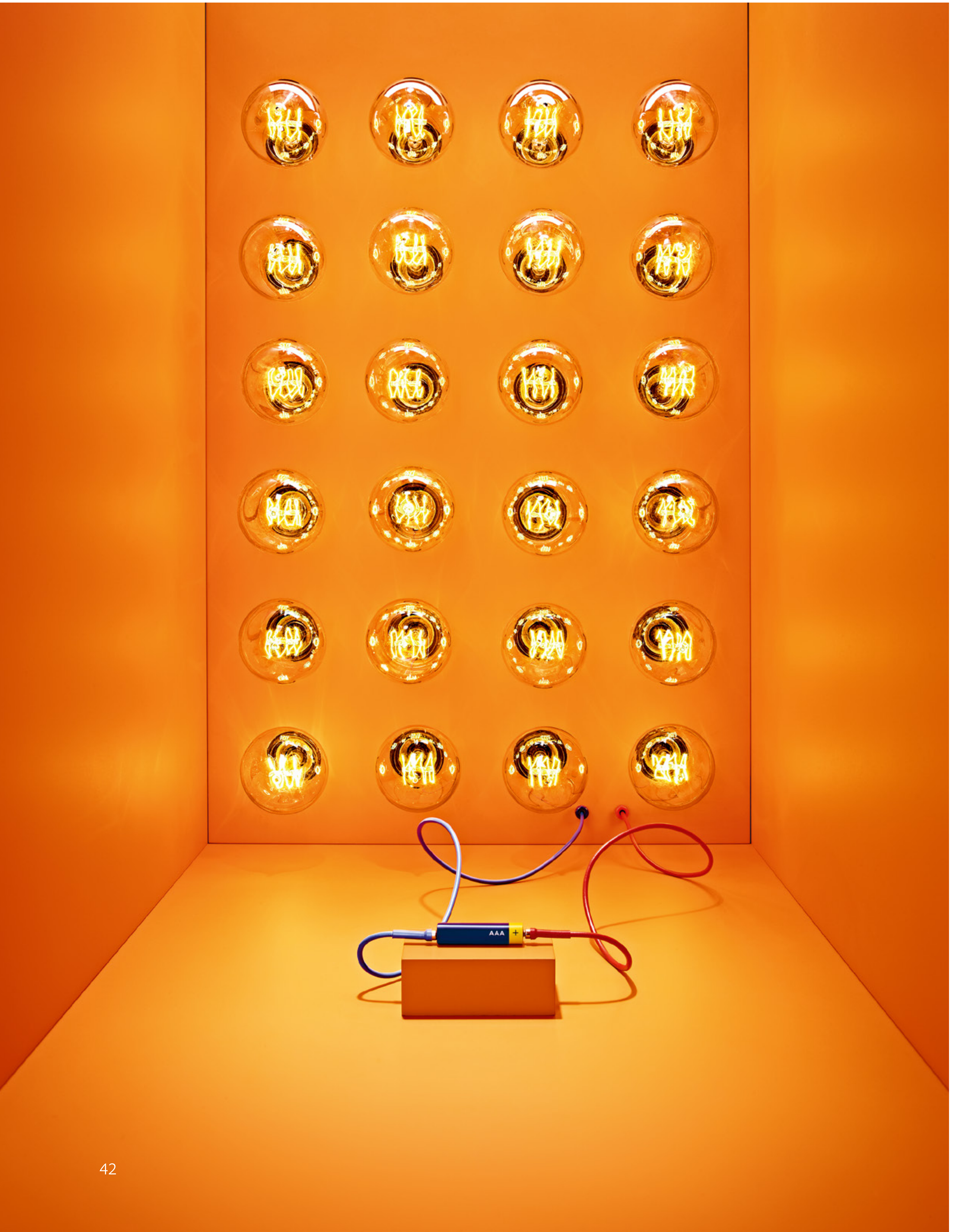


CHARGED AND SAFE

TEXT **TOM RADEMACHER**

Improved batteries are playing a key role in the energy transition and in sustainable mobility. Evonik is working to make energy storage systems more efficient and cost-effective. Even well-known technologies have substantial amounts of potential that is still untapped

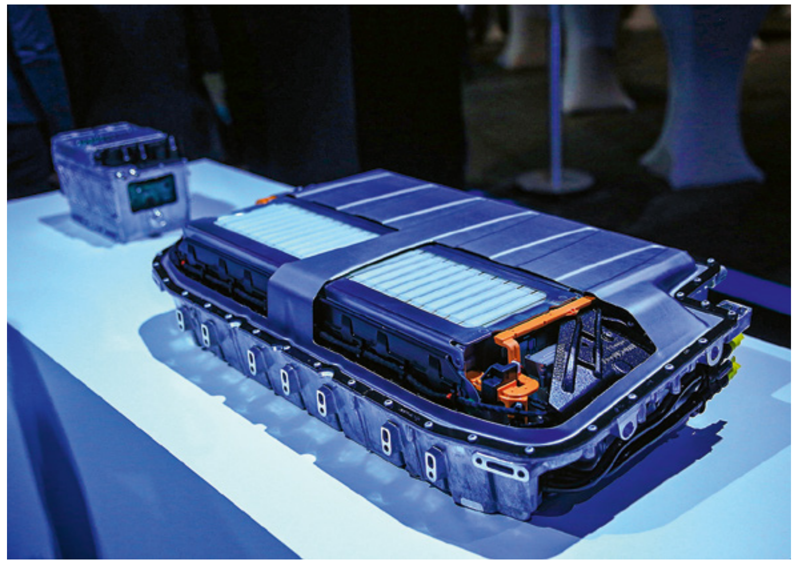
The *New York Times* doesn't often carry reports about the small town of Arnstadt in the German state of Thuringia. And if it does, it's because a young man named Johann Sebastian Bach was the town's organist three centuries ago. But since the summer of 2018, a very different star has attracted international media attention to this provincial town: This is where the Chinese company Contemporary Amperex Technology Limited, or CATL for short, is building its first battery factory outside China.

CATL, the world's biggest producer of batteries for electric cars, plans to invest two billion euros in this facility. The cornerstone has been laid, and the first rechargeable batteries for BMW cars will roll off the assembly line this year. BMW has ordered batteries costing a total of €1.5 billion. Up to 2,000 new jobs are to be created, and a decommissioned rail freight depot is being reactivated specially for CATL. "People are happy that a company that will offer jobs for their children and grandchildren is setting up a plant here," said the local director of Germany's federal employment agency to a *New York Times* reporter. Arnstadt residents are setting high hopes on battery technology.

And in this they are not alone. Energy storage systems have the potential to fundamentally change our economy and our society. Electric mobility, renewable energy sources, information technology, consumer electronics—just about every area of our lives depends on efficient energy or heat storage systems. These systems range from pumped storage plants that balance out the performance peaks of solar, wind, and hydroelectric power plants to dual-layer capacitors in electric cars' braking systems and electrolytic processes for generating energy-rich hydrogen from electricity (see the diagram on pages 50/51).

A CONSTRUCTION PRINCIPLE FROM THE 1990S

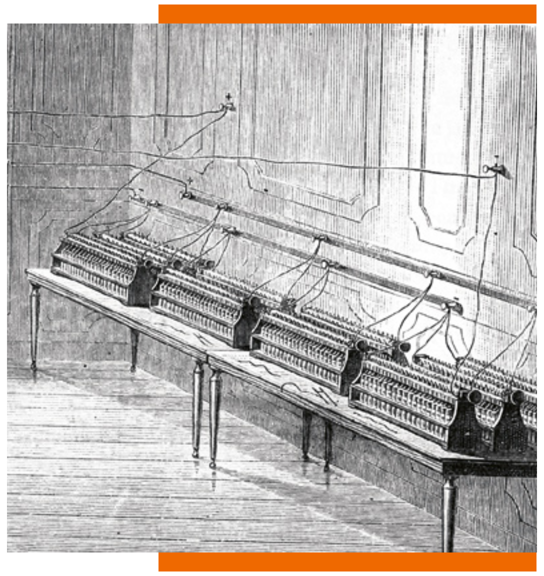
These systems' market opportunities are huge. During this decade, the automotive sector alone will invest US$300 billion in the development of electric vehicles, according to the Reuters news agency. The International Energy Agency (IEA) estimates that as many as 44 million electric cars may be sold worldwide in 2030. The forecasts of the French consulting company Avicenne Energy are much more conservative, but even it has predicted that the market for lithium-ion bat- →



Power pack Hybrid batteries for cars must be compact and deliver large amounts of energy within a short time

"The principle underlying the lithium-ion battery has not changed since the 1990s"

FRANK MENZEL, DIRECTOR APPLIED TECHNOLOGY SOLUTIONS AT EVONIK



The first lead batteries (based on the lead-sulfuric acid-lead dioxide system) were used around 1850—for telegraphic experiments, for example

teries in electric vehicles will almost quadruple over the next ten years to more than US$120 billion.

There are good reasons why modern lithium-ion batteries (or LIBs for short) play a key role in electric mobility: They are more high-powered and more efficient than anything that has come before. Their suitability for daily use is due to three inventors who received the Nobel Prize in Chemistry in 2019 for their work in this field (see the box on page 48). Even decades ago, lithium-ion batteries set the technical standard.

"The principle underlying the lithium-ion battery has not changed since the 1990s," says Prof. Frank Menzel, who teaches at the Technical University Ilmenau and is responsible for application technology for special oxides at Evonik. Menzel's statement might sound heretical to some. After all, developers have worked for three decades to lengthen lithium-ion batteries' service life, increase their capacity, and decrease their production costs. Between 2010 and 2019 alone, the price per watt-hour of storage capacity was reduced from one US dollar to less than 16 US cents. However, current LIBs basically still replicate the original structural design: The cathode consists of a lithium metal (mixed) oxide, and the anode is made of carbon. The cathode and the anode are kept apart by a thin separator, and all of the cell's components are soaked in a liquid electrolyte.

EVER STRONGER, EVER CHEAPER

In order to coax even better performance out of this established technology, Evonik is tinkering with almost all of its components. The goal is to achieve higher capacity, longer service life, and improved safety. And the road to this goal runs through the town of Rheinfelden near the Swiss-German border. This is where Evonik produces nanostructured particles of aluminum oxide and titanium dioxide. These particles could solve a whole series of problems, explains Dr. Daniel Esken, the head of the Application Technology Batteries unit at the Hanau location. Esken is also responsible for the battery projects conducted by the Silica Business Line at Evonik. "One of the challenges we face is the cathode material's reactivity with the liquid electrolyte," he says. "Undesirable reactions occur at this interface as a result of electrochemical processes as well as the high cell voltage." He points out one such reaction on an image that was captured with an electron microscope. Here the round cathode particles, which initially looked somewhat like shortbread cookies, have partially disintegrated after 250 charging cycles and literally crumbled. This disintegration over time irreversibly reduces the battery's total capacity.

A fine piece of work At the Applied Technology unit in Hanau, Evonik demonstrates how separator films are provided with a ceramic coating

THE MIRACLE CURE: ALUMINUM OXIDE

This effect can be significantly limited if the cathode particles are coated with aluminum oxide or titanium dioxide. In the coating process, the nanostructured oxidic powder is mixed with the component material of the cathode. The powder coats the particles, and in the finished battery it reacts with the electrolyte to form a sort of glaze that allows ions to penetrate it but prevents the particles from disintegrating.

A brutal test clearly shows the beneficial effect of aluminum oxides on the separator in a lithium-ion battery. Behind a sheet of bulletproof glass, nails are driven through two battery cells. The first battery cell explodes, but the second one doesn't—thanks to the aluminum oxide in the separator. "During the extrusion process our material can be incorporated into the plastic or, alternatively, it can be applied as a thin ceramic coating onto the separator film," Esken explains. The porous separator is only about 20 micrometers thick—that's less than the diameter of a human hair.

Esken's team is also working with Hanyang University in Seoul on the use of aluminum oxide in electrolytes—in combination with methacrylate as a functional group on the surface of the oxide particles. "Our material is applied onto the separator as a ceramic layer, and it polymerizes with additives in the electrolyte after the cell has been filled," says Esken, the battery expert. Through this process, a gel is formed. This not only prevents the LIB cell from leaking but also improves the adhesion between the cell's components.

Not far from Esken's office, Dr. Julia Lyubina from the Strategy & New Growth Business Unit is focusing her research on the anode. She too is using a helpful product from Rheinfelden, in this case a completely new one. "Today's anodes consist of graphite," explains Lyubina, a materials physicist. "But we know that if we integrate additional silicon into the anode we can significantly increase its capacity." Unfortunately, there's a problem: When silicon particles are charged with lithium ions, they can swell up to as much as 300 percent of their previous size. That can burst the anode; worse yet, the particles disintegrate all over again. In order to solve this problem, Lyubina's team has developed an innovative composite material along with its own production process. The spherical particles that are used in the anode are about 200 nanometers in diameter. They consist of silicon and carbon, with the silicon mainly filling up the core and the concentration of carbon increasing toward the surface of the particle. "If ten percent of the anode's weight is made up of silicon, we can double its ion capacity," explains Lyubina. Until a few years ago, Evonik's Rheinfelden location was →

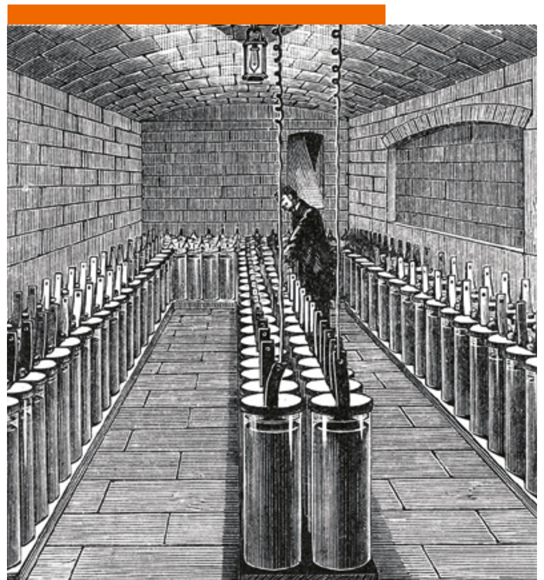
still producing pure silicon for the solar industry. An existing installation has now been converted to make the new product and is due to start pilot operation this year.

AN OLD TECHNOLOGY WITH POTENTIAL

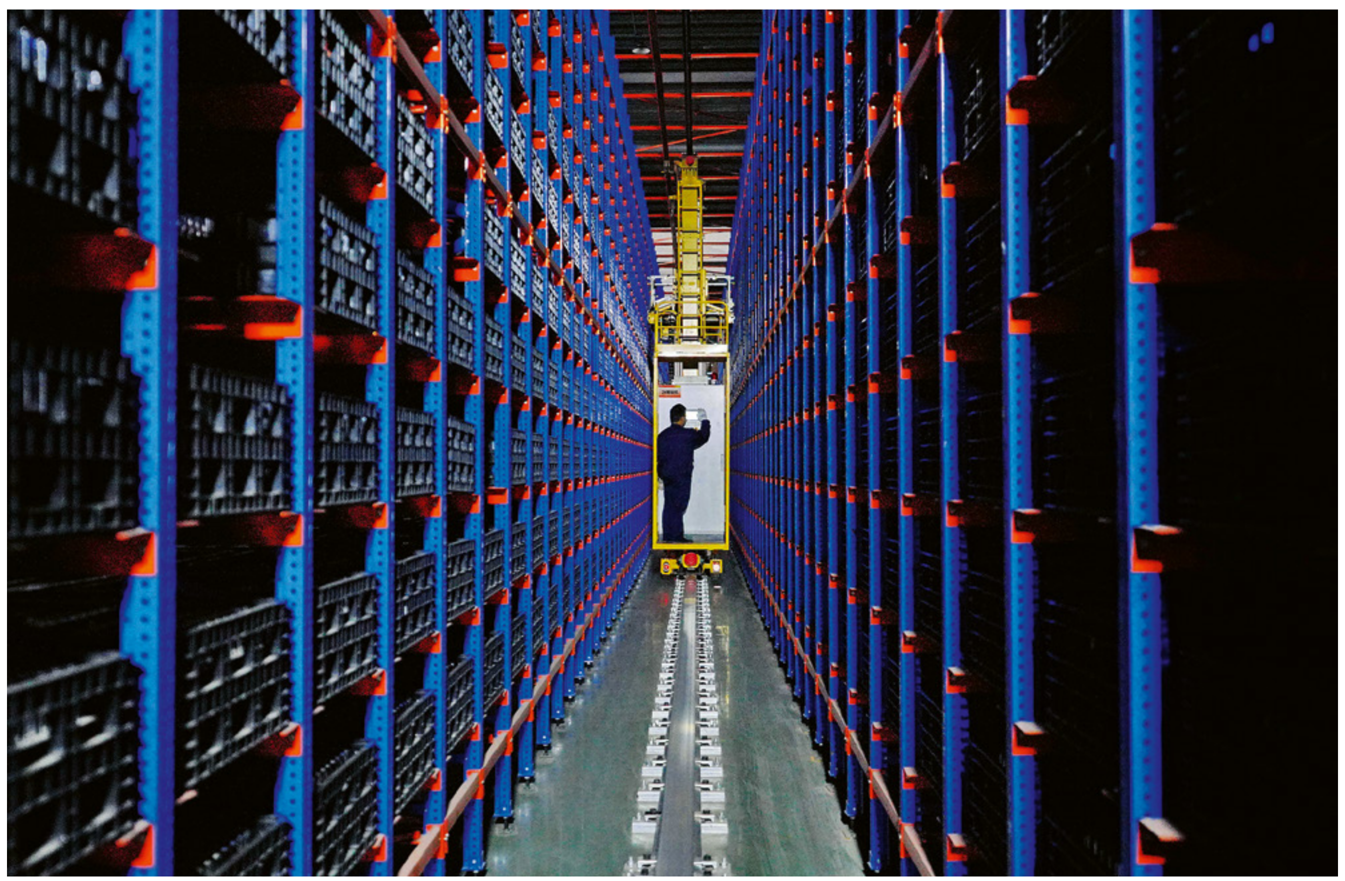
In the effort to extract even better performance from the currently available storage technologies, the lead-acid battery cannot be ignored. The traditional "automobile battery" is definitely not dead. In terms of the total storage capacity sold, it accounts for 70 percent of the world market. Lead-acid batteries with a total storage capacity of 400 gigawatt-hours are sold every year, and this figure is growing. Three quarters of these batteries are operating in automobiles with combustion engines.

Today these batteries as well are expected to perform better than they did in the past. Start-stop systems that switch off the engine when the car stops at a red light significantly increase the number of charging cycles and make demands on the battery in a wide range of states of charge. "The lead-acid battery really doesn't like these systems at all, but the most advanced versions of the battery cope with them well," says Dr. Jochen Settelein from the Fraunhofer R&D Center for Electromobility Bavaria (FZEB) in Würzburg. Settelein, an expert in the field of nanostructures, is the head of the Lead Acid Technology working group at the center.

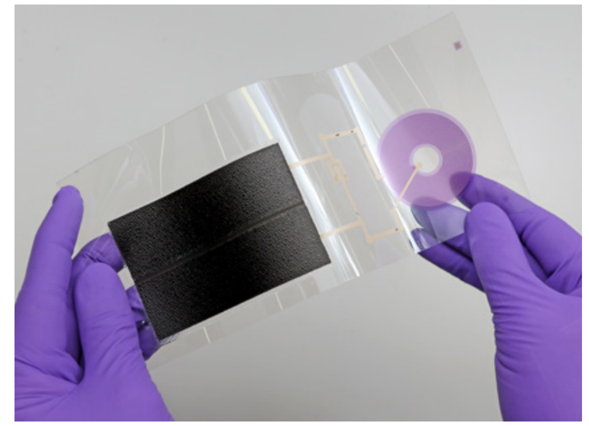
This type of battery is too heavy, and its energy density is too low, for use in hybrid and electric cars. But that doesn't matter in other applications. For example, in a forklift a lead-acid battery actually provides the necessary tail weight that prevents the forklift from tipping forward during operation. In stationary power storage systems in particular, this supposedly age-old



In the 19th century, before a network of power plants and cables existed, buildings such as the City Hall of Paris were supplied with electricity by batteries



A storage depot for lithium-ion batteries: According to the International Energy Agency, 44 million new electric vehicles could be on the road as soon as 2030



Rechargeable batteries made of plastic

In the spring of 2019 Evonik presented a technology that makes it possible to print batteries made of plastic onto almost any surface. These batteries are wafer-thin, flexible, and environmentally friendly to boot. This technology, which is known as TAeTTOOz®, is based on redox polymers—plastics that can hold and discharge an electric charge. Polymer batteries work without any metal or liquid electrolytes and are manufactured using a conventional printing process. They open up possibilities for using sensors to monitor supply chains or the integrity of food or medicines in the logistics and packaging industry, for example. Another interesting area of application for these flexible energy storage units is wearables—mobile devices that can be used to measure the wearer's bodily functions.

technology still has lots of future potential. The more that natural energy sources such as the sun and the wind are used, the more energy has to be retained in storage systems in order to balance out fluctuations in the power supply. According to the International Energy Agency (IEA), the worldwide installed power storage capacity almost doubled in 2018 alone. Most of this increase was due to electric batteries and "behind-the-meter storage"—in other words, consumers' individual power storage systems.

But major energy producers are also increasingly depending on electric batteries as temporary storage systems in order to smooth out network fluctuations and discrepancies between supply and demand. The IEA anticipates that the installed battery capacity for power grids will increase almost tenfold by 2040.

Lithium-ion batteries are in demand in this segment as well. For example, old batteries from electric cars can be reused here. And this is where the advantages of lead-acid batteries come to the fore. That's because their high weight and bulky dimensions play a very minor role in such applications, whereas their low price is all the more important. Lead-acid batteries cost only a third as much as lithium-ion rechargeable batteries per kilowatt-hour. What's more, they require no complicated charge control or cooling and they are environmentally friendly: About 99 percent of their component materials are recycled. The reusable-material cycle for lead has been well-established for decades, whereas for lithium it is still a distant goal.

ONE PROJECT, SIX PARTNERS

In order to exploit these advantages of lead-acid batteries for the benefit of the energy transition, Germany's Federal Ministry of Education and Research has been promoting the "AddESun" project at Settelein's Fraunhofer research center since 2017. The project's name mimics that of the electricity pioneer Thomas Edison →

> "With this configuration we are moving toward a physically determined performance plateau"

CHRISTOS SARIGIANNIDIS, A CHEMICAL ENGINEER AT CREAVIS, ON THE LIMITS OF LITHIUM-ION BATTERY TECHNOLOGY

The applications engineer Herbert Habermann checks a separator that has been coated with aluminum oxide on both sides

Award-winning battery researchers

The excellent daily utility of the lithium-ion battery is due to three inventors who were honored with the Nobel Prize for Chemistry last year.

The British-American solid-state chemist **Stanley Whittingham** (below right) conducted experiments with tantalum sulfide and potassium for the multinational oil company Exxon in the 1970s. He discovered that layered sulfide takes up ions from a metal anode in its interstices. Experts call this process "intercalation." It generates an electric voltage between the anode and the cathode. Whittingham subsequently replaced the tantalum sulfide in the cathode with the lighter substance titanium and used the less volatile element lithium instead of potassium as the ion donor in the anode. Whittingham's first battery cell already generated two volts of electrical power, but it was highly explosive. After several charging cycles, the anode metal forms needle-like structures called dendrites. If they penetrate the cell and reach the cathode, they cause a short circuit. Back then, the local fire department had to rush to Whittingham's laboratory so often that it threatened to send him a bill for its services.

Not long after that, the American physicist **John Goodenough** (middle), who was working at the University of Oxford, took up Whittingham's idea. He suspected that oxides could take up more ions than sulfides do—and he was proven right. His cathode, which was made of lithium cobalt oxide, promptly generated four volts instead of two. In addition, Goodenough was the first scientist to realize that the batteries did not have to be manufactured in the charged state; they could also be charged after they had been assembled.

The last component of lithium-ion batteries, which was the key element of their safety, was contributed by the Japanese scientist **Akira Yoshino** (left). Unlike his forerunners, he was employed by a company that had its own electronics department, the Asahi Kasei Corporation in Japan. In the early 1980's, the company was placing great hopes in portable consumer electronics. Sony had just recently scored a global success with the first Walkman. Yoshino developed an anode made of cobalt that smoothly intercalated the lithium ions. If no metallic lithium is present, the danger of dendrites is eliminated. Thus Yoshino had discovered the structural design of the lithium-ion battery that is still valid today. Sony launched the first one on the market in 1991.

BERND KALTWASSER

and is a combination of the words "additive," "energy," and "sun." Evonik, which is one of the six project partners, is providing the additives—in particular, nanostructured oxide particles from Rheinfelden.

"With the additives from Evonik, such as aluminum oxide, we can increase the porosity of the electrodes," explains Settelein. The aim is to have the electrolyte penetrate more efficiently into the electrodes that have received the additives, just as a liquid soaks into the pores of a sponge. That way the electrolytes can reach the maximum area of reactive surface. This ambitious goal can be summed up in the formula "3×30": 30 percent more charging cycles should become possible, thus further extending the battery's service life. The battery's chargeability—its capacity for taking up electricity—should increase by 30 percent. And the battery's energy density—its storage capacity per kilogram of material—should also increase by 30 percent.

Settelein admits that when he started working at FZEB seven years ago, he himself was skeptical about just how much potential remained in the lead-acid battery. He adds that this makes it all the more fascinating to see what can still be coaxed out of it today.

THE NEXT GENERATION OF RECHARGEABLE BATTERIES

However, the researchers at Evonik are turning their attention to new technologies as well. That's because the theoretical limits of the established lithium-ion battery technology, for example, are becoming ever more clearly visible. "With this configuration we are moving toward a physically determined performance plateau," says Dr. Christos Sarigiannidis, a chemical engineer who is working on the next battery generation at Creavis, Evonik's central innovation unit in Marl. "We are investing great hope in solid-state batteries," he says. These rechargeable batteries function without liquid electrolytes—a property that should make them safer and more powerful. That would be reflected in increased ranges for electric cars, for example.

The first prototypes already existed in the late 1950s, but this technology has only been approaching market maturity for about the last five years. Many companies, ranging from the gigantic battery producer Panasonic to automakers such as Toyota, Nissan, BMW, and VW, are working to develop a practicable version of the solid-state battery.

True blue Lithium mining, shown here in the Uyuni salt flats in Bolivia, is a target of criticism by advocates of environmental protection and human rights. A five-person team led by Dr. Alessandro Dani at Evonik recently started working on a technology for recovering lithium from used batteries with the help of a selective ceramic membrane. The idea behind the project, which is called "Blue Lithium," was recognized with an in-house Evonik innovation award in 2019. Dani now has a six-digit budget to spend one year working exclusively on refining this idea

Even one of the inventors of the lithium-ion battery, John Goodenough, who is now 97 (see the box on the left), has joined the race. In 2017, his team from the University of Texas presented a solid-state battery that uses glass powder as the electrolyte. It is claimed to be at least twice as powerful as traditional lithium-ion batteries. What's more, it may be possible to replace the lithium it contains with sodium.

ENERGY FROM THE OCEAN

The sodium battery is a long-cherished dream of the battery industry. Lithium exists in large quantities on our planet, but it's not available everywhere. Today the largest producers are Australia and Chile. China has secured access to massive deposits of lithium. An even rarer substance is cobalt. Some 60 percent of the world's supply of cobalt is mined in the Democratic Republic of the Congo—often by means of slavery and child labor, practices condemned by advocates of human rights. By contrast, sodium is available all over the globe, at least in coastal countries. Every liter of seawater contains ten grams of this element on average.

Evonik is primarily interested in the solid-state battery. More than two dozen solid electrolytes are currently under consideration. They can be roughly categorized into three groups as inorganic materials, organic polymers or composites. "The crux of every solid-state battery is the balance between the electrolyte's ion conductivity and its mechanical properties," says Sarigiannidis. Each of the materials mentioned above has advantages and disadvantages. For example, as yet there is no polymer electrolyte with good conductivity at room temperature. Creavis is working together with various Evonik business units to evaluate a wide range of solid-state electrolyte technologies based on Evonik materials.

However, it will take quite some time before the next generation of batteries can be used in mobile phones or even in electric cars. "Solid-state batteries will probably not hit the market until about 2030," Sarigiannidis estimates. In view of today's continuously growing need for energy storage, the currently available technologies will continue to dominate for quite a while.