running on the roads all over Europe – high time the cocktail of exhaust emissions from these engines were examined closely.

In the spring 2014, the GasOMeP project (Gasoline Vehicle Emission Control for Organic, Metallic and Particulate Non-Legislative Pollutants) got underway. The Paul Scherrer Institute (PSI), Bern University of Applied Sciences, the University of Applied Sciences and Arts Northwestern Switzerland, several industrial partners and Empa were all involved. The project was funded by the ETH Domain's Competence Center for Energy and Mobility (CCEM) and coordinated by Empa chemist Norbert Heeb, who has made a name for himself in the last 25 years by analyzing diesel emissions and studying filter systems.

The team selected seven direct-injection gasoline cars, including a Mitsubishi Carisma (2001 model, exhaust emission standard Euro 3). The other vehicles were all built between 2010 (VW Golf, Euro 4) and 2016 (Citroën C4, Euro 6b). By way of comparison, a current Peugeot 4008 (2013, Euro 5b) with a diesel engine and a particle filter was also included. All the vehicles were tested based on the WLTP cycle (Worldwide Light-Duty Vehicles Test Procedure), which will be mandatory for newly licensed models as of September 2017 (see p. 10).

Soot particles as Trojan horses

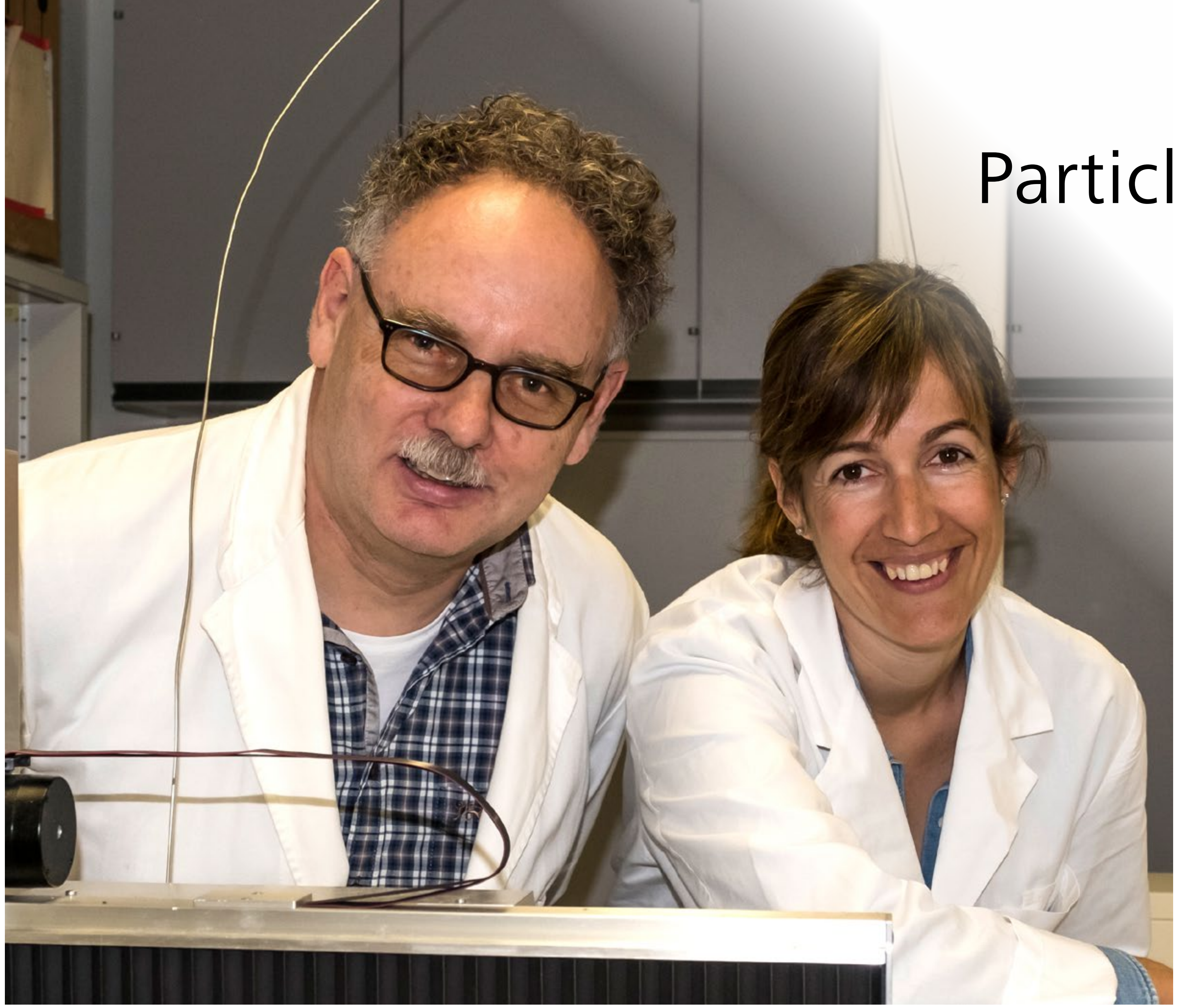
The results were sobering: every single one of the tested gasoline cars emitted ten to 100 times more fine soot particles than the diesel Peugeot. Under the microscope, the particles from the gasoline engines were similar in size to the soot particles that had given diesel a bad name: primary particles measuring ten to 20 nanometers in size, which congregate into particle agglomerates measuring 80 to 100 nanometers before leaving the exhaust. "Once inhaled, these particles remain in the body forever," explains Norbert Heeb. The evidence shows that they can penetrate the membrane of human alveoli in the lungs and thus get into the bloodstream.

Benzo(a)pyrene – a well-known smoker's killer

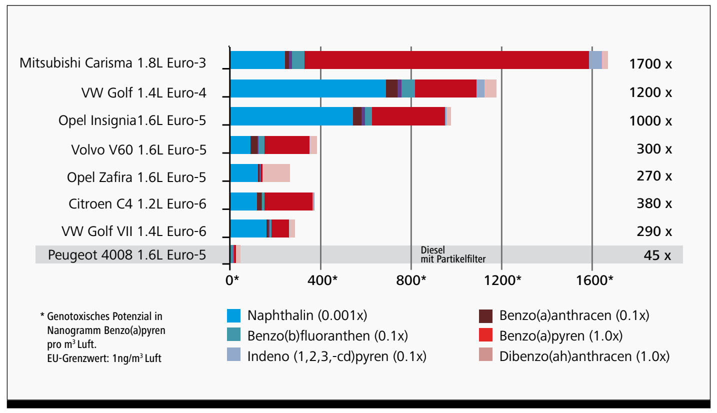
However, the particles are not the only problem, as Heeb is well aware: "Liquid or solid chemical toxins from the combustion process, including polycyclic aromatic compounds, accumulate on the surface of the particles, which can then smuggle these substances into the bloodstream – like a Trojan horse." Maria Munoz, a colleague of Heeb's from Empa's Advanced Analytical Technologies lab, took a closer look at the exhaust emissions from the vehicles tested in the GasOMeP project – and discovered the combustion product benzo(a) pyrene, a known carcinogenic substance also found in cigarette smoke.

The World Health Organization (WHO) considers even the tiniest dose of benzo(a)pyrene harmful. The EU settled on an air limit of one nanogram per cubic meter. Levels in exhaust emissions were found to be as much as 1,700 times above this limit. Or to put it another way, one cubic meter of exhaust gas transforms up to 1,700 cubic meters of clean air into a mixture deemed carcinogenic according to the EU standard.

Once again, the diesel vehicle with particle filter fared much better: in the test, the Peugeot emitted only 45 nanograms of carcinogenic substances – 6 times less than the best one of the analyzed gasoline cars.



Successful chemical tracking: Empa researchers Norbert Heeb and Maria Munoz discovered large quantities of benzo(a)pyrene (red bar in the table) – a combustion product responsible for cutting short the lives of cigarette smokers – in the exhaust gas emitted by gasoline direct injectors. Dibenzo(ah) anthracene (pink) is also carcinogenic.



GRAPHIC: Empa

The carcinogenic potential in one cubic meter of exhaust gas from gasoline direct injectors is up to 1,700 times higher than the EU limit for clean air. By contrast, diesel cars with particle filters exceeded the limit only 45-fold.

Researchers push for action

The results of the GasOMeP project were presented during a conference held at the Empa Academy in late March. The conclusion of the researchers involved: particle filters are established in diesel vehicles and have offered advanced technology for years; based on the current data, they should now also be mandatory for gasoline vehicles.

"At the moment, they don't incorporate the best available technology," criticizes Heeb, urging haste: "New exhaust emission technologies launched on the market usually take around 13 years to become fully effective. Only then will nine out of ten cars from the vehicle stock be replaced. So the sooner particle filters are made mandatory for gasoline vehicles, the better it will be for everyone's health." //

Soot from high-performance engines

The problem with increased particle emissions is not limited solely to direct-injection petrol vehicles. An Empa team headed by engine researcher Potis Dimopoulos Eggenschwiler has spent the last few months studying six current Euro 6b diesel vehicles and six current Euro 6b petrol vehicles, including a VW Golf R with a direct injection engine and a Fiat 500 twin air with an intake manifold injection engine. While all the petrol vehicles complied with the current particle limits, the emissions from the direct injectors were ten times higher than in diesel vehicles with filters. Surprisingly, particularly powerful turbo petrol vehicles with (classic) intake manifold injection engines emitted a similar number of particles to (newer) direct injectors. Only weaker engines with little power per liter of cubic capacity were really clean (see list). For the time being, this problem remains unresolved: while the more stringent Euro 6c limits for direct injectors come into force in the fall 2017 (and will often render particle filters necessary), petrol cars with intake manifold injection engines will still be allowed to emit as many particles as they like. Engine researchers like Christian Bach are therefore advocating technology-neutral limits for all kinds of engines.

Tested petrol cars

High particulate emissions:
VW Golf R I BMW 428i I Fiat 500 twin air I Alfa Romeo Giulietta 1.4

Low particulate emissions:
Skoda Octavia 1.8 I Suzuki SX4 Cross

Warmed up and raring to go

When an engine cold-starts, it produces far more pollutants than during the actual journey. This is because a cold catalytic converter is much less efficient at cleaning the exhaust gas. So what's the answer? Preheat the cat with microwaves.

TEXT: Rainer Klose / PICTURES: BAFU, PSI

90 percent of all pollutants are produced in the first minute after a modern gasoline engine is cold-started. Or to put it another way: the first 500 meters on the road pollute the air just as much as the next 5,000 kilometers if the vehicle were to be driven nonstop.

Catalytic converters for cars that warm up as fast as possible or – even better – already clean the exhaust gas efficiently during the first engine revolution are thus vital if we want to improve air quality. Potis Dimopoulos Eggenschwiler, an exhaust gas treatment specialist at Empa's Automotive Powertrain TechnologiesLaboratory, has spent the last two years searching for a solution to the cold-start problem, which especially pollutes the air in cities (see box). The project is funded by the Swiss National Science Foundation (SNSF) and the Federal Office for the Environment (FOEN).

For a catalytic converter to be heated to 250 degrees Celsius by the car's power supply using as little energy as possible before the engine starts, it needs to be small and as heat-conductive as possible. Dimopoulos Eggenschwiler proposes an open-pored structure with a special coating, which can be heated up by a small microwave transmitter within ten seconds – much like the microwave oven at home. Back in 2012, the Empa team already developed a particularly efficient catalytic converter: a ceramic cast of a polyurethane foam that swirls the exhaust gases more effectively and generates less counter-pressure than a catalytic converter with its conventional honeycomb structure.

Ceramics from the 3D printer

The Foamcat then sparked the next idea: a geometric grid structure made of thin ceramic struts that makes do with a coating containing a low amount of precious metal yet still cleans the exhaust gas swirling inside it efficiently. "First of all, we looked for an ideal structure on the computer," says Dimopoulos Eggenschwiler. "A structure that heats up rapidly, accelerates chemical reactions and hampers the gas flow as little as possible. Then we set about recreating the structure in ceramics." Specialists at the Scuola universitaria professionale della Svizzera italiana (SUPSI) in Lugano constructed the lattice designed on the computer using stereolithography, a kind of 3D print from liquids and UV light. Experts at Empa then coated the ceramics with silicon carbide, zirconium oxide and aluminum oxide – and the active catalytic converter substances consisting of platinum, rhodium and palladium.

Expectations met

What is probably the world's first 3D-printed catalytic exhaust converter lived up to expectations in field tests: in the exhaust from Empa's model gas reactor the polyhedron-shaped cat actually cleaned the pollutants even more effectively than the 2012 Foamcat. In the wake of their successful initial lab tests using small model cats, the researchers are now talking to industrial partners to integrate one of these catalytic converters in full size in a test vehicle.

The next step for Dimopoulos Eggenschwiler will be to incorporate the microwave heating. "It's important that we don't heat up the entire ceramic structure," he says. "We want the microwaves that are generated by using precious battery power to only affect the ultrathin catalytic coating."

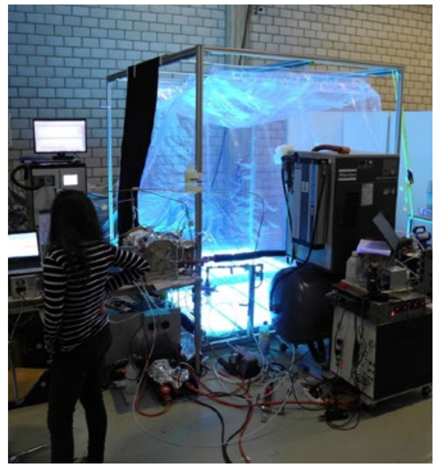
According to the exhaust gas specialist, one to two kilowatts can easily be diverted from a vehicle's battery for ten to 20 seconds. "That should be enough." As soon as the engine is running, the exhaust gas and the chemical reactions in the catalytic converter supply sufficient heat to keep it hot, at which point the microwave can be switched off. //

Left
Potis Dimopoulos Eggenschwiler (right) heads the project initiated by the Federal Office for the Environment (FOEN) to develop a novel exhaust gas catalytic converter for gasoline cars. Alberto Ortona (left) from the University of Applied Sciences and Arts of Southern Switzerland (SUPSI) 3D-printed the ceramic structure.

Large Photo below
The geometric ceramic structure of the test catalytic converter designed on the computer. Specialists at Empa coated it with the catalytically active layer and tested the cleaning effect in an artificial stream of exhaust gas.

Particles for breakfast

Particulate matter in city centers isn't just caused by diesel vehicles without filters; petrol cars also play a role – especially when they start up from cold in the carpark or an underground garage.
A team of researchers headed by André Prévôt from PSI succeeded in demonstrating how these fine particles develop in a so-called smog chamber. Within the scope of the GasOMeP project (see page 14), the researchers collected exhaust gases from test vehicles in a 12-cubic-meter blow-up chamber with transparent Teflon film walls. Inside, the car exhaust gases are mixed with dampened air and irradiated with UV lamps for several hours to simulate a sunny day. The "fresh" exhaust gas, which initially contains gaseous substances such as benzene, toluene, nitric oxides and ammonia, now transforms into something completely different: salt particles such as ammonium nitrate. The unburnt hydrocarbons oxidize in the air and are converted into a liquid or solid state, which produces a toxic fog that accumulates on the newly formed salt particles and the soot particles from the engine. Some days, as much as



90 percent of the fine dust pollution can be generated in this way.
Studies conducted at the University of Bern in 2015 revealed that secondary fine particulate matter from a Euro 5 petrol engine harms the pulmonary tissue directly and can affect the ability of the lungs to fight off infections.

Electric cars – no silver bullet

Electric cars aren't always the answer. After all, the power grid also contains CO_2. Anyone who switches to electromobility and thus saves on fossil fuels at the gas station should make sure that the electricity they "refuel" comes from renewable sources.

TEXT: Rainer Klose / GRAFIC+PICTURE: Empa

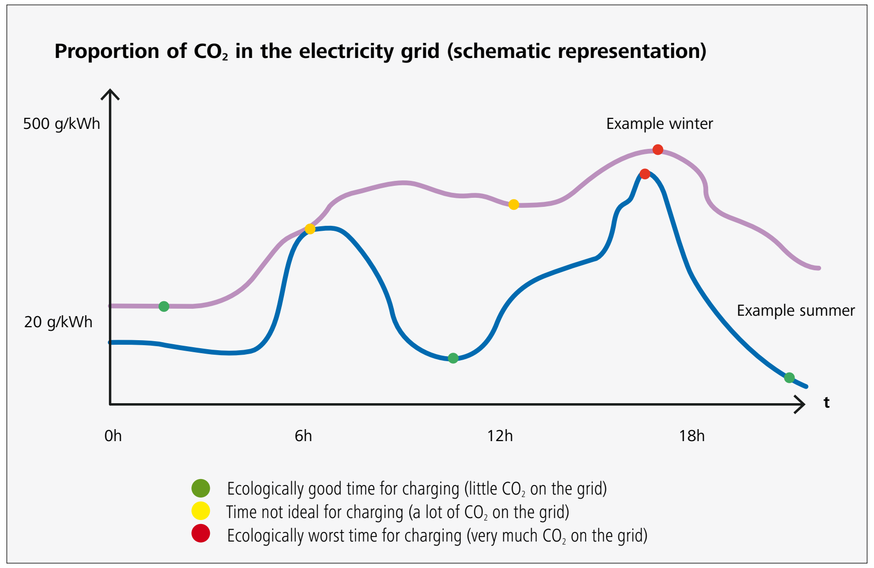
If combustion engines emit many harmful substances (see page 08 onwards), shouldn't we just switch to electric cars? Are cars without an exhaust pipe the answer? As Urs Elber, Head of Empa's Research Focus Area "Energy", states: "Electricity is never completely CO_2-free, not even in Switzerland." This is because renewable energy also contains "gray" energy. Although ever more electricity can be generated by hydro, wind, solar and biomass pow-er stations, electricity is also produced from fossil sources in large parts of Europe. Due to the international electricity trade, this electricity, which often contains high levels of CO_2, also reaches Switzerland – sometimes more, sometimes less depending on the time of day and year.

In his talks, Elber likes displaying a current European electricity map (www.electricitymap.org), which shows that Swiss electricity contained 111 grams of CO_2 per kilowatt hour (kWh) at 11 a.m. on April 4, for instance. At the same moment, the level was 506 grams over the border in Germany. As a simple calculation reveals: anyone who drives a Tesla Model S and, according to the manufacturer, consumes 22 kWh of electricity in 100 kilometers, therefore, emits 111 grams of CO_2 per kilometer using electricity from the German grid; with Swiss electricity, this goes down to around 25 grams per kilometer.

Good times, bad times

The more electricity is used at the same time, the higher the CO_2 burden of the electricity as additional fossil power stations have to plug the gaps. This is often the case in the evening, when people head home, cook, heat their houses and plug in their electric car. The electricity charged from the grid is thus not necessarily "greener" than an efficient, fossil-powered car – especially in the wintertime. "Charging an electric car when the network load and CO_2 proportion is low or the electricity is produced in a decentralized, directly renewable way makes both ecological and economic sense," says Elber. "This is because the power grid doesn't need to be expanded for electromobility."

In order to make the most of the solar power in the summertime, many more seasonal storage systems are needed in future. Solar and wind power can be stored in the form of hydrogen or natural gas (in power-to-gas plants like at Empa). Energy stored this way can then also be used to power fuel cell vehicles or natural gas cars with a low CO_2 footprint. //



Charging electric cars is not always equally environmentally friendly. More electricity with high CO_2 emissions is especially produced in the evening, when commuters head home. In the summertime, solar power could be channeled into commuter cars. However, this would require charging stations at the workplace.

"We have to talk about what the future holds for us."

In May 2016, Patrick Wäger took over the helm at Empa's Technology and Society lab. Closing material cycles and performing life cycle and technology assessments are just some of the topics that now come under his dominion.

TEXT: Patrick Wäger / PICTURE: Empa

Patrick Wäger spent the majority of his childhood and youth as a Swiss expat living in Milan, Paris, Strasbourg and Königstein im Taunus (Germany). As he moved so frequently, sometimes even at short notice, he had his fair share of goodbyes and fresh starts. Wäger soon learned how to find his bearings in changing environments, develop his own way of seeing things and not take everything for granted. And the best way to learn languages is when you're a child – where they are spoken, he adds. The nomadic aspect of his childhood is still in his blood. Every so often, he gets itchy feet and explores new avenues. Sometimes he might simply immerse himself in a good book, other times he really does set off on his travels.

After leaving school, the Swiss expat returned to his homeland, studied chemistry at ETH Zurich and did a PhD on indoor toxins at the Institute of Toxicology of ETH Zurich and the University of Zurich. He followed up his degree with a job as an environmental adviser at the company Elektrowatt Ingenieurunternehmung AG in Zurich's Seefeld district and eventually joined Empa in 1993 for a research project on the disposal of filter dust from waste incineration plants.

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> "We researchers can't tell society what to do; that's where the political process comes in."

A few years later, he moved back to academia to embark on a university degree in philosophy and sociology. According to Wäger, it is important for scientists who deal with sustainability issues to develop a certain sensitivity to ideas and concepts from other scientific fields. Ultimately, he believes that technology were inconceivable without the people who develop and use it for certain purposes, and vice versa.

Wäger sums up the goal of the Technology and Society lab thus: to create and pass on knowledge in order to facilitate and enable the transition to a more sustainable society. With this in mind, the lab focuses on analyzing the materials and energy flows that go hand in hand with the production, use and disposal of new materials and technological applications, and assessing them in terms of natural (ecological) and social (ethical) framework conditions.

Rare metals, plastic in abundance

One of the material categories the Technology and Society lab examines is rare metals, which are essential for numerous technological applications such as information and communication technologies (ICT) or energy conversion and storage. Many rare metals, such as indium, platinum metals or rare earth elements like neodymium and dysprosium, are classed as being in critically scarce supply. With regards to recycling them from what is dubbed the "urban mine", the Technology and Society lab, therefore, studies how these materials are distributed in the manmade world, the anthroposphere.

Another key material category that the lab focuses on is microplastics, i.e. small plastic components measuring less than five millimeters in diameter, which could pose a potential risk to humans and the environment. The Environmental Risk Assessment and Management (ERAM) research group led by Bernd Nowack, one of Empa's four "Distinguished Senior Researchers", studies how they behave in the environment.

"My goal is to create knowledge that might be useful to shape society," explains Wäger. Such a "transition" is especially important in his specialist field – sustainability. The knowhow from his research should help shape and change society. However, data is not enough by itself; society's behavior patterns also need to be factored in. "We try to tally people's behavior with the classic life cycle assessment data," explains Wäger. "We can't tell society what to do; that's where the political process comes in. But we can support the process by highlighting the actual or potential consequences of our conduct, which is inextricably linked to the use of new materials and technologies, from a scientific perspective." He believes it is up to environmental researchers to reveal and talk about potential future developments and the associated impact on nature and the environment.

Disposal of electronic equipment

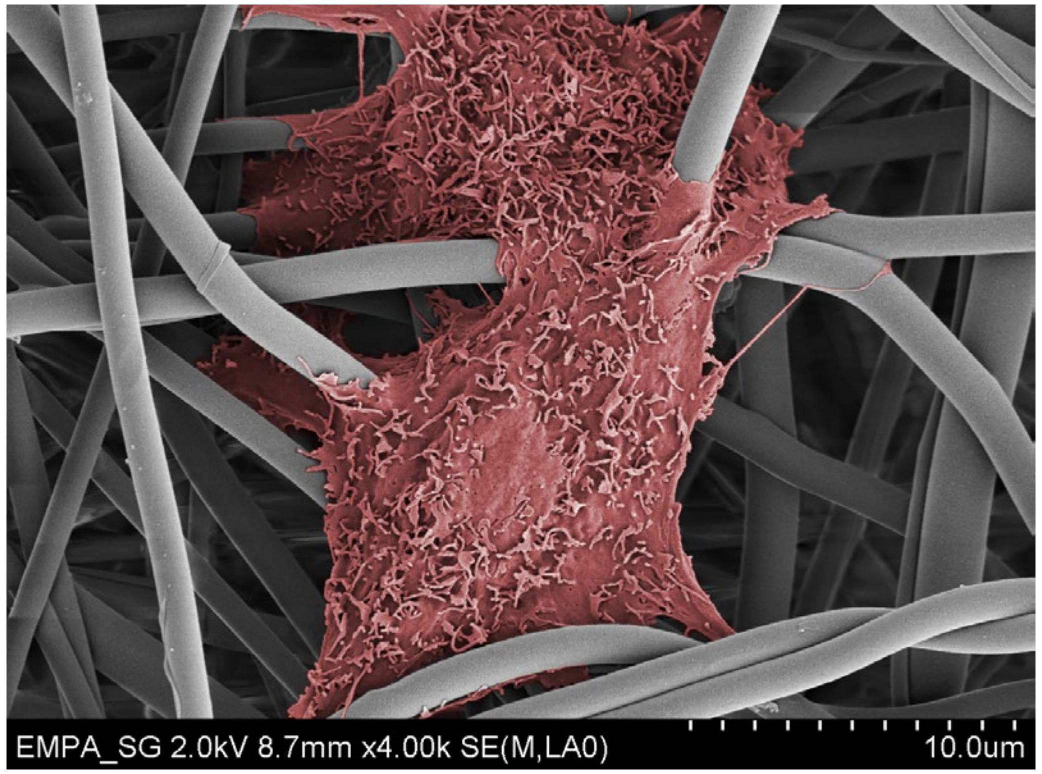
The knowhow garnered in the lab and the team's long-standing experience in disposing of old electrical and electronic equipment (EEE) is therefore channeled into existing or new standards and regulations. Wäger cites the current revision of the Electronic Scrap Ordinance (VREG) and the CENELEC standard on the collection, logistics and treatment of EEE as examples.

For Wäger, the topic is also a personal matter – one which he tackles in the same way as his research: practically and within a reasonable framework. Whenever possible, for instance, he uses public transport. But that does not stop him from flying away with his children on vacation from time to time. "Becoming a fundamentalist isn't the answer, either," he explains. "But looking after things and the environment is necessary – and a decent start." //

A magic hood for artificial heart pumps

Ten million people in Europe alone suffer from cardiac insufficiency, or a weak heart. One day, many of them may require a heart transplant. Artificial heart pumps are frequently used to bridge the wait for the transplant. However, these pumps also have their drawbacks. A project involving Empa offers a possible solution.

TEXT: Martina Peter / PICTURES: Empa



A human muscle cell grows on a fleece made of micrometer-thin polymer fibers. This enables the synthetic membrane to be camouflaged and "look" like a normal blood vessel to the immune system.

Artificial heart pumps can be tricky: blood clots may develop, causing a stroke, and the immune system may attack what it recognizes as foreign. In order to tackle this and other problems with artificial hearts, in 2011 researchers at the University Hospital Zurich launched the Zurich Heart project in collaboration with colleagues at the University of Zurich and at ETH Zurich. Meanwhile, the consortium boasts more than 75 MDs, engineers, biologists and materials scientists. Zurich Heart aims to refine current heart pumps and find completely new, original solutions. The goal of the project is to develop a fully implantable artificial heart. Around 20 research groups in Switzerland and at the German Heart Institute in Berlin have pooled their outstanding expertise to realize this ambitious goal.

As a materials research institute, Empa was a logical partner to contribute innovative solutions. "We'd like to make an artificial heart pump that works in a similar way to the human heart and has its inner surface covered with the patient's own cells," explains Edoardo Mazza, Head of Empa's Mechanical Integrity of Energy Systems lab, professor at ETH Zurich and co-leader of Zurich Heart. Two teams from Empa, one from the field of biotechnology/biointerfaces, the other from the textiles sector, are working on this heart pump, which is "invisible" to the body's blood clotting and immune system.

Textiles and human tissue

But what have textiles got to do with human organs? More than you might think: after all, aren't we talking about human tissue, about muscle fibers that can tear? And aren't veins and arteries essentially nothing more than hollow fibers, through which our blood flows? "These days, textile development has nothing anymore to do with cotton T-shirts and the like," says René Rossi, Head of Empa's Biomimetic Membranes and Textiles lab. For him, a textile is when a one-dimensional material – a fiber – is turned into a

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two-dimensional entity. This might be fabric or tissue. "Theoretically, there are no bounds to the materials and properties," explains Rossi. "The fibers can be made of metal, wood or synthetic material, and used to produce textiles or entities that are malleable, elastic, lightweight etc."

One of the main problems of current heart pumps is the fact that blood can start coagulating when it comes into contact with them. Blood clots can form, which roam around the body and can cause strokes or embolisms. If the surface of the artificial heart pump is given a kind of coating that the body perceives as a "natural" environment, however, blood clots could – at least in theory – be prevented.

The inner surface of natural blood vessels is lined with a layer of endothelial cells, which control the exchange between the blood and body's tissues. Therefore, Empa scientists are now working on an ultra-thin lining made of sticky polymer fibers that are less than a micrometer thick. Living endothelial cells are placed on this "fabric", where they form a monolayer – as they do in all lymphatic and blood vessels. This kind of tissue surface could trick blood cells into thinking the pump is one of the body's own organs. For the endothelial cells to feel at home in the artificial tissue, however, they need to be able to effectively "cling onto" the lining. A simple lining made of polymer fibers is ill-suited.

Electrospinning and living cells

This is where Empa's electrospinning unit comes in. The technique is used to produce polymers, i.e. purely organic and hybrid fibers measuring less than a micrometer in diameter, which makes novel membranes for use in medical engineering, catalysis and filter technology possible. An electric current is applied between a cannula, from which a polymer solution is squeezed, and a counter electrode – and this pulls threads. Thanks to the electric field, the threads twirl until they form a tissue-like membrane. Holding it in your hand, it feels like a wafer-thin, elastic cloth. "The membrane for the heart pump needs to be stable, firm and stretch-able in all directions," says Giuseppino Fortunato from the Biomimetic Membranes and Textiles lab. "It really has to withstand a lot." After all, the heart beats around 100,000 times a day.

Muscle cells form the foundation

This Mixed tissue made of fibers and cells can also be produced in the incubator. The Biointerface lab headed by Katharina Maniura is in charge of the cells, using smooth muscle cells that form a cellular structure on the hybrid membrane – as found in natural blood vessels. Endothelial cells are then supposed to settle on this "substructure".

The cells feel particularly at home if they find a substructure that reminds them of the body's own structures – more specifically, collagenous fibers such as from connective tissue. "We have to get muscle cells to produce collagen so the endothelial cells stick to it permanently," explains Maniura. "If the tissue is composed of two types of cells, they emit signals and thus communicate with each other. This also has the effect that the endothelial cells are stabilized on the surface and readily perform their natural functions." In order to render the electrospun fibers particularly attractive for the cells, the polymer fibers should be functionalized with cell adhesion peptides. The idea is for both the endothelial and the muscle fiber cells to be "presented" with their typical natural environment so the multi-layered structure lives as long as possible.

Verifying process in the bioreactor

Whether this also works in practice is being examined in a bioreactor. The material system, i.e. the synthetic elastomer pump wall developed by the Zurich Heart consortium, is exposed to "real" conditions together with Empa's cell-textile mixture.

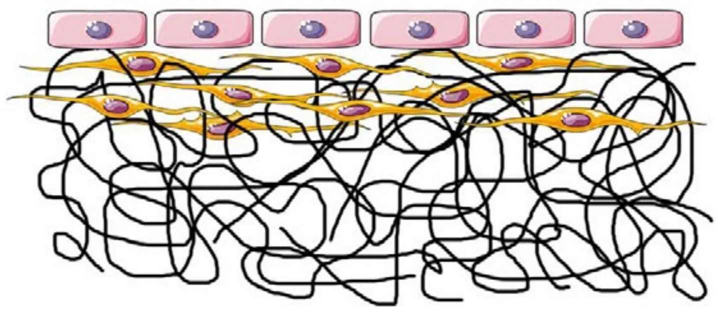
The reactor recreates the situation in the human body, allows a cell culture liquid instead of blood to flow by, and simulates pulsations that mimic the movement of the heart muscle. This should show the researchers whether the "camouflaged" materials can withstand the heavy strain in the human body.

"We will conduct a study using the first prototypes of the biomimetic heart pumps before the end of the year. But it will be many years before they can be used clinically," says Mazza. The pumps each have to be "grown" individually using the patient's own cells. Eventually, this will involve taking cells from the patients' blood, vessels or fatty tissue. These will then be grown in the lab for two to three weeks before the heart pump with the endothelial layer can be implanted.

"The concept would be too slow for emergency operations," explains Mazza. Nonetheless, patients with a cardiac insufficiency could use the biomimetic pump to relieve the strain to such an extent that the heart is able to regenerate under its own steam – help it to help itself, as it were. //

www.zurichheart.ethz.ch/hybridmembrane/

Camouflaging the pump membrane perfectly takes two layers of cells: muscle fibers nestle into the fleece itself. They form the carrier structure for the endothelial cells on the surface, which simulate the inner wall of blood vessels.



Events (in German)

9. Mai 2017
Kurs: Die Welt der Stähle
Zielpublikum: Industrie und Wirtschaft
www.empa-akademie.ch/staehle
Empa, Dübendorf

10. Mai 2017
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www.empa-akademie.ch/tblaser
Empa, Thun

18. Mai 2017
Kurs: Die Wärmebehandlung
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1. Juni 2017
Kurs: Elektrochemische Charakterisierung und Korrosion
Zielpublikum: Industrie und Wirtschaft
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Empa, Dübendorf

1. Juni 2017
Workshop: Massgeschneiderte Oberflächen an der Grenze zwischen Nass und Trocken
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