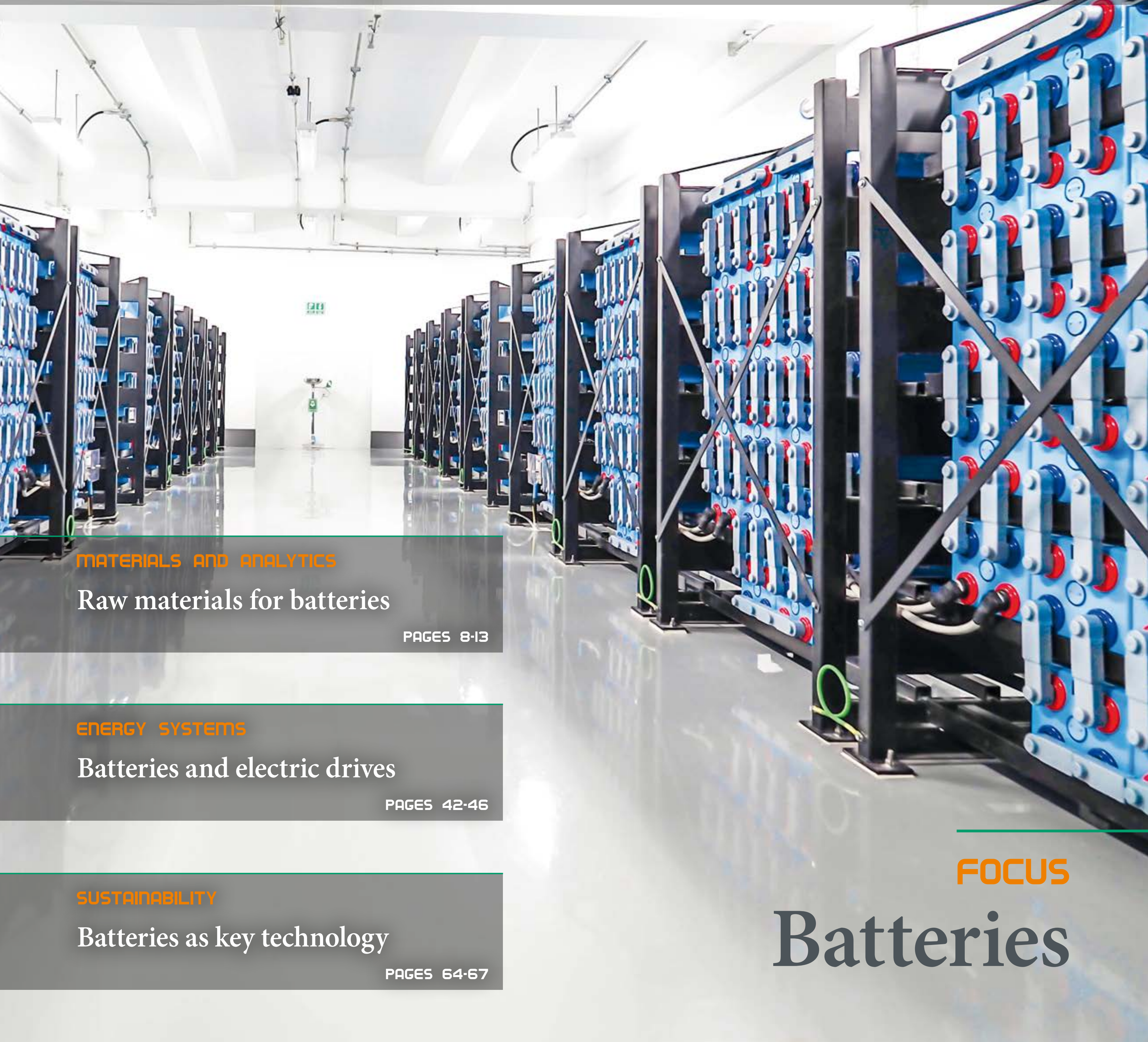
UNIVERSITÄT BAYREUTH

SPEKTRUM

The Science Magazine of the University of Bayreuth ■ Volume 15 ■ Issue 1 ■ August 2019



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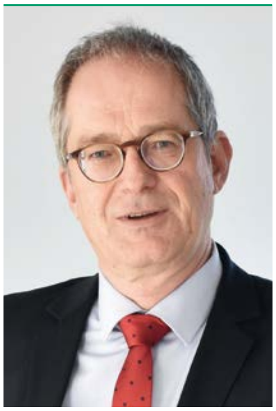
Batteries

Dear Readers,



■ *Prof. Dr. Stefan Leible, President of the University of Bayreuth.*

As we face a future of climate change, environmentally sustainable energy supply is one of the crucial issues of the 21st century. New energy storage technologies play a key role here. With its Bavarian Centre for Battery Technology (BayBatt), the University of Bayreuth is resolved to spur onward innovative developments in this field.

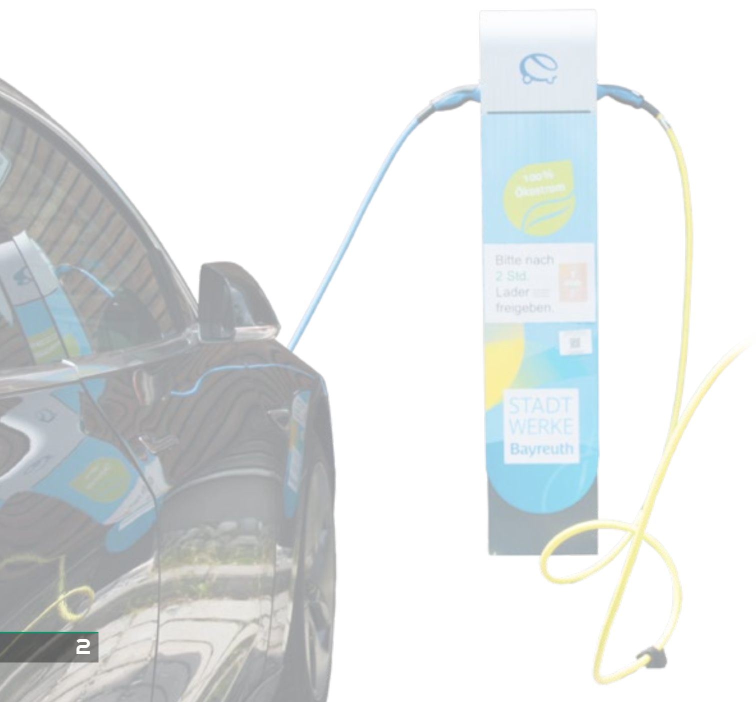
The aim is not to reduce CO_2 emissions simply by expanding e-mobility. Stationary storage systems in private households, industrial plants, and public institutions that are integrated into intelligent energy systems will all help to further increase the share of renewable energies in the electricity we consume. Nevertheless, today's state of the art in battery technology alone will not be enough to achieve this. We therefore intend to intensify basic research in the field, and use our findings to help develop more effective, safe and marketable storage technologies. Once again, we can be sure the excellent interdisciplinary cooperation that has characterized our campus university for more than four decades will show its mettle in these efforts. Indeed, physics and chemistry, the engineering sciences and information systems will have the means to network more closely than ever before. Meanwhile, the social and ecological problems associated with the mining of raw materials for today's batteries in African and South American countries must not be overlooked: In fact, the development of battery storage systems based on other, readily available and recyclable materials is high on the agenda.

The decision of the Bavarian State Government to locate the Bavarian Centre for Battery Technology at the University of Bayreuth has once again shown without a doubt: In the field of energy research and energy technology, this Campus is a veritable hothouse of science for our future.

Kind regards,

Your

Prof. Dr. Stefan Leible
President of the University of Bayreuth



Further SPEKTRUM issues

On the homepage of the University of Bayreuth you will find previous issues of SPEKTRUM on the following topics:

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1/2018:	Planet Earth
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When the state premier of Bavaria announced in April 2018 that the University of Bayreuth would receive a new research facility – namely a Bavarian Centre for Battery Technology (BayBatt) – the response on Campus was unanimous: we surely meet the preconditions for this endeavor. The focus area of „Energy Research and Energy Technology“ is, after all, firmly established in both research and teaching in the science and engineering at the University of Bayreuth, and the Centre for Energy Technology (ZET) has been bundling the relevant competencies for battery storage from various disciplines for many years now.

BayBatt is set to continue this campus-wide cooperation, and keen to develop this matter of „batteries“ on several scales. These range from the investigation of molecular structures and processes, to the modelling of individual electrodes and cells, all the way to the control and coordination of batteries in an intelligent energy system. The new issue of SPEKTRUM you are holding seeks to highlight the variety of exciting questions facing battery researchers in Bayreuth.

Especially our junior scholars will find the challenging research projects at BayBatt to their taste. Master's students, doctoral students and postdocs from Germany and abroad are most welcome to contribute their own ideas and concepts. In the medium term, we also plan to set up a course of study in battery research and technology. Like the University of Bayreuth as a whole, its Centre for Battery Technology has a „third mission“: In view of the technical, economic and socio-political challenges associated with Germany's energy transition, BayBatt will cooperate with companies and public institutions in its search for innovative solutions.

Indeed, batteries have the potential to initiate a paradigm shift in the energy and transport sectors which will ultimately affect all citizens. On this note, I trust you will find new and intriguing food for thought in our latest issue of SPEKTRUM.

Enjoy!

Yours sincerely

Prof. Dr.-Ing. Michael Danzer
Head of the Bavarian Centre for Battery Technology (BayBatt) at the University of Bayreuth

Prof. Dr.-Ing. Michael Danzer is the Chair of Electrical Energy Systems (EES) at the University of Bayreuth.

SPEKTRUM-Magazine of the University of Bayreuth

Circulation:
German edition: 1.500 copies
English edition: 500 copies

Published by:
University of Bayreuth
Press, Marketing &
Communications (PMK)
95440 Bayreuth
Phone 0049 - 921 55 - 53 56 / - 53 24
pressestelle@uni-bayreuth.de

Editorial management:
Christian Wißler (V.i.S.d.P.)

Translation:
Ralph Reindler, Daniel Mook

Printing:
bonitasprint gmbh, Wurzburg

Layout and Design:
GAUBE media agentur, Bayreuth

Image source labelling:
sst: www.shutterstock.com

Christian Wißler M.A., PMK staff division of the University of Bayreuth, Research Communications.

Cover figure: Battery room in a power plant (sst).

Fig. left: Electric filling station on the Campus of the University of Bayreuth (Photo: Christian Wißler).

Batteries

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The Bavarian Centre for Battery Technology (BayBatt) on the Campus of the University of Bayreuth was inaugurated in September 2018 beside the representation of a hi-tech battery (Photo: Peter Kolb).

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Energy storage – one of the central questions of the future

Q&A with Bernd Sibler, MdL, Bavarian State Minister for Science and the Arts

Fig. 1: „Sun disk“ by the glass artist Florian Lechner in front of the Faculty of Engineering Science (Photo: Christian Wißler).

Mr. Sibler, not a year has passed since your ministry set up the Bavarian Centre for Battery Technology – BayBatt for short – on the Campus of the University of Bayreuth. What prompted the Bavarian State Government to set up a new centre in this field of energy research? And why was BayBatt founded as an institute of the University of Bayreuth – and not at a different location, for example as a non-university institute?

Energy storage is one of the central questions of the future! In the international search for answers, we want to create innovative initiatives here in Bavaria. Having our own research centre enables us to bundle our expertise and carry out in-depth research. Our goal is to initiate promising developments along the entire value chain of battery storage systems. In addition to research, we also focus on educating and training young professionals. After all, we need visionaries and problem solvers in this future field! For this reason, we want to be able to offer attractive opportunities.

The University of Bayreuth's plan for establishing a research and development centre for battery technology took all these points into account. The orientation and focus of the university made it possible for us to open the Bavarian Centre for Battery Technology in September of last year – just a few months after its announcement.

After all, Energy Research and Energy Technology has been an important research focus at the University of Bayreuth for years, involving several disciplines and faculties. We are now able to build on this expertise and these competencies.

In his government statement of April last year, in which he announced the research and development centre for battery technology at the University of Bayreuth, Prime Minister Söder stated: „Electromobility is the future.“ What impact does the state government expect from research at the University of Bayreuth?

If we want to lead the way in climate protection and reduce our dependence on fossil fuels, we cannot avoid electric mobility. However, there is still some room for improvement here, for example in terms of range and the question of what will happen to the batteries when they are no longer usable. In these areas, BayBatt´s interdisciplinary approach, which focuses on the entire life cycle of a battery, could become a driving force for developing an efficient and sustainable battery of tomorrow.

The coalition agreement of the state government consisting of the CSU and Free Voters has extended battery research at BayBatt to include stationary energy storage devices. What is the significance of research into innovative storage technologies for regional and national energy system transformation?

Continuing to develop stationary energy storage systems is the key to the energy supply of tomorrow.

Fig. 2: The central Campus of the University of Bayreuth (Photo: UBT).

In Bavaria, we have already achieved great success in expanding renewable energy sources. However, stationary energy storage systems are essential for the economic and sustainable use and networking of this decentrally produced green energy. They allow us to compensate for the fluctuations of wind and solar power and guarantee wide-ranging security of supply in our electricity grids – thus we can make our lives a bit better in a concrete and tangible way.

The next generation of safe, intelligent, and sustainable energy storage systems will come from Bayreuth – this was announced by the state government in its Ministerial Council resolution of September 2018. It also promised interdisciplinary cooperation and close networking between science and industry. How can this be achieved?

The University of Bayreuth is integrated into a broad and above all extremely successful network of expertise together with non-university partners. BayBatt will also benefit considerably from this! For example, the research groups involved are already linked to industry in a variety of ways within the framework of projects or industrial contracts. In addition, the BayBatt Advisory Board, composed of representatives from science and industry, will provide an important external impetus.

What direct and indirect effects do you expect to see with regard to the Bavarian economy? What role will battery technology play in the country´s future industrial policy?

BayBatt is closely linked to the economy. Accordingly, research will focus on the needs of the economy and provide support in solving concrete problems in the field of battery technology. In addition, we are responding to the existing demand for specialists in this area with a range of courses planned.

Fig. 3: Bernd Sibler, MdL, Bavarian State Minister for Science and the Arts (Photo: ©StMWK).

Battery technology undoubtedly plays a central role in Bavaria´s industrial policy when it comes to mastering the current challenges in the transport and energy sectors. Modern and efficient batteries play a key role in both electric mobility and energy supply. Successful research and development projects in the field of battery technology are therefore immensely important for the future viability of Bavaria as a location for the industry. Above all, the innovations that result from such projects help to strengthen Bavaria as a business location.

Let´s look to the future: What will BayBatt look like in 2028? What achievements and successes do you expect to look back on 10 years after the establishment of this research centre? And what do you want to do as the Bavarian Minister of Science to make this vision a reality?

I am convinced that BayBatt will successfully position itself as a highly visible research institution in the years to come! In many houses, appliances, and cars, we will surely find a range of applications for battery technology that originated in Bayreuth. I will continue to closely monitor BayBatt´s development to ensure this success. And I will do my utmost to support this unique research institute in Upper Franconia!

The questions were posed by Michael Danzer and Christian Wißler.

■ Thorsten Gerdes

Raw materials for batteries

Performance isn't everything

■ *Salar de Uyuni in the Southwest of Bolivia, at an altitude of 3,653 metres above sea level, is not only the largest salt pan in the world, but also contains one of the world's largest deposits of lithium (sst).*

> „The energy requirements in the extraction and refining of battery materials are often considerable."

Since the Italian physicist Alessandro Volta invented the battery in 1800, new types of battery have been developed time and again. Whether smartphone, hearing aid, remote control, pacemaker, starter motor, or uninterrupted power supply for large systems – the batteries used are as varied as their applications. In view of climate change and the need to improve air quality, especially in large cities, batteries have gained new significance as energy storage devices, to a degree that was unimaginable just a few years ago. Batteries today are expected to be rechargeable, contain as few toxic substances as possible, and consist of raw materials that are readily available and inexpensive. Even under critical conditions such as overheating or mechanical damage, batteries must be safe, and recycling should be mandatory at the end of the longest possible service life.

All the batteries sold on the global market these days per annum have a total storage capacity of around 500 gigawatt hours. A nuclear power plant would need about half a year to fully charge them from new. The energy storage roadmap of the Fraunhofer Institute for Systems and Innovation Research (ISI) forecasts a demand for storage capacity of 8,000 to 10,000 gigawatt hours (GWh) per year for 2050.[1] And sufficient raw material resources, manufacturing technology and capacity are not the only prerequisites for meeting this demand. Battery materials, cells and systems must also be optimised or even completely redeveloped.

For 15 years, research groups at the Chair of Materials Processing in Bayreuth have been developing battery materials and manufacturing processes, manufacturing cells, characterizing and evaluating them physically and electrochemically. The focus has been on anode materials for lithium-ion batteries, anode and cathode materials for rechargeable zinc-air batteries, separators for separating the anode from the cathode, and analyses to elucidate the ageing processes in cell components. In addition, the research work also deals with the question of how to replace battery raw materials that have come under criticism from an economic, social, ecological, or political point of view.

Availability of raw materials

The production of batteries requires raw materials such as lithium, cobalt, nickel, manganese, and graphite, which are not in infinite supply in the earth's crust, and are much sought after for applications in other areas as well. At the same time, global demand is rising. In 2015, the global demand for storage capacity for lithium-ion batteries was still around 70 GWh, but by 2025 it will already be 535 GWh – even based on moderate growth scenarios. The good news is that the global reserves of all battery raw materials will clearly exceed the forecast demand for the next few years. However, this does not rule out the possibility of temporary shortages or price increases for individual raw materials.

Despite optimistic forecasts, however, the fact that the production of battery raw materials is often accompanied by social and ecological problems, even today, should not be ignored. Working conditions in the mines are harmful to health in many raw material-rich countries around the world, and wages are low. Moreover, it is not uncommon for conflicts to arise between mining companies and the local population over water consumption. Polluted waste water resulting from the mining and processing of battery raw materials can damage the environment. In addition, the energy requirements in the extraction and refining of battery materials are often considerable, which increases „grey energy"[2] but also the costs. Five important battery raw materials – lead, lithium, cobalt, graphite, and zinc – will be examined in more detail below.

Lead

Since the 1950s, the most important battery raw material has always been lead. This refers to both world demand of almost nine million tons per year, and to demand for battery capacity. This currently stands at just under 400 GWh per year, which is four times higher than for lithium-ion batteries. As a toxic heavy metal, lead has a special position among battery materials. Many established applications, e.g. lead-containing screen tubes, have lost their technological significance. Other applications, e.g. lead in metal solders, are prohibited by law. Therefore, a good 80 percent of the lead available worldwide is available for use in lead batteries.[3] In addition, the recycling rates are very high compared to other battery raw materials. This is not only due to the sophisticated recycling technology, but also to a deposit system

AUTHOR

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for lead-acid batteries in Germany, which is unique in comparison with other battery raw materials. Of the 370,000 tons of lead processed in Germany every year, around 65 percent comes from recycled lead.[4]

■ Fig. 1: Lead-acid batteries post mortem (above). The formation of lead sulphate crystals (below) has led to the blocking of the lead electrode (Images: Tobias Michlik).

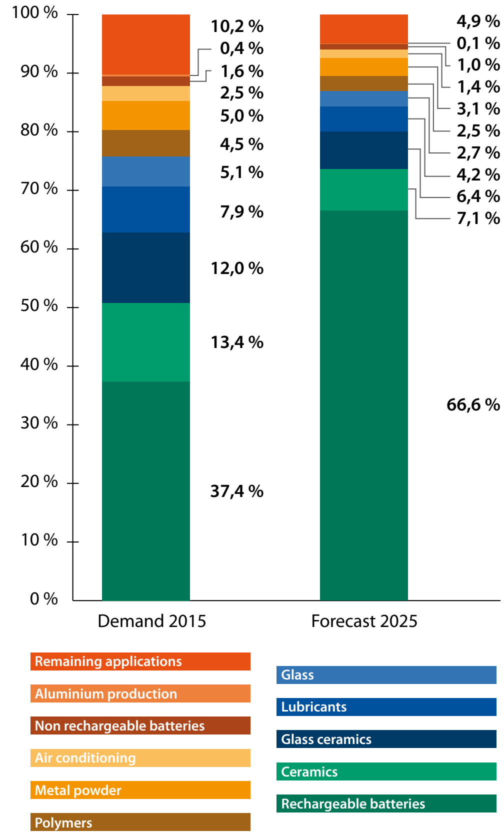
Lead-acid batteries are well suited for use as starter batteries in vehicles, or to ensure an uninterrupted power supply in industrial plants. They have acceptable cycle stability and the price-performance ratio is favourable. However, cycle stability drops drastically when the depth of discharge increases – for example in electric vehicles that are equipped with an automatic start/stop system to save energy. In this respect, there is still scope for development of this old type of battery. It will probably take until 2025 for the decades-old dominance of lead-acid batteries to be ended by other battery types, in particular lithium-ion batteries.

Lithium

Lithium is an important component not only in glasses, glass ceramics and ceramics – for example in hobs or dental prostheses - but also in batteries. Because it reacts most strongly with moisture among all alkali metals, the battery cells must be manufactured under absolutely dry conditions. Today, well over a third of the lithium produced worldwide is already used in lithium-ion batteries. Even cautious growth forecasts predict that this share will rise to two thirds by 2025.[5]

The main raw materials used for battery production are lithium-bearing minerals, which are mined especially in Australia, and lithium-bearing brine deposits in Chile. The combined output of the two countries currently covers about 80 percent of global lithium demand. Due to the expected steep increases in demand, many countries are expanding their production capacities or putting disused mines back into operation. New mining projects launched. The price of lithium, which has more than tripled since 2015, also favours mining deposits with a low lithium content, which requires higher processing costs. Recently, however, the price of lithium has fallen so sharply that the profitability of some projects has become an issue.

The Zinnwald deposit in Saxony near the German-Czech border could also be used to produce significant quantities of lithium in the future. Current



■ Fig. 2: Lithium demand in 2015 compared to forecast 2025 (Illustration: Andreas Gaube). Sources: Roskill Information Services Ltd.: Lithium: Global Industry, Markets & Outlook. London 2016 (Demand 2015); DERA Rohstoffinformationen: Raw Material Risk Assessment - Lithium Berlin 2017 (Prognose 2025), cf. Remark 5. This forecast is based on a scenario in which total demand growth is 9.2 percent.

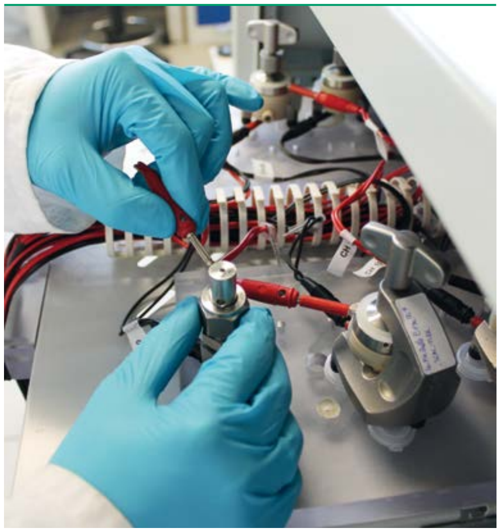


Fig. 3: Test stand for the electrochemical characterization of experimental battery cells (left), experimental cells for the electrochemical analysis of novel battery materials (right) (Photos: Christian Wißler).

RECOMMENDED READING

T. Michlik et al.: Improved Discharge Capacity of Zinc Particles by Applying Bismuth-Doped Silica Coating for Zinc-Based Batteries. Batteries (2019), Vol. 5 (1). DOI:10.3390/batteries5010032.

estimates point to 25 million tons of mineral, with an average lithium content of 0.45 percent.[6] The most important mineral in this deposit is tin forestite with a lithium content of about 1.6 percent.[7]

Cobalt

Cobalt is an important component in superalloys, hard metals, steels, enamels, and glasses. However, almost half of the 117,000 metric tons produced worldwide in 2017 were used for battery production. The raw material cobalt is often regarded as particularly critical: it can be replaced by other raw materials to a limited extent only, and deposits are restricted to a few countries. The DR Congo, for example, is responsible for over 64 percent of global cobalt mining, the Russian Federation for 4.6 percent, and Australia for 4.2 percent.[8] The DR Congo is by far the most important cobalt supplier and, with 3.5 million tonnes, possesses about 48 percent of the world's cobalt reserves. The country risk – resulting from uncertain political, economic and social conditions – is considered particularly high in this Central African country. Here mining is often associated with child labour and illegal small-scale mining to finance militias.

About 75 percent of the cobalt required worldwide comes from industrial mining, 10 percent from recycling, and about 13 percent from small-scale mining. Today, the certification of mining and cooperatives helps to at least partially prevent the most serious abuses of the past. Small-scale mining, which employs 150,000 to 200,000 people in Congo, will thus continue to make a substantial contribution to the global supply of cobalt in the future.[9]

As a result of the growing economic importance of e-mobility, which relies on lithium-ion batteries, demand for cobalt is expected to double by 2026.[10] This forecast already takes into account the fact that the cobalt content in these batteries is set to decrease, thanks to new cathode materials being used instead. Like all raw materials, cobalt is likely to become more expensive in coming years. This development favours investment decisions to expand primary

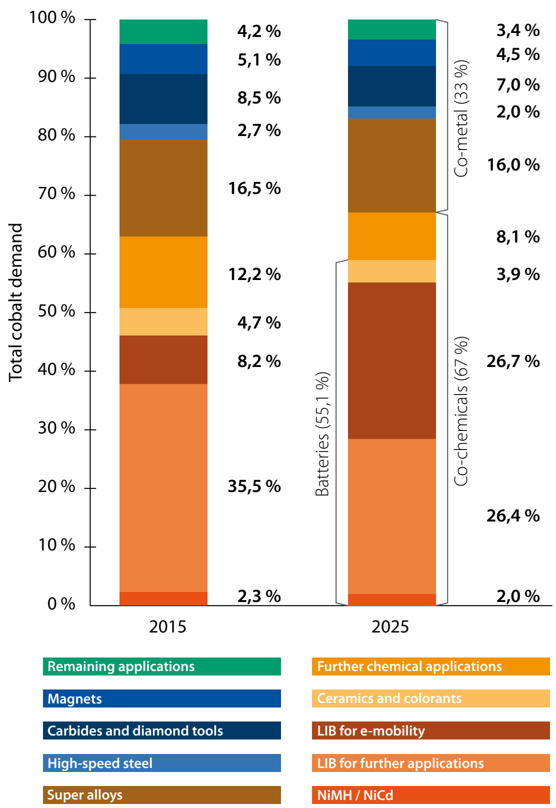


Fig. 4: Cobalt demand by application areas in 2017 and 2026 (Illustration: Andreas Gaube). Data from S. Al Barazi: Raw Material Risk Assessment – Cobalt. DERA Rohstoffinformationen 36. Berlin 2018.

Fig. 5: The Bou Azzer cobalt mine in the Lesser Atlas mountains in Morocco (Foto: Sunart Media / Shutterstock.com).

Fig. 6: Working group of the project „Coatemo" in the graphite mine Kropfmühl in Bavaria. The material mined here and refined into graphene is further processed in Bayreuth into graphite-silicon anodes for lithium-ion batteries (Photo: Landshut University of Applied Sciences).

production, so that there is no need to fear supply bottlenecks in the medium term.

Graphite

No graphite, no pencils. The material is even more important in the refractory industry, in foundries, in brake linings, as an electrode material in metallurgy, but also in batteries and fuel cells. About 1.2 million tons of graphite flakes are produced annually.[11] However, only 380,000 tons of these are of sufficient quality to be used for anodes in lithium-ion batteries. The special thing about graphite is that it is not only available as a natural resource, but can also be produced synthetically. In fact, the advantages of natural and synthetic graphites are mutually complementary, meaning that battery anodes can be optimized by combining them. Prices for graphite, at about 1,000 euros per ton, are moderate and relatively constant compared to other battery raw materials.[12] Nevertheless graphite is considered a critical raw material - not because of a lack of availability, but because of the fact that world supply is concentrated in China and India, with market shares of 71 and 14 percent, respectively.[13]

In Bavaria graphite is traditionally mined in the Kropfmühl graphite mine. The mine operator, AMG Kropfmühl, is developing the refining of graphite into graphene in a project sponsored by the Federal Ministry of Education and Research (BMBF). These two-dimensional modifications of the graphite are further processed by Future Carbon and the Institute for Innovative Process Technology (InVerTec) in Bayreuth into new silicon-carbon anodes. These anodes are characterized by high cycle stability and would therefore be suitable for a new generation of lithium-ion batteries.

Zinc

Zinc is a readily available, inexpensive, and long-established raw material for primary batteries. A distinction must be made between zinc-carbon, alkali-manganese, silver oxide, and zinc-air batteries. Every year 13.7 million tons of the metal is offered on the world market, which is mainly used for corrosion protection of steel, in cast alloys, or as a component of brass. In contrast, the demand for zinc for batteries is of secondary importance.[14] However, battery zinc of very high purity is still required, in fine powder form, precisely doped with other metals (bismuth, indium). This leads to an increase in production costs. These days, zinc is used very frequently in the primary batteries of hearing aids.

Zinc-air batteries differ from other zinc batteries in that zinc reacts with atmospheric oxygen, and is oxidized in the process. Because the cathode material is not an integral part of these batteries, they are lightweight and compact. At around 1,000 watt hours per kilogram, they have a theoretical energy density that is three times higher than that of lithium-ion batteries. The dream of battery researchers is therefore a rechargeable zinc-air battery, which combines this high energy density with great cycle stability, as it is realized in modern lithium-ion batteries. Such a secondary battery would be excellent for recycling, and the raw material costs would be low.

1 Fraunhofer Institute for Systems and Innovation Research ISI: Energy Storage Roadmap (Update 2017) – High Energy Batteries 2030+ and Prospects for Future Battery Technology. Karlsruhe 2017.
2 "Grey energy" is the energy required for the production, transport, and disposal of a product.
3 S. Mohr, D. Giurco et al.: Global Projection of Lead-Zinc Supply from Known Resources, Resources (2018), 7(1), 17. DOI 10.3390/resources7010017.
4 Federal Institute for Geosciences and Natural Resources: Raw Material Science Profiles - Lead. Hannover 2018.
5 M. Schmidt: Raw Material Risk Assessment - Lithium DERA Rohstoffinformationen 33, Berlin 2017.
6 A. Stark: Lithium from Saxony to provide supply security for batteries, Process – Chemie.Pharma.Verfahrenstechnik, 19. Feb. 2019.
7 The Zinnwald Lithium Project: Lithium compounds from Germany. DERA Industrieworkshop 27. Juni 2017, Berlin.
8 S. Al Barazi: Raw Material Risk Assessment – Cobalt. DERA Rohstoffinformationen 36: Berlin 2018.
9 S. Vetter: Current developments and field of players in the Congolese small-scale mining sector, DERA Industrieworkshop zur Verfügbarkeit von Kobalt für den Industriestandort Deutschland. Berlin, 2. Juli 2018.
10 Ibid.
11 U.S. Geological Survey: Mineral Commodity Summaries, 2018.
12 Federal Institute for Geosciences and Natural Resources (BGR): Preismonitor Oktober 2018.
13 Federal Institute for Geosciences and Natural Resources (BGR): Raw Material Science Profiles - Graphite, March 2014.
14 U. Dorner: Raw Materials Risk Assessment – Zinc. DERA Rohstoffinformationen 25. Berlin 2015.

However, today's zinc-air batteries still have the disadvantage that they age comparatively quickly. During the discharge of the anode, soluble zincate ions are formed which, in high concentrations, form an electrically non-conductive zinc oxide layer. As a result, the conductivity of the anode and thus also the cycle capacity of the battery decreases steadily. This is where the BMBF-funded „PrintEnergy" project at the Chair of Materials Process Engineering comes in. In order to improve cycleability, researchers are developing a glass coating for the zinc particles contained in the anode. As a result of the coating, a gel electrolyte is formed on the anode during discharge, which absorbs the zincate ions and still remains electrically conductive. Bismuth oxide is integrated into the glass network to increase conductivity and further improve the rechargeability of the battery.

And the Bayreuth researchers are working on the optimisation of zinc-air secondary batteries in one other respect: In order to reduce the use of the critical raw material cobalt, they are developing materials for the cathode of these batteries – the so-called air cathode – which contain little or no cobalt. The air cathode differs from other battery cathodes in that it draws the oxygen required for the generation of electrochemical energy from the surrounding air. It ensures a continuous supply and discharge of oxygen because it essentially consists of a gas-permeable layer and a catalytically active layer. Only the processes in this reactive layer enable the partial reactions necessary for charging and discharging the battery: the reduction of atmospheric oxygen (O_2) and the re-oxidation of the discharge product (OH-) to oxygen. Although precious metals such as platinum and iridium are suitable for use in air cathodes thanks to their high catalytic activity, they are very expensive and not very stable. The Bayreuth research work in this area therefore concentrates on the development of catalyst materials which not only contain as little cobalt as possible, but are also free of precious metals.

Even if the geological availability of the battery raw materials is basically given, resource conservation through efficiency increases and recycling strategies remains imperative, as does the development of substitution strategies. Research, development and an in-depth understanding of materials are therefore all indispensable for the sustainable transformation of our energy supply.

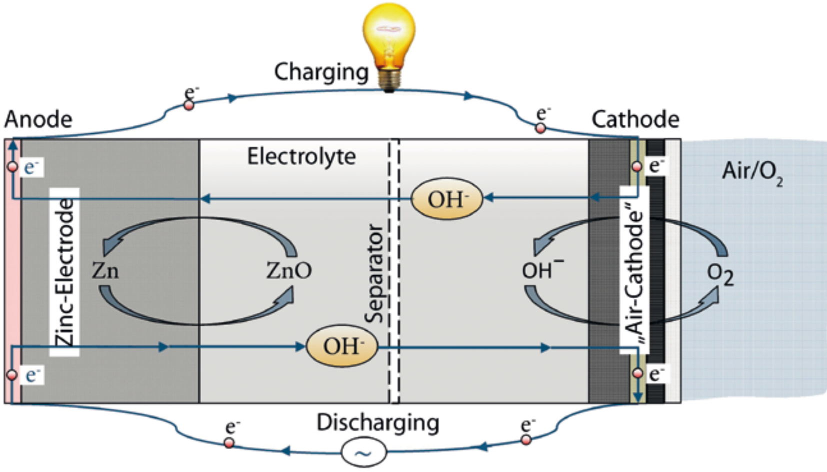
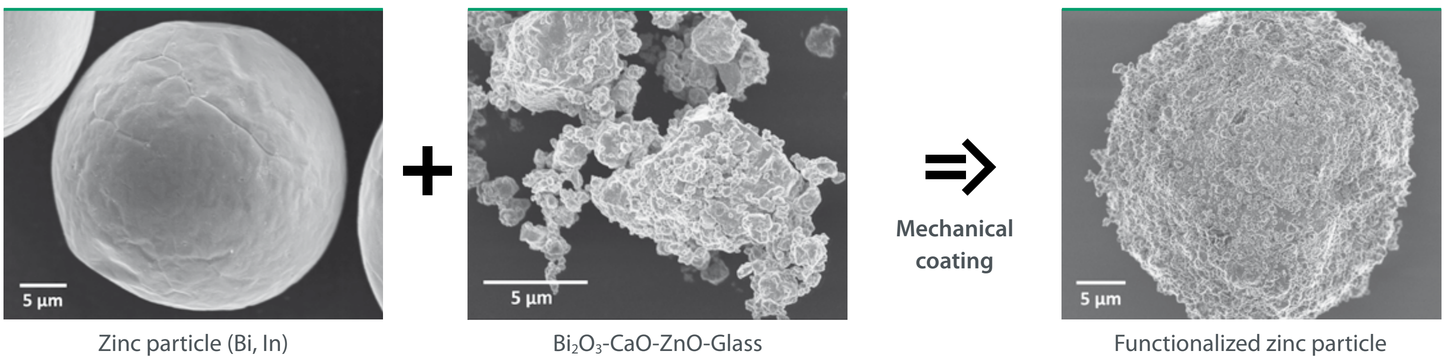


Fig. 7: Functional principle of a zinc-air secondary battery (Illustration: Michael Fink).

Fig. 8: Test cell for investigating the electrochemical properties of the active materials (Photo: Michael Fink).



Prof. Dr. Monika Willert-Porada was Chair of Materials Processing at the University of Bayreuth until her death in December 2016. Her work will be continued into the future by Chair of Materials Process Engineering Prof. Dr.-Ing. Christina Roth, and at Keylab Glass Technology by Prof. Dr.-Ing. Thorsten Gerdes.

Fig. 9: At the Chair of Materials Process Engineering, glass-coated zinc particles are being developed as anode materials for rechargeable zinc-air batteries in order to improve cycle stability, which remains inadequate (REM-pictures: Tobias Michlik).

Christina Roth

All in the flow

Flow batteries store solar and wind energy

The Application Centre for Renewable Energies at the Fraunhofer Institute for Chemical Technology (ICT) in Pfinztal couples a wind turbine with flow batteries. The Chair of Materials Process Engineering at the University of Bayreuth is cooperating with the ICT in the joint project "DegraBat: Degradation Processes in All-Vanadium Redox Flow Batteries", which is funded by the Federal Ministry of Economics and Energy (BMWi) (Photo: Application Centre for Renewable Energies at Fraunhofer Institute for Chemical Technology ICT).

When the sun shines and the wind blows, the conditions to feed energy from renewable sources into our supply network are just right. Unfortunately, however, electricity is used less often at these times, for example when tens of thousands of citizens want to switch on their coffee machines early in the morning when it's still dark. In order to achieve a better balance between supply and demand and to buffer resulting power peaks in the grid, flow batteries (redox flow batteries) are an interesting option. Unlike lithium-ion batteries, which work with solid electrolytes, the energy is stored in aqueous solutions. Pumps cause these liquid electrolytes to flow through porous electrodes. So the battery can be quickly charged and discharged when necessary. Moreover, flow batteries are especially suitable for large stationary applications in which the excess energy from wind farms and solar fields must be stored temporarily. Furthermore, they are comparatively low-maintenance and characterized by the fact that energy and power can be scaled over a wide range.

Already 70 years ago, the flow battery was presented in a patent application by Walter Kangro as a process for storing electrical energy.[1] In the following years it was intensively researched at the TU Braunschweig. In the 1980s, the research group of Maria Skyllas-Kazacos at the University of New South Wales in Australia developed the vanadium redox flow battery, a milestone on the road to commercialising this technological development.[2]

Structure and function of the vanadium redox flow battery

The special feature of a vanadium redox flow battery is that the only electrolyte used is vanadium - in its different oxidation states V^{2+} (violet) and V^{3+} (green) as well as V^{4+} (blue) and V^{5+} (yellow). These electrolyte pairs are distributed over two containers (tanks), each of which is connected to an electrochemical half-cell. The two half cells contain the electrodes and are physically separated by a non-conductive polymer membrane: At the cathode, in the positive half-cell, V^{5+} (yellow) is reduced to V^{4+} (blue), while at the anode in the negative half-cell V^{2+} (violet) is oxidized to V^{3+} (green). Meanwhile, an ionic current flows through the polymer membrane. The complementary processes of reduction and oxidation result in the release of electrons to the electrodes and their transfer to an external conductor circuit when the battery is discharged. This is where the electricity which is fed into the power grid flows, to be used by the end consumer to operate their electrical appliances.

With the help of the flow battery as an electricity storage system, the German citizen in need of caffeine could operate his coffee machine in the morning with electricity that has been temporarily stored overnight. Even if all the supposed hordes of morning coffee drinkers in Bayreuth got up at once, they would not cause main fluctuations or blackouts.

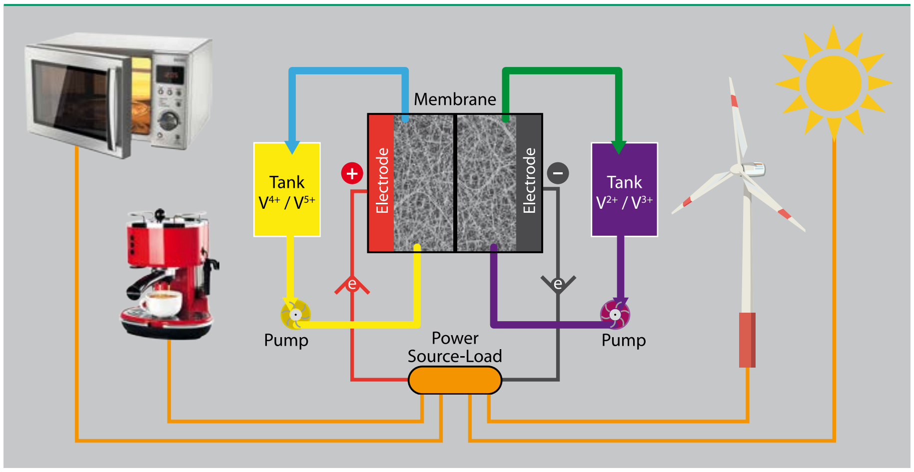


Fig. 1: Functional principle of a vanadium flow battery. Both electrolyte containers holding vanadium ensures that the electrolytes are not contaminated by other chemical elements (Illustration: Christina Roth / Christian Göppner / Andreas Gaube, Photos: sst).

Robust electrodes thanks to carbon

The vanadium used in the flow battery is a heavy metal and must be dissolved in diluted sulphuric acid. Unfortunately, this gives rise to two problems at once:

- So far only a comparatively small amount of vanadium can be dissolved. However, the amount of electricity that can be stored in the battery depends directly on how much is dissolved. For this reason, additives such as phosphoric acid are currently being researched in order to increase the concentration of vanadium.
- Yet the sulphuric acid used to dissolve vanadium salts is very corrosive. The materials used for the electrodes must therefore be particularly resistant so that they are not damaged by constant contact with the acid solutions. However, most corrosion-resistant materials, including high-alloy steels and precious metals such as platinum, are expensive. Carbon materials are therefore an exciting alternative.

AUTHOR

Prof. Dr.-Ing. Christina Roth has been the Chair of Material Process Engineering at the University of Bayreuth since April 2019.

RECOMMENDED READING

J. Noack et al.: The Chemistry of Redox-Flow Batteries, Angewandte Chemie (2015), Vol. 127, 9912-9947. DOI: 10.1002/anie.201410823.

A. Fetyan et al.: Comparison of Electrospun Carbon–Carbon Composite and Commercial Felt for Their Activity and Electrolyte Utilization in Vanadium Redox Flow Batteries, ChemElectroChem (2019), Vol. 6, 130-135. DOI: 10.1002/celc.201801128.

Fig. 2: Vanadium flow batteries work with four aqueous vanadium solutions. The colours correspond to the different oxidation states of vanadium (Photo: Joachim Langner).

Currently, carbon felts – commercially available fabrics made of carbon fibres - are used as porous electrodes. The acidic vanadium solutions are pumped through this material. Indeed, carbon is well suited for this purpose for several reasons: It is resistant to acidic solutions, conducts electrons well, and is comparatively inexpensive. However, the carbon felts used so far have not been designed for use in flow batteries. Originally, they were used as furnace insulation due to their flame retardant properties. In order to be able to catalyse the reduction and oxidation of the vanadium solution when charging or discharging the flow battery, they must first be activated. This can be done, for example, in the furnace by heat treatment at 400 degrees Celsius for a period of 30 hours in an air atmosphere, or by contact with strongly oxidizing acids. This increases the wettability of the felts and improves the contact between them and the vanadium solution. In addition, the contact of the carbon surface with the atmospheric oxygen produces functional groups which accelerate the desired reduction or oxidation of the vanadium. The exact function of this mechanism has yet to be completely revealed by research.

Carbon felts are therefore in principle well suited as materials for corrosion-resistant electrodes in flow batteries. However, the commercial fabrics used to date have a number of drawbacks that remain a challenge for research and development:

- The electrodes have only a comparatively small surface area for catalytic reactions.
- Although the wettability of the electrodes and their reactivity are improved by the activating pre-treatment, their catalytic efficiency remains very limited.
- And, although the pre-treatment does not require much effort, the question arises as to whether it should be carried out by the carbon felt manufacturer or by the customer. This is particularly important for liability issues. Who assumes liability if the felt activation does not lead to the desired performance?

Felt manufacturers are therefore in close contact with scientists to eliminate these disadvantages. The aim is to provide the electrodes with surfaces that are directly active and do not require any additional activation in order to fulfil their role as catalysts. If such optimized felts could be produced industrially, they could be delivered by the manufacturer to the battery producers without pre-treatment and installed directly in the flow battery.

„Flow batteries are suitable for large stationary applications in which the excess energy from wind farms and solar fields must be temporarily stored.“

Innovative strategies for optimization of electrodes

The Chair of Materials Process Engineering at the University of Bayreuth has also been dealing with the challenge of optimizing the electrodes of flow batteries. In recent years, the working group led by Prof. Dr.-Ing. Christina Roth at the FU Berlin has pursued a number of new approaches:

- A better understanding of the processes that take place when a battery is recharged and discharged over and over again is essential for optimizing the electrodes. Indeed, the amount of energy that can be stored and released decreases continuously. Electrochemical impedance spectroscopy is used to better understand this ageing phenomenon in commercially available felt electrodes. In this method, the resistance of the alternating current is determined and related to its frequency. However, it is important to distinguish the power loss caused by electrode degradation from the ageing of other battery components, such as the polymer membrane or vanadium solution. The knowledge gained from the electrochemical investigations can contribute to counteracting the ageing of the felt electrodes by appropriate pre-treatment.[3]

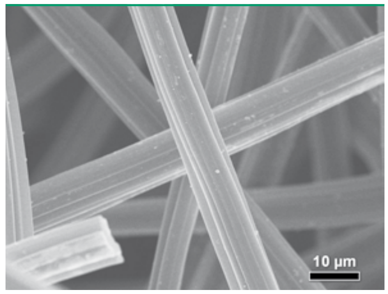
Fig. 3: Dr. Igor Derr, former doctoral student in the working group of Prof. Dr.-Ing. Christina Roth, setting up the laboratory to test battery performance (Photo: Manoj Krishna Kayarkatte).

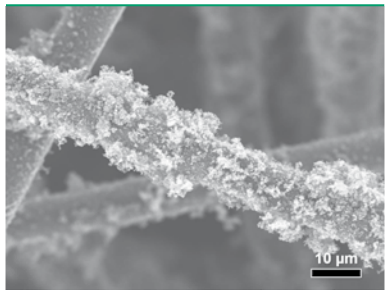
■ Another strategy for optimizing the electrodes is aimed at eliminating the need for pre-treatment in air to activate them. For this purpose, commercially available felts are coated with a second carbon phase before they are inserted into the electrodes, so that a carbon-carbon composite is formed. While the fibres in the felt mainly conduct electrons, the carbon coating has a catalytic function. It is supposed to accelerate the reaction in contact with the vanadium solution.[4]

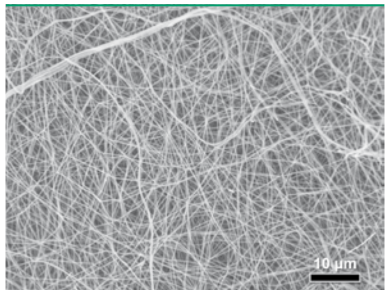
■ A further strategy does without the commercial felts completely. It uses the electrospinning process to produce the required carbon electrodes itself. In electrospinning, a polymer solution is „pulled" out of the tip by applying a high voltage between the needle tip and the collector plate, swirled and deposited on the collector plate similar to cotton candy. During the production of the fabric, the high voltage, the distance between needle tip and collector plate as well as the viscosity of the solution can be varied. In this way, a huge variety of structures can be obtained, differing, for example, in fibre diameters, pore sizes and branches. Since the polymer fabric is not yet electron-conductive immediately after manufacture, it must be heated in an oven filled with inert gas to at least 1,700 degrees Celsius. What remains is a carbon felt that has a surface area 100 times larger than that of commercial electrodes and is therefore much more efficient.[5]

Alternative materials for better environmental compatibility

In the future, the availability of battery raw materials and their return to the materials cycle will also become more central to research projects on the Bayreuth Campus. What happens if a battery can no longer store enough energy because it has exhausted itself over its lifetime? From the point of view of recycling, vanadium as a heavy metal is certainly not the best choice. A new research approach developed at the University of Jena aims to replace vanadium with recyclable polymers.[6] In this case, polymers that absorb and release charges are decisive for the storage capacity of the battery. At the University of Bayreuth, an interdisciplinary team is increasingly targeting iron systems, and investigating whether, based on more readily available materials, they can replace vanadium. In comparison with vanadium, both alternatives are not only expected to improve environmental compatibility, but also offer a considerable price advantage.





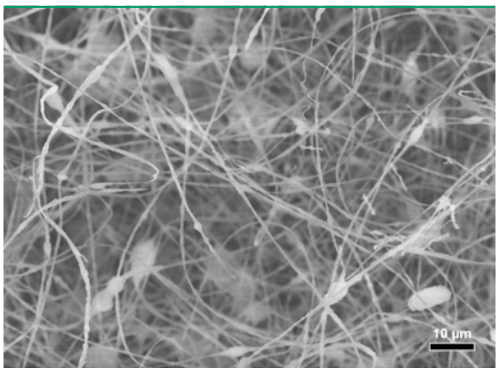


Carbon materials in the scanning electron microscope:

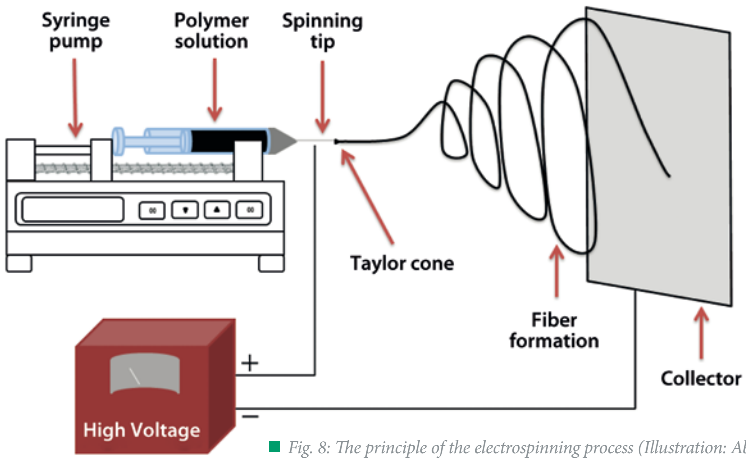
■ *Fig. 4: Commercial felt electrode (Image: Abdulmonem Fetyan).*

■ *Fig. 5: Carbon-carbon composite like Pretzel sticks (Image: Maike Schnucklake).*

■ *Fig. 6: A fabric electro-spun by AG Roth with a surface area 100-times larger (Image: Abdulmonem Fetyan).*



■ *Fig. 7: Scanning electronic image of fibre with spindle structure that can be produced with the electrospinning process (Image: Mahboubeh Maleki).*



■ *Fig. 8: The principle of the electrospinning process (Illustration: Abdulmonem Fetyan).*

1 W. Kangro, DE Patent 914264 (1949).
2 E. Sum et al.: Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery, Journal of Power Sources (1985), Vol. 16, 85-95. DOI: 10.1016/0378-7753(85)80082-3.
3 J. Schneider et al.: Degradation phenomena of bismuth-modified felt electrodes in VRFB studied by electrochemical impedance spectroscopy, Batteries (2019), 5(1), 16. DOI: 10.3390/batteries5010016.
4 M. Schnucklake et al.: Salt-templated porous carbon-carbon composite electrodes for application in vanadium redox flow batteries, Journal of Materials Chemistry A (2017), 5, 25193-25199. DOI: 10.1039/C7TA07759A.
5 A. Fetyan et al.: Electrospun Carbon Nanofibers as Alternative Electrode Materials for Vanadium Redox Flow Batteries, ChemElectroChem (2015) 2, 2055-2060. DOI: 10.1002/celc.201500284; siehe auch Literaturtipps: A. Fetyan et al., ChemElectroChem (2019).
6 Cf. the press release dated 5 July 2017: https://idw-online.de/de/news698945.

The authors team of the Department of Functional Materials

Process technologies for new solid electrolytes

Innovations for the lithium-ion battery of the future

Constructing the cell of a lithium-ion battery and testing it (Photo: Christian Wißler).

These days, primary batteries and accumulators – the latter can be recharged and are also called secondary batteries – are ubiquitous. The spectrum of applications ranges from simple devices such as watches, remote controls, and battery-powered tools, to smartphones, tablets, e-bikes, and electric vehicles, to off-grid decentralised power supply units.

Depending on the application in which they are later to be used, batteries have different characteristics which largely determine their suitability. First and foremost, however, safe operation is essential for all battery types. Here, the prevention of spontaneous combustion and the toxicity of the materials are two important parameters. In addition, batteries must also meet the requirements of their respective applications with regard to the following parameters:

- Energy density:
  gravimetric: the ratio of storable energy to battery weight
  volumetric: the ratio of storable energy to battery volume

- Power density:
  gravimetric: the ratio of the retrievable power to the weight of the battery
  volumetric: the ratio of the retrievable power to the battery volume

Accumulators in smartphones, for example, ideally contain sufficient energy to ensure long periods of operation while taking up as little space as possible. Accumulators for electric cars, on the other hand, not only require a high energy density but also a high power density so that energy can be quickly stored or retrieved. In addition, accumulators must have a long service life – both in terms of storage (calendar service life) and of frequent charging and discharging (cyclic service life). Because the numbers of electric vehicles are constantly increasing, it is assumed that demand for battery storage capacity will increase sharply in the medium term (Fig. 1).

In order to be able to meet future requirements in terms of energy and power density as well as high demand, many fundamental innovations and major improvements will be necessary. In the first place, these will concern the material systems used, then the design of the battery cells, and finally the level of the overall system.[1] After all, the finished battery is competing with other energy storage devices on the market. Costs for the consumer will therefore remain a decisive factor. These in turn depend directly on processing costs, availability, recyclability and above all on the prices of the materials used.

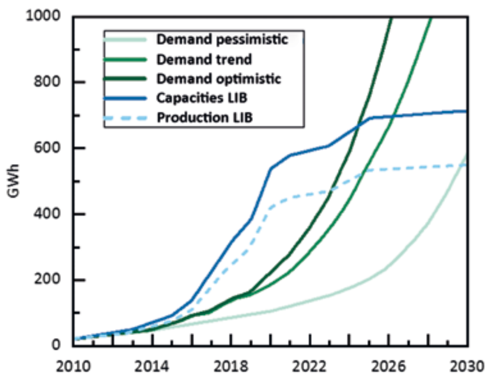


Fig. 1: Forecast development of global demand, capacities and production of lithium-ion batteries up to 2030.[2] (Illustration: Dominik Hanft).

„Ceramic solid electrolytes often have a very wide range of electrochemical stability."

Lithium-ion batteries

A conventional lithium-ion battery (LIB) contains – in simplified terms – four components: The two electrodes, the cathode on the one hand and the anode on the other, consist of two different energy-storing materials. Between them there is a liquid electrolyte and a separator. The latter ensures that the electrodes have no direct contact with each other, which would lead to an internal short-circuit. To discharge the battery, a contact is established between the electrodes via electronic current collectors so that electrical current flows from the anode to the cathode. At the same time, an ionic current flows inside the battery from the anode to the cathode. Besides the electrode materials, the electrolyte also has a special role to play: it must have the highest possible

AUTHORS

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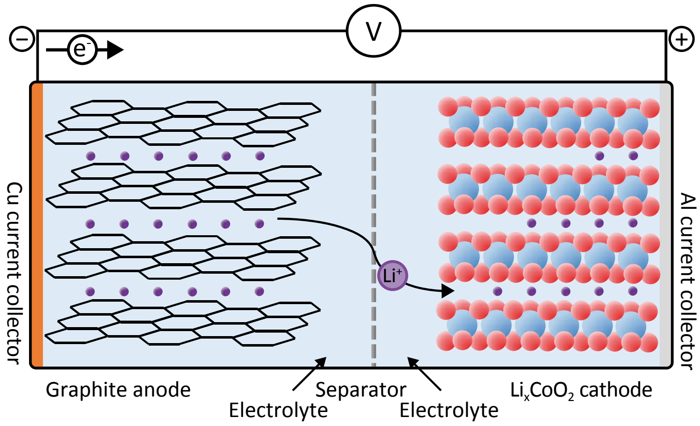

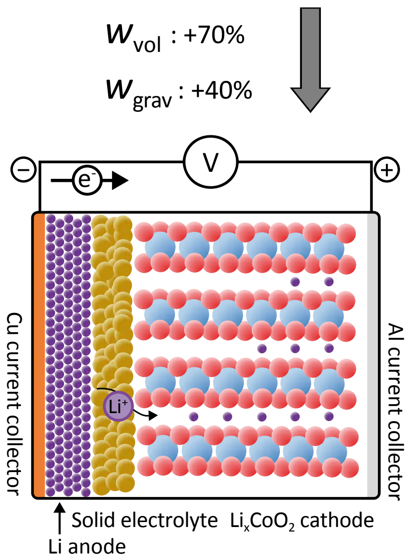

Fig. 2: Schematic representation of the structure of different battery concepts. Above: Commercial lithium ion cell with $LiCoO_2$ cathode, liquid electrolyte, and graphite anode. Below: Concept of a solid battery with $LiCoO_2$ cathode, solid electrolyte and Li-Metal anode. Compared to conventional cells, solid batteries have significantly higher energy gravimetric and volumetric densities (W_{grav} and W_{vol}) (Illustration: Yannick Jännsch / Tobias Nazarenus, edited by Christian Göppner).

ionic conductivity and the lowest possible electronic conductivity. At the same time it must be (electro-) chemically stable in relation to its neighbouring components, the anode and the cathode. All this represents a major challenge in the search for suitable new materials.

Materials in the focus of research and development

The materials currently used in common lithium-ion batteries are in the public eye, not least because of geopolitical issues in the producing countries. On the cathode side, mixed oxides based on cobalt, nickel and manganese oxide are frequently used as active materials. The reason for choosing the mixed oxide compound is the high cell voltages that can be achieved with these components, and material prices. Further advantages of mixed oxides are the comparatively large gravimetric and volumetric capacity for rapid reversible storage of lithium ions, high cycle stability and high Coulomb efficiency.

This type of active material is an intercalation material, which, similar to a sponge, can absorb lithium ions when the accumulator is discharged and release lithium ions when it is charging. During the charge-discharge cycles, the skeleton remains intact, and free spaces in the crystal lattice can be filled similarly to the pores of a sponge.

On the anode side, graphite is chosen as state-of-the-art intercalation material. In order to further increase storage capacity on the anode side, silicon particles are added in small quantities during the production of the anode. Silicon has a very high storage capacity, but is associated with a particular challenge: Charging and discharging is accompanied by an extreme change in the volume of the silicon particles. This leads to mechanical stresses and consequently to loss of contact. As a consequence, the more often an accumulator is cyclically charged and discharged, the lower is its energy density and thus also its service life.

A possible alternative to the use of graphite and silicon particles currently being discussed is to use metallic lithium as anode material. In this way, cell voltage could be raised, and the capacity increased significantly. During cyclic operation, the anode would be constantly eroding and reforming. A surplus of lithium can be used there to improve the connection to the current collector.

Meanwhile, solid electrolytes based on polymers or (glass) ceramics are considered to be a promising technology that can enable the commercial realization of metallic lithium as an electrode material. Ceramic solid electrolytes in particular often exhibit a very wide electrochemical stability range, so that decomposition of the electrolyte material at the electrodes will not occur – as is usual with liquid electrolytes. In addition, the use of a ceramic ionic conductor can increase operational safety, since it neither leaks out nor is flammable. Although ceramics have a higher specific weight than liquid electrolytes, this disadvantage can be countered by adapting cell design. In fact, the mechanical stability of ceramics promises to counteract the risk of short circuits. Furthermore, if solid electrolytes were used, self-discharge would no longer be an issue.

New directions in Bayreuth: Powder aerosol-based deposition at room temperature

Although research activities in the field of materials have increased significantly in recent years and although it has been possible to demonstrate the technical functionality of solid-state batteries on a laboratory scale, there is still a lack of process technologies for mass production of lithium-ion batteries with the aforementioned (glass) ceramic solid electrolytes. Indeed, the production of dense ceramic solid electrolyte layers, which are only a few micrometres thick, represents a major challenge for process technology. The aim is to create layers that are less than half as thick as a human hair, which is typically around 60 micrometres in diameter. Conventional ceramic process technology is characterized by high

1 Cf.. T. Placke et al.: Lithium ion, lithium metal, and alternative rechargeable battery technologies: the odyssey for high energy density. J. Solid State Electrochem. (2017), 21, 1939-1964. DOI: 10.1007/s10008-017-3610-7; J. Janek, W.G. Zeier: A solid future for battery development. Nat. Energy (2016), 1, 16141. DOI: 10.1038/nenergy.2016.141.

2 Data according to A. Thielmann et al: Energiespeicher-Roadmap (Update 2017): Hochenergie-Batterien 2030+ und Perspektiven zukünftiger Batterietechnologien. Karlsruhe 2017.

processing temperatures and correspondingly high plant and operating costs.

The Department of Functional Materials at the University of Bayreuth is therefore breaking new ground with a novel ceramic coating process. Powder aerosol-based deposition at room temperature (Aerosol Deposition Method, ADM) makes it possible for the first time to produce thick films at room temperature directly from the ceramic starting powders. This spray coating process stands out for enabling the cost-effective production of layers ranging from a few micrometres to several hundred micrometres in thickness. The ceramic particles are accelerated to almost the speed of sound and directed onto the surface to be coated. Here, the particles form a dense nanocrystalline layer. The process is also characterized by excellent bonding to a wide variety of base materials. A unique feature of the process is that, in addition to ceramic and metallic materials, glasses and even plastics can be coated.

This points to some highly interesting applications in the field of battery development: The strong bonding of the ceramic coatings creates the prerequisite for the build-up of the electrolyte layer on the cathode substrate. Furthermore, the almost free choice of process gases and the low process temperatures involved make inert processing of moisture-sensitive and reactive materials highly feasible. This applies to most common solid electrolytes for future lithium-ion batteries. What is particularly promising for the construction of an „All-Solid State Battery“ is that a direct connection of electrolyte and cathode is possible without having to consider the coefficients of thermal expansion or the limits of chemical stability at elevated temperatures of the two components.

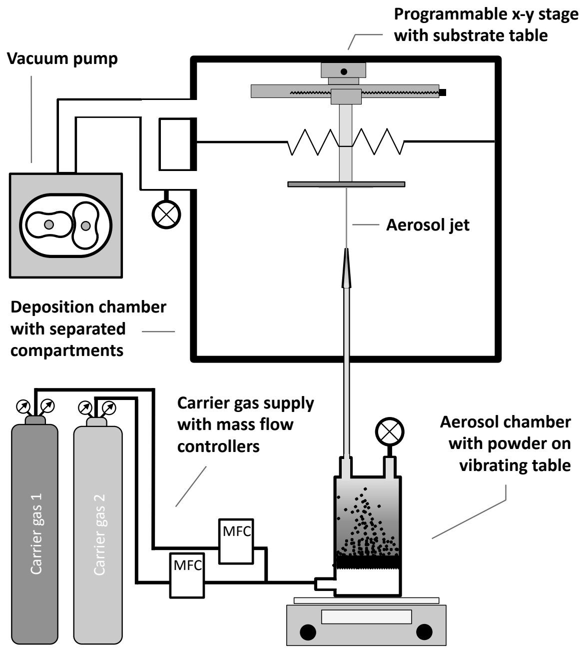

Fig. 3: Schematic representation of an apparatus for powder aerosol deposition (Illustration: LS for functional materials).

Outlook

In addition to research into materials and process technology for novel accumulators, research at the Department of Functional Materials extends to other areas of energy storage and conversion. Materials for thermoelectric generators are being researched that can convert thermal energy directly into electrical energy. In electrochemical CO_2 reduction, electrical energy – for example as excess energy from renewable energy sources such as wind or photovoltaics – is used to produce hydrocarbons from CO_2 in an electrolysis process. In this field, the Department of Functional Materials is researching catalyst materials (electrode materials) and suitable process management to improve yields, selectivity and process stability.

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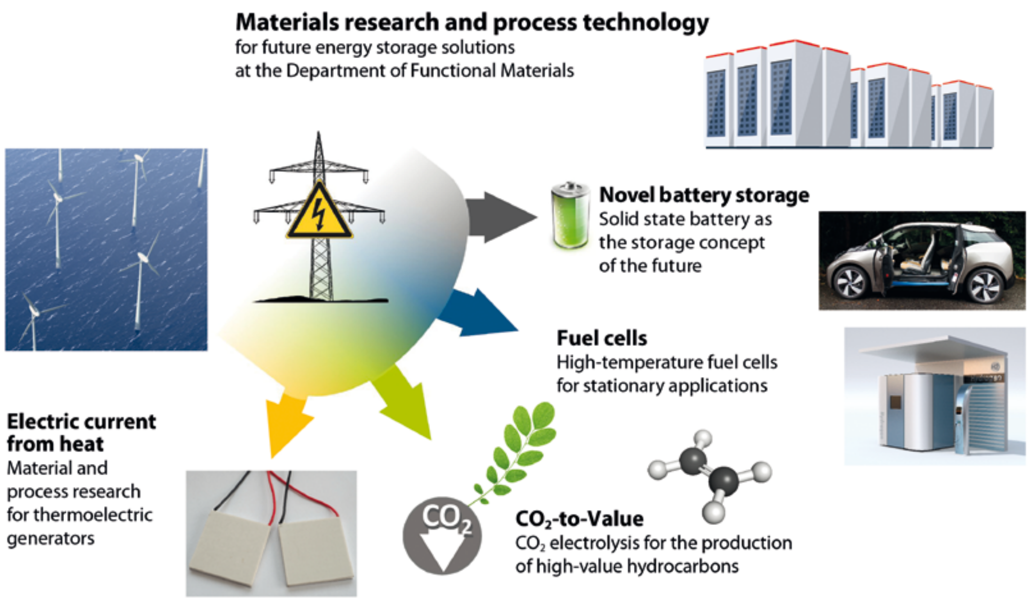
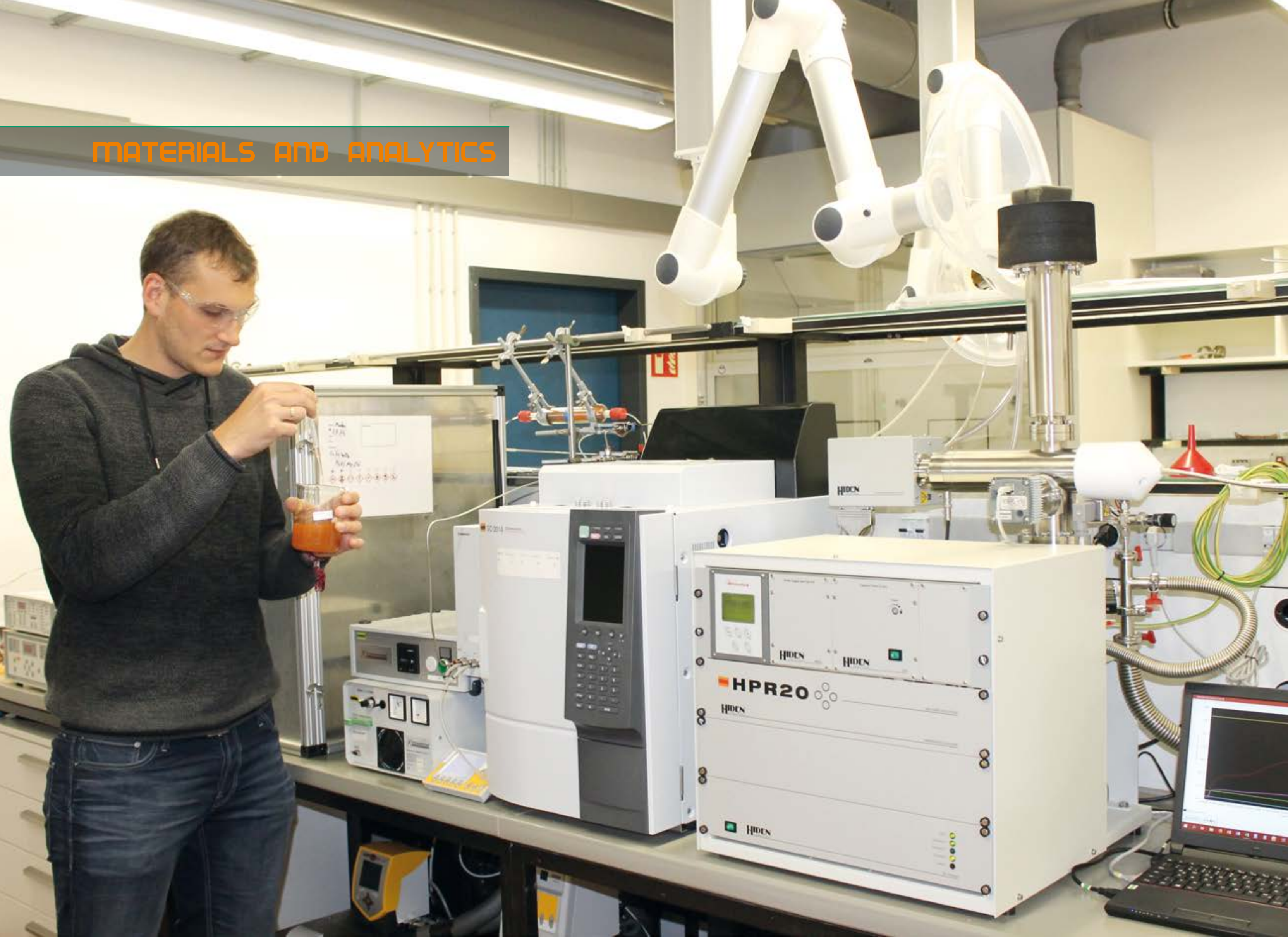


Fig. 4: Spectrum of research at the Department of Functional Materials in the field of energy technology (Illustration: Dominik Hanft, Images: sst).



Roland Marschall

Nanostructured oxides

Functional materials for electrochemical energy storage and conversion

A suspension of $MgFe_2O_4$ nanoparticles is prepared for investigation in photocatalysis / water splitting by gas chromatography (Photo: Christian Wißler).

Functional materials belonging to the class of metal oxides have found their way into our everyday lives in a variety of ways. Indeed, especially in the field of small electronic appliances, whether in touch screens or Li-ion accumulators, but even in everyday items such as toothpaste, they are more or less omnipresent. Metal oxides are compounds of metals and oxygen. They occur in a multitude of composites and crystal structures which differ in the metals they contain, their composition ratio and the size of the constituent atoms (metal cations and oxygen anions O^{2-}).

In order for metal oxides to possess exactly those properties that are required in the respective context for their optimal application, it is necessary that the method of their production is capable of the respective modification in a straightforward manner. There are numerous possibilities for the production of metal oxides: wet chemical methods, hydrothermal syntheses and solid phase reactions. Wet-chemical methods – which belong to the field of sol-gel chemistry – offer the advantage that metal oxides can be obtained in the form of tailor-made morphologies. These can be used, for example, for coating components.

In sol-gel synthesis, cation-containing precursor compounds are reacted with alcohols or water. This process is called alcoholysis or hydrolysis (Fig. 1). Subsequently or in parallel, the OH groups formed can condense to form a network: *the result is a sol*. As the reaction continues, the network condenses over time and becomes increasingly viscous under the influence of the solvent incorporated at the beginning: *a gel is formed*. If this gel is now exposed to temperatures of more than 100 degrees Celsius, the network loses its gel character, and all water or alcohol are removed: *the metal oxide is formed*.

In recent decades, chemists have studied in detail which physical parameters influence this type of synthesis – with the result that today they are able to control the speed of the individual steps. This enables the use of sol-gel synthesis to produce metastable structures, highly ordered porous particles, size-controlled nanoparticles, and fibres with tailor-made diameters. In many areas of application, the main objective is to increase the surface area by nanostructuring, as the following example illustrates.

Suppose a metal oxide in the hypothetical shape of a cube has an edge length of 1 cm and a specific surface area of 6 cm². These 6 cm² are then available for surface reactions, for example catalytic reactions or the storage of electrical charge in double layer capacitors. If this cube is now divided into 1,000 smaller cubes with an edge length of 1 mm, a surface area of 1,000 x 6 mm² = 6,000 mm² = 60 cm² is obtained (Fig. 2). The smaller the cubes become, the greater the effect of surface enlargement. Chemists today can easily and quickly produce form-controlled „cubes" of a few nanometres (1 nanometre = 0.0000001 cm) in length by sol-gel chemistry. If one were to divide the cube in Fig. 2 into cubes with an edge length of 1 nanometer, one would obtain a surface area of 60,000,000 cm².

The following examples show how nanostructured metal oxides can be produced which are of particular interest for electrochemical energy storage and conversion.

Iron spinels from the microwave

Spinels of iron have aroused great interest in recent years for electrodes in lithium-ion batteries, especially in the field of conversion anodes. Meanwhile it is possible to produce size-controlled nanoparticles of these ternary iron oxides (AFe_2O_4, A= Zn, Mg, Mn, Fe, Co, Ni) in order to obtain, for example, better distribution in the active anode. Microwave-assisted syntheses are particularly well suited for this purpose, as temperatures required by sol-gel chemistry can be very efficiently and quickly achieved

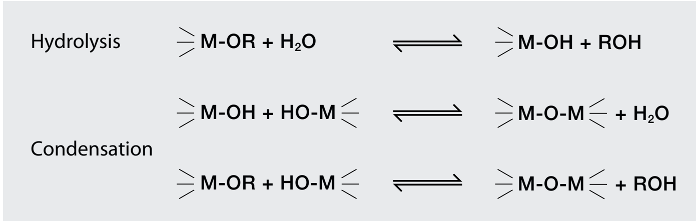


Fig. 1: Chemical reactions during hydrolysis and condensation to form a metal (M) oxide.[1]

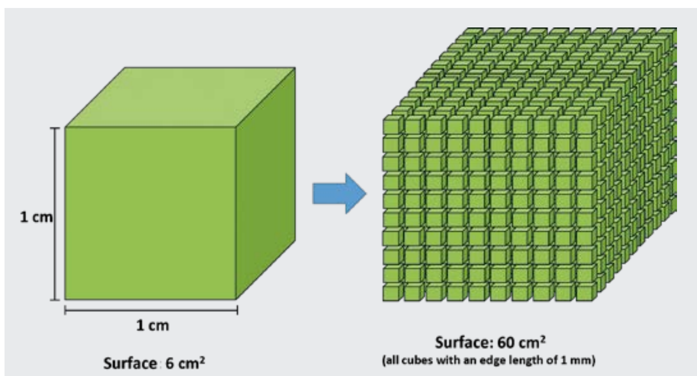


Fig. 2: Surface enlargement by structuring. (Photo: Roland Marschall).[2]

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M. Einert et al.: Electrospun CuO Nanofibers: Stable Nanostructures for Solar Water Splitting. ChemPhotoChem (2017), 1, 326-340. DOI: 10.1002/cptc.201700050.

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■ *Fig. 3 and 4: A suspension of $MgFe_2O$ nanoparticles is removed from the laboratory microwave (Photos: Christian Wißler).*

in a laboratory microwave. In some cases, metal oxides produced in this way do not require the above-mentioned subsequent temperature step and can therefore be conveniently produced in a time-saving manner.

„Electrospinning opens up the possibility of synthesizing electrode coatings directly."

AUTHOR

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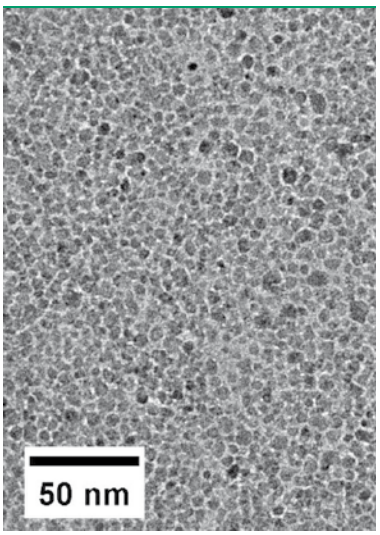
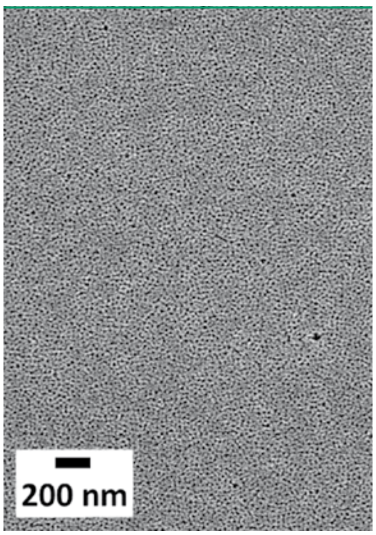
For example, it is possible to produce the ternary metal oxides $ZnFe_2O_4$ and $MgFe_2O_4$ in an anhydrous sol-gel synthesis in the microwave.[3] By controlling the reaction temperature, crystalline nanoparticles with a spinel structure smaller than 10 nanometers can be produced (Fig. 5). If a certain distribution in a medium is particularly important for further use, the particles can be processed accordingly: $MgFe_2O_4$ nanoparticles can be modified on the surface so that they can be ideally distributed in aqueous or organic dispersions.

The precursor solutions involved in such a microwave synthesis are relatively stable without temperature treatment: they will not react by forming the gel or metal oxide. Therefore, these solutions can also be used to coat surfaces to produce thin-film electrodes of the metal oxide. If so-called porogens are added to this deposition, porous thin-film electrodes are obtained (Fig. 6). These can be used in many areas, for example for lithium uptake in batteries and photoelectrochemistry.



■ *Fig. 5: Transmission electron microscope image of $MgFe_2O_4$ nanoparticles (Image: © American Chemical Society. First published in K. Kirchberg et al (2017), see recommended reading).*



■ *Fig. 6: Scanning electron microscope image of a $ZnFe_2O_4$ thin film (Image: © Wiley-VCH, First published in K. Kirchberg et al. (2018), see recommended reading).*

Copper oxide fibres

Copper oxide (CuO) is a highly interesting material for conversion electrodes in sodium ion batteries[4] and photoelectrochemistry, but also for sensor technology for toxic gases. Nanoparticles made of copper oxide are easy to produce, but their production by electrospinning is far more attractive. Although the process poses a particular technical challenge, it opens up the possibility of synthesizing electrode coatings directly.[5] Electrospinning is a simple and scalable method for the production of polymer and oxide fibres. For CuO oxide fibres, the sol-gel chemistry must be controlled during electrospinning, and the fibre morphology must be maintained in the subsequent temperature treatment. The results are temperature-dependent fibre morphologies (Fig. 7) that could be used in battery electrodes.

Copper oxide is of considerable interest for solar energy conversion in photoelectrochemistry due to its small band gap and its p-type semiconductor behaviour. This shows up as a dependence of photoelectrochemical performance on morphology. This is because fibres consisting of smaller crystallites have a higher number of grain boundaries, which can be disadvantageous for the transfer of photogenerated charge carriers. In this case, fibres with larger crystallites are the better material for photoelectrochemical water splitting.[6]

Mesoporous proton conductors

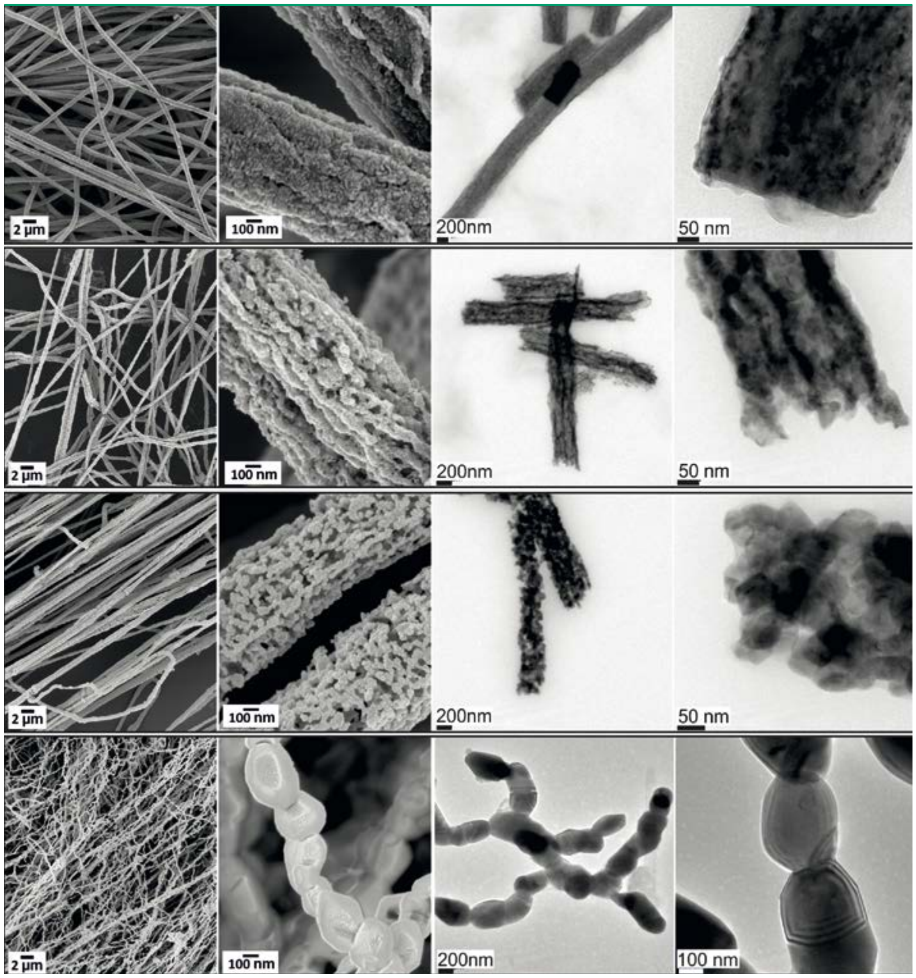
Proton-conducting membranes are used in a variety of applications, for example in desalination plants, in photoelectrochemistry, and also in energy technology – in fuel cells, but not in batteries.[7] In order to improve the stability and water balance of such membranes at temperatures above 100 degrees Celsius, proton-conducting additives and porous proton conductors are being researched. In particular, mesoporous SiO_2-based particles with a highly ordered pore structure can be loaded with a large number of proton-conducting functional groups (e.g. SO_3H or imidazole) in order to be incorporated into membranes. This functionalization was recently achieved even from the gas phase, meaning the effect of pore blocking during surface functionalization was eliminated.[8] Here, the advantage of mesoporous proton conductors with their enormous specific surface areas as compared to non-porous additives, which do not reach the proton conductivities of porous systems, is particularly evident.[9] Recently, mesoporous proton conductors were also produced in monolithic form for the first time.[10]

Porous aromatic and organic polymers are an alternative to SiO_2-based proton conductors. They are also porous proton conductors, partly for anhydrous proton conduction. These have also been intensively researched in recent years[11] and offer great variability in composition for proton conduction.[12]

Outlook

Functional and nanostructured metal oxides can be produced by various methods and used in many areas. The Bavarian Centre for Battery Technology (Baybatt) at the University of Bayreuth is conducting research into new metal oxides and their nanostructuring for (photo-)electrochemical energy storage and conversion.

Fig. 7: CuO nanofibers produced by electrospinning with different morphologies depending on the temperature treatment (from top to bottom: 300, 400, 550 and 800 degrees Celsius) (Image: © Wiley-VCH. First published in M. Einert et al. (2017), see recommended reading).



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Mukundan Thelakkat

Batteries based on polymers

Solvent-free polymer electrolytes for the next generation batteries

Alexander Krimalowski (M.Sc.), a doctoral student in the Research Group for Applied Functional Polymers, evaluating measurement results on potentiostats (Photo: Christian Wißler).

The production of renewable energy is based on very different energy sources and fluctuates with the time of day and the seasons. For this reason, appropriately adapted forms of energy storage are needed to ensure the availability of energy whenever and wherever it is needed. At the same time, the efficient and widespread conversion of photovoltaic energy into solar power yields an energy surplus that must be stored – either in the form of electrochemical energy storage or by conversion into fuels. In 2017, the energy produced by photovoltaic systems in Germany amounted to around 40 terawatt hours, thus covering almost 7.2 percent of local electricity consumption. There is also a growing demand for energy storage to provide transportable energy, especially for electrically powered vehicles.

This constellation of interests has intensified battery research and technology in recent years and driven it forward on a broad front. In contrast to the use of batteries in portable electronic devices such as cameras, laptops, and smartphones, the use of lithium-based batteries in electric vehicles requires more safety, a larger application temperature window, significantly increased service life, and increased energy and power density.

Materials research in this field focuses on solvent-free batteries and new materials for the electrodes (anode and cathode). Research to date has concentrated primarily on developing highly conductive liquid electrolytes in such a way that they are suitable as a medium for lithium-ion transport in today's batteries. These liquid electrolytes are usually flammable, low-molecular organic carbonates combined with additives. However, such research using flammable liquid electrolytes has contributed significantly to making lithium-ion batteries commercially viable – for example by controlling the formation of the solid electrolyte interphase (SEI) layer. A stable SEI layer contributes significantly to the stability of a battery by preventing the uncontrolled growth of lithium dendrites in the cell. Current commercial lithium-ion batteries with liquid electrolytes also require costly separator membranes that are permeable to lithium ions but prevent any contact between the two electrodes during operation.

At present, battery research is increasingly focusing on electromobility and is therefore concentrating more and more on the use of non-inflammable electrolytes instead of liquid organic carbonates. Solvent-free solid polymer electrolytes (SPEs) are considered to be particularly promising candidates for lithium-ion transport materials. They are a mixture of a solid-phase, ion-conducting polymer and

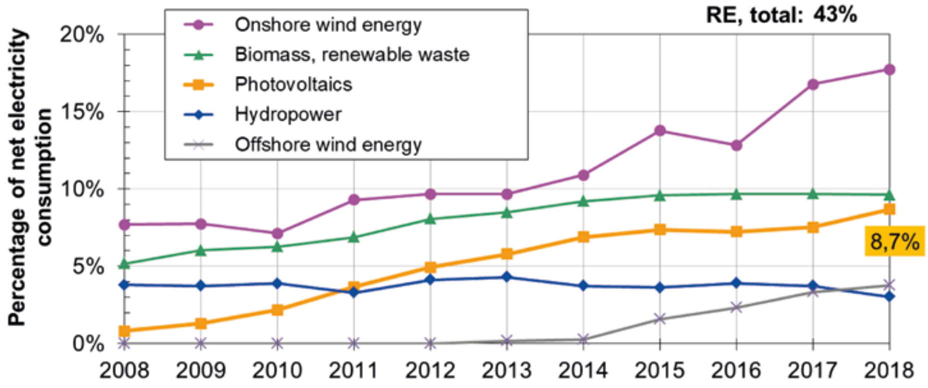

Fig. 1: Share of renewable energy in net electricity consumption in Germany.
Data sources: Total expenditure of energy data – data from the BMWi, 12 Jan. 2016; Monthly report on the development of renewable electricity generation and output in Germany: Research Group for Renewable Energy Statistics (AGEE-Stat), Dec. 2018; Development of net electricity consumption in Germany: BDEW, Feb. 2018.[1] (Illustration: © Fraunhofer-Institut für Solare Energiesysteme ISE).

a suitable lithium salt. Such SPEs can replace liquid electrolytes that have a high risk of flammability, such as those currently used in commercial batteries. Provided that sufficient ionic conductivity and mechanical stability are guaranteed in an SPE, the SPE concept has numerous advantages:

- Battery safety can be drastically improved using solvent-free electrolytes.
- SPEs can be laminated and printed in large quantities and then assembled into lightweight batteries with very high energy density.
- Costly separator membranes can be avoided.
- In combination with an SPE, pure lithium metal can be used as an anode instead of lithium-intercalated graphite, which would significantly increase the capacity of the cells.
- New cathode materials with further increased capacity, such as sulphur cathodes, can be used in conjunction with an SPE since the solid electrolyte can prevent the formation and dissolution of lithium polysulphides.

Although the principle of the SPE was already demonstrated in 1980, this topic has long been ignored. Battery research focused mainly on solving safety and stability problems in liquid electrolyte systems. Since then, experiments on SPEs have essentially been limited to a single polymer class, polyethylene oxides (PEOs). This is a semi-crystalline polymer with a glass transition temperature of approximately minus 40 degrees Celsius and a melting point between 50 and 60 degrees Celsius. Due to the segment mobility of the PEO chains, ion transport takes place in the amorphous domains of the poly-

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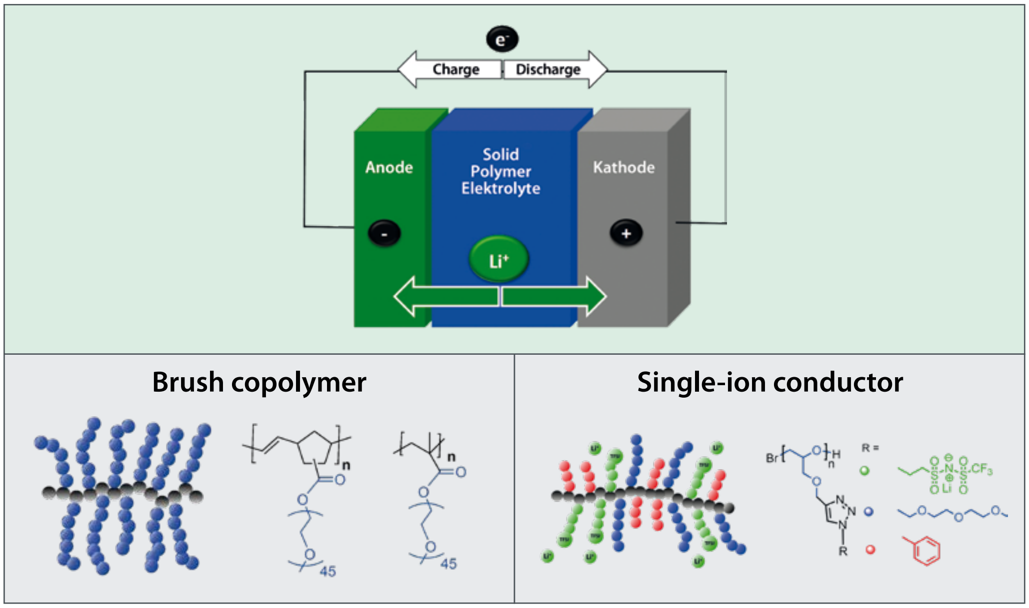
■ *Fig. 2: Above: Diagram of a lithium-ion battery with a solid polymer electrolyte as medium for ion transport. Bottom left: Polymer brushes with differently structured parts of the backbone to which short polyethylene oxide (PEO) chains are attached. Bottom right: Single ion conducting solid plastic electrolyte in which both the backbone and the side chains contribute to lithium-ion transport (Illustration: Mukundan Thelakkat).*



RECOMMENDED READING

A. Krimalowski, M. Thelakkat: Sequential Co-click Reactions with Poly(glycidyl propargyl ether) toward Single-ion Conducting Electrolytes, Macromolecules (2019), 52 (11), 4042-4051. DOI: 10.1021/acs.macromol.9b00206.

mer. As previously mentioned, there are two fundamental challenges in SPE research:

- to increase the conductivity of lithium ions within a large temperature window (if possible also at room temperature)
- and to ensure sufficient mechanical stability without impairing the ionic conductivity.

> “Solvent-free solid polymer electrolytes are considered to be particularly promising candidates for lithium-ion transport materials.“

New ion-conducting polymers

The research group for Applied Functional Polymers at the University of Bayreuth aims to find innovative solutions to these challenges. One focus is on the design and synthesis of new ion-conducting polymers. The scientists are also breaking new ground in the development of systems without PEOs. Actually, PEO-based systems generally perform well: As mixtures with well dissociating lithium salts (e.g. LiTFSI) they have an ionic conductivity in the range of 10^{-3} and 10^{-4} S·cm^{-1} if the SPE has a very low glass transition temperature (below 0 degrees Celsius) and is completely amorphous. However, this efficient ionic conductivity is only achieved at the expense of mechanical stability. Bayreuth’s researchers are therefore pursuing the goal of maintaining mechanical stability, avoiding crystallization processes, and maintaining the highest possible ionic conductivity in the material.

The starting point for new ion-conducting polymers is, among other things, the architecture of brush polymers. The backbone of these polymers can be used to attach short PEO side chains. In this case, the system has a less pronounced tendency to crystallize.[2] A brush architecture enables the simple synthesis of polymers with a very high molecular weight, since the molecular weight can be adjusted both over the

■ *Fig. 3: ECC-Std® electrochemical test cell for the electrochemical characterization of polymer solid electrolytes (Photo: Christian Wißler).*

length of the backbone and over the length of the side chain.

In some cases, the backbone can also be cross-linked via heat treatment to improve mechanical stability. In addition, the established concept of microphase separation of a diblock copolymer is used in Bayreuth. One of the blocks (usually the softer phase) provides the ion transport, while the second (usually the harder phase) provides the mechanical stability. Such a microphase-separated system thus combines two opposing properties in a single polymer: Softness in one domain and mechanical stability in the other. Most of the concepts presented so far can be transferred to so-called single-ion conductor systems in which the anions are immobilized. This means that lithium ions alone contribute to charge transport.[3]

In addition, the Research Group for Applied Functional Polymers is taking up the proven idea of fluorinating organic molecules. The aim is to develop partially fluorinated SPEs in order to suppress the flammability of the electrolyte even more. This has already been achieved in spacecraft materials.[4]

High-tech infrastructure in Bayreuth

In the Keylab for Device Engineering, which was established at the University of Bayreuth under the umbrella of the Bavarian Polymer Institute (BPI), the Research Group for Applied Functional Polymers has a complete electrochemical test and measurement station. Here a multi-channel potentiostat was installed in combination with a thermostat chamber for temperature-dependent electrochemical impedance spectroscopy and for the measurement of current-voltage curves. On the basis of this infrastructure, the scientists are building and developing battery prototypes in button cell geometry. They are investigating the ionic conductivity, the electrochemical stability, and the lithium transport number (which corresponds to the actual charge transport by lithium ions). Cyclization tests examine the capacity, charging speed, and reliability of batteries over a long period with many charging and discharging cycles. Newly produced electrolyte materials can thus be tested directly within the Research Group for Applied Functional Polymers with respect to their suitability for real battery applications.

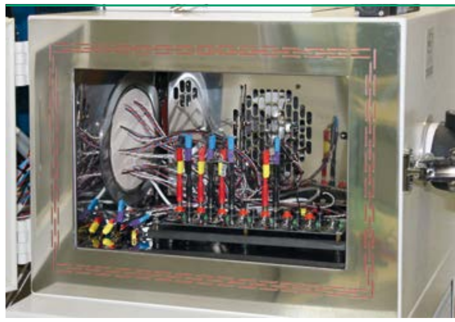


Fig. 4: Climatic chamber with button cell holder for temperature-dependent measurement of electrochemical parameters of polymer solid electrolytes.

Fig. 5: Inside the climatic chamber.

(Photos: Christian Wißler).

Within the framework of BayBatt, the research group cooperates with the Research Group for Electrical Energy Systems. Together, the electrochemical processes that take place within the solid electrolyte material and at its interfaces are analysed. For this purpose, the distribution of relaxation times (DRT) is calculated from the electrochemical impedance measurements in order to derive more precise statements about the processes within the battery system.

In the future, questions of electrolyte research and electrode research will be combined, and a basic understanding of electrochemical processes in SPE systems will be established in order to implement sustainable and technology-relevant concepts in battery research.

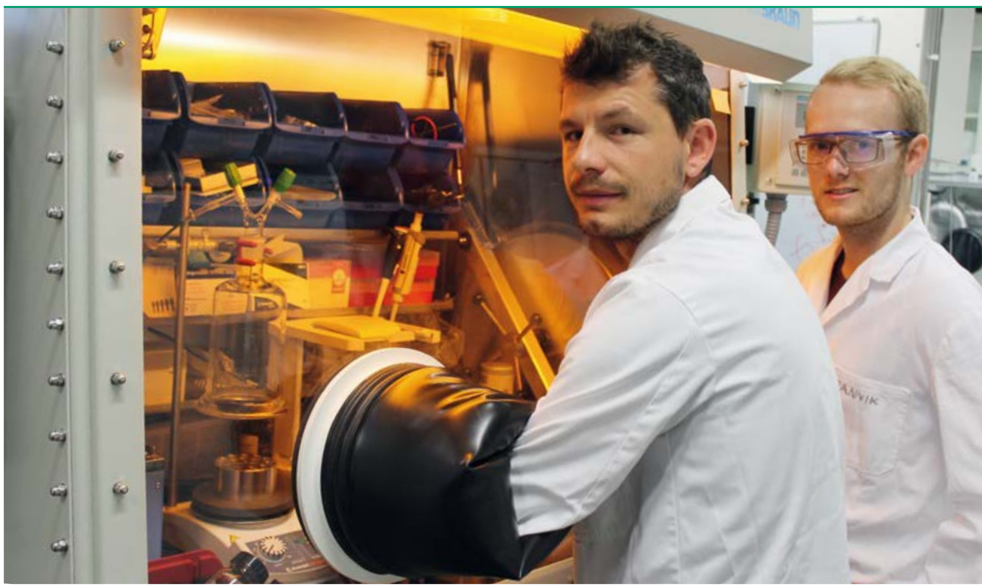


Fig. 6: Dominic Rosenbach (M.Sc.), a doctoral student, and Jannik Petry, members of the Research Group for Applied Functional Polymers, at the glovebox during production of battery button cells (Photo: Christian Wißler).

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Sebastian Weiß
Josef Breu

Lithium-ion batteries

Challenges of current technology

Salt lake in the Atacama Desert in Chile. In this region lithium is obtained by pumping brine from the ground into flat evaporation basins and drying it in the hot desert sun to form lithium-containing salts (sst).

Lithium-ion batteries (LIB) became the driving force behind the global revolution in consumer electronics, energy storage systems and other key applications shortly after their introduction in the early 1990s. Within a few decades, energy and power density, cycle life, rate capability, and cell design were all significantly improved and new horizons opened up for the green energy market. In order to enable fossil energy sources to be substituted effectively and appropriately, however, a further improvement in the cell performance of stationary energy storage systems is key.

Since the diesel scandal and the „Fridays for Future" demonstrations, the application of LIB technology in electric vehicles (EVs) has moved into the center of attention. In this field of application, the requisite space and weight are much more important than with stationary energy storage systems. Modern battery cells can provide 260 Wh/kg and 780 Wh/L gravimetric and volumetric energy density respectively. This is, however, only sufficient for ranges of 150 to 300 kilometres in mid-sized cars. This range is insufficient to meet the requirements of long-distance traffic. If performance comparable to that of modern internal combustion engines is to be achieved, larger batteries are required. Yet these are heavier and require more space than the sum of engine and tank in a conventional vehicle. A higher transport weight, however, again results in higher consumption of electricity and resources, putting additional strain on the ecological balance.

As a result, more efficient and sustainable solutions are called for[1], and a commensurate investment in research. With the establishment of the Bavarian Centre for Battery Technology, the Free State of Bavaria is now taking its first steps in this direction.

Possibilities and limits of the current LIB technology

A commercially available lithium-ion battery is typically composed of several components and contains no lithium metal but only Li^+ ions.[2] In order to achieve high performance, i.e. to draw or store a lot of current from the battery in a short time, the Li^+ ions must be able to move back and forth between anode and cathode chambers as quickly as possible, whereby the direction depends on whether the battery is currently being charged or discharged. To ensure this, the cell is typically filled with a liquid organic solvent mixture.[3]

For electric vehicles, capacity and retrievable power are the most important parameters, and the field is dominated by NMC and NCA cathodes. However, depending on the area of application (portable electronic devices, stationary memory, aircraft construction), other specifics such as costs, safety and service life can play a much more important role (Fig. 1). The various commercial materials hence all have their respective niche and reason for being on the market. There will probably never be „the" LIB cell, but always several application-specific technologies.

Actually, the component limiting the performance of the modern LIB is the cathode. This determines the capacity and performance of the cell. The most common commercial cathode materials are $LiCoO_2$ (LCO, ~140 mAh/g), $LiMn_2O_4$ (LMO, ~120 mAh/g), $LiFePO_4$ (LFP, ~140 mAh/g), $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ (NCM, ~160 mAh/g) and $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA, ~160 mAh/g). In EVs, battery capacity correlates directly with vehicle range, and indirectly with available power („PS"). With regard to the performance data, no disruptive leaps in technology are to be expected. Rather, incremental innovations will bring moderate improvements in the energy density and safety of lithium-ion batteries in the coming years.

Safety

Unfortunately, the charging and discharging processes when using existing electroactive materials are not ideally reversible. More energy needs to be invested in charging than can be taken out again when discharging. The lost energy is released as waste heat. In combination with the organic solvent involved, the low melting point of the polymer separator currently in favour, and the associated risk of short circuits, this heat release therefore represents a real safety risk. It is therefore necessary to electronically limit the performance of EVs in order to prevent thermal runaways. An increase in reversibility could passively reduce this risk. The anode and cathode are preferably made of layered materials because the absorption and release of Li^+ ions associated with the (dis-)charging process can then take place relatively quickly involving only small activation energies. A research group in inorganic chemistry headed by Prof. Dr. Josef Breu is set to pursue an approach that will further reduce the activation energy associated with the storage/removal of Li^+ ions, and thus hysteresis, by keeping the gap between the layers open („pillared") by spacers and thus minimizing the change in volume.

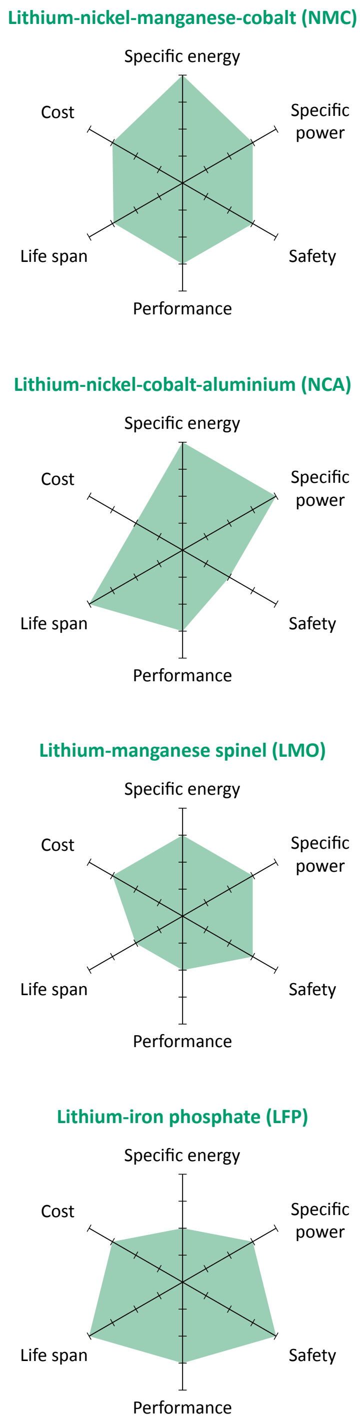

Fig. 1: Comparison of different commercial cathode materials (Illustration: BCG).[4]

„There will probably never be ‚the' LIB cell, but always several application-specific technologies."

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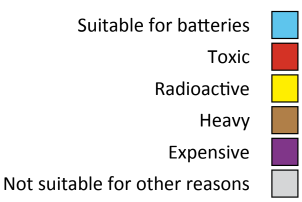
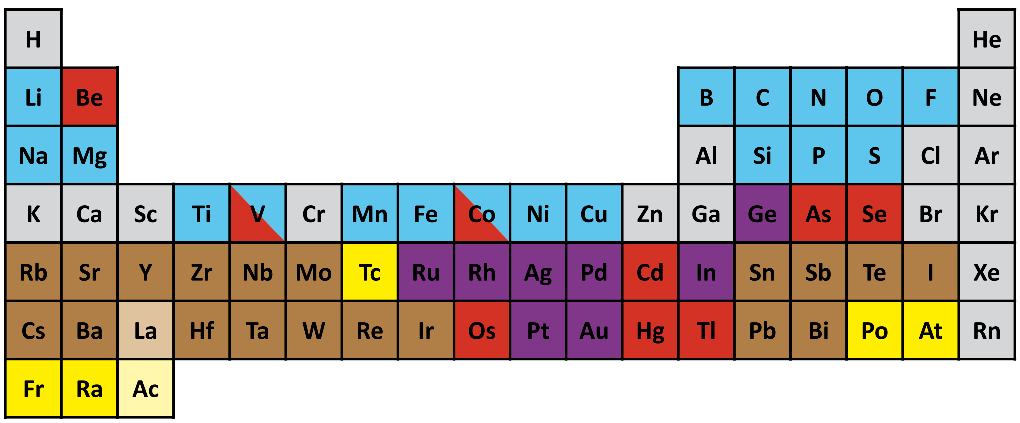
Availability of resources

The transition to e-mobility only makes sense if the availability of the necessary resources (materials) can be secured sustainably and at an commercially reasonable price. All established electric car manufacturers currently rely on cobalt-containing layered compounds, which have the highest energy density and service life compared to other available battery types. In view of the ambitious EV plans of many car manufacturers, massive shortages of lithium and above all cobalt are forecast in the production of this type of battery cell. Unfortunately, specific gravity, toxicity, price, and availability all narrow down the selection of chemical elements that are principally suitable for batteries to a small shortlist (Fig. 2). In addition, these are concentrated in only a few deposits that can be viably exploited. The concentration of critical raw material deposits in such a limited space always implies uncertainties regarding long-term availability.[6]

Lithium is the central component of LIBs, and availability is estimated to be sufficient to meet even the most optimistic demands. The hunger of the world economy for this metal, however, even now points to unmistakable socio-ecological and economic problems appearing in connection with its mining. Lithium salts are readily soluble, and lithium-containing minerals have therefore accumulated over geological periods primarily in the arid regions of the high Andes of Chile and Argentina. At the same time, lithium extraction requires large quantities of water, which is taken from valuable groundwater resources in this region. The lithium industry competes for this resource with the indigenous population, who are thus deprived of the basis pf their way of life and economy that has been adapted to these harsh living conditions for thousands of years. This is accompanied by political tension as the state uses expropriation and displacement of the indigenous population as means to valorize the area. In view of these uncertainties, rising demand is reflected in the price, which has risen after enormous fluctuations from approx. 4,000 dollars/tonne in 2000 to 12,000 dollars/tonne in 2018.[7]

More than half of world production and reserves of cobalt (Co) originates from the Democratic Republic of Congo, which has been devastated by civil war in recent years. The continuity of the cobalt supply is therefore repeatedly called into question, affecting market certainty. This political instability is the reason for strong price fluctuations and doubts about the sustainability of the supply of this critical element. Cobalt is toxic in high doses, and can lead to health problems in mining areas, rendering the common practice of child labour in mines even more problematic.[8] Cobalt, with an average concentration in the earth's crust of 25 ppm, is not as rare as gold ($4 \cdot 10^{-3}$ ppm), but still much rarer than the neighbouring elements manganese (Mn, 950 ppm), iron (Fe, $56 \cdot 10^{3}$ ppm) and nickel (Ni, 84 ppm).[9] The relative scarcity and uncertainty of supply have resulted in a sharply rising price, which has gone from 30,000 dollars/tonne in 2000 to as much as 94,000 dollars/tonne in 2018. This raises the central question of what proportion of the global vehicle fleet can/should be equipped with cobalt-based batteries.





■ *Fig. 2: Overview of the suitability or disadvantages of elements for use in batteries (Illustration: Sebastian Weiß / Christian Göppner).*[5]

A central goal of the BayBatt research project mentioned above will therefore be the development of cobalt-free, iron-based cathode materials. Iron is well distributed, available worldwide in unlimited quantities and is completely harmless to health. In contrast to the already commercialized lithium iron phosphate, however, a pillared layer structure promises to achieve capacities comparable to those of the NMC and NCA materials, as required for electric vehicles.

Ecological balance

In order to achieve the long-term goals of reducing CO_2 emissions, politicians and industry are increasingly setting store by electric mobility. In contrast to cars with internal combustion engines, these can drive emission-free locally. However, it must be taken into account that the production of the car, the battery and above all the electricity to charge it is associated with CO_2 emissions. Heavier vehicles or more powerful vehicles with internal combustion engines may even have a better environmental footprint than electric counterparts.

Therefore, it is not possible to make a blanket statement on the environmental friendliness of drive systems covering all vehicle classes. Small cars with low-powered engines typically have small batteries. Their CO_2 emissions summed over lifetime are significantly lower, and the advantage will only become larger as the share of regenerative energy in the electricity mix increases. If the electricity can be provided entirely by renewable energies, the operation of electric vehicles will be emission-free, and the climate and environment will not be polluted by CO_2 or nitrogen oxides. At present, however, electric mobility only has clear advantages if light and low-powered, smaller medium-sized cars are used in local road traffic, and if they can draw on completely renewable energies.

The bottom line

The electric car is often praised as a panacea for the climate crisis without us having to suffer restrictions on the individual mobility we have become so fond of. However, e-mobility is only ever as clean or low in CO_2 emissions as the ecological balance of battery production and country-specific electricity production/distribution – and the whole thing is framed by the electricity consumption per kilometre driven. The new breed of luxury SUVs with their heavy and bulky battery packs and enormous engine power, that are currently so much in demand among car buyers, will provide a lot of driving pleasure, but will not be able to make any real contribution to climate protection.

Meanwhile, diesel drivers are used to ranges of more than 1,000 kilometres from an engine output of more than 100 kilowatts, and an engine life of more than 300,000 kilometres. Although these specifications are not really essential for the vast majority of customers, the limited range resulting from the low energy density and high price of batteries does pose a serious entry problem. Performance and dynamism are currently the most convincing sales arguments, but they are dramatically worsening the ecological balance. Without an adaptation of expectations on this emotionally charged product aka our beloved cars, the ecological revolution in mobility will not succeed given the state of battery technology.

Moreover, the mining and recovery of essential critical metals for the battery is also concentrated in just a few areas in the world, which themselves can only be classified as socio-ecologically problematic. If climate protection and air purity in Europe's cities are paid for with child labour, working conditions dangerous to human health, the destabilisation of fragile ecosystems, or with the destabilising weak, politically fragile state structures, the global benefit is questionable.

Unsurprisingly, the high energy density super battery which packs huge storage capacity and thus range into a small installation space, is nowhere in sight at BayBatt either, for the time being. Rather, the focus here is on replacing critical raw materials with cheap, globally available ones, and on increasing safety.

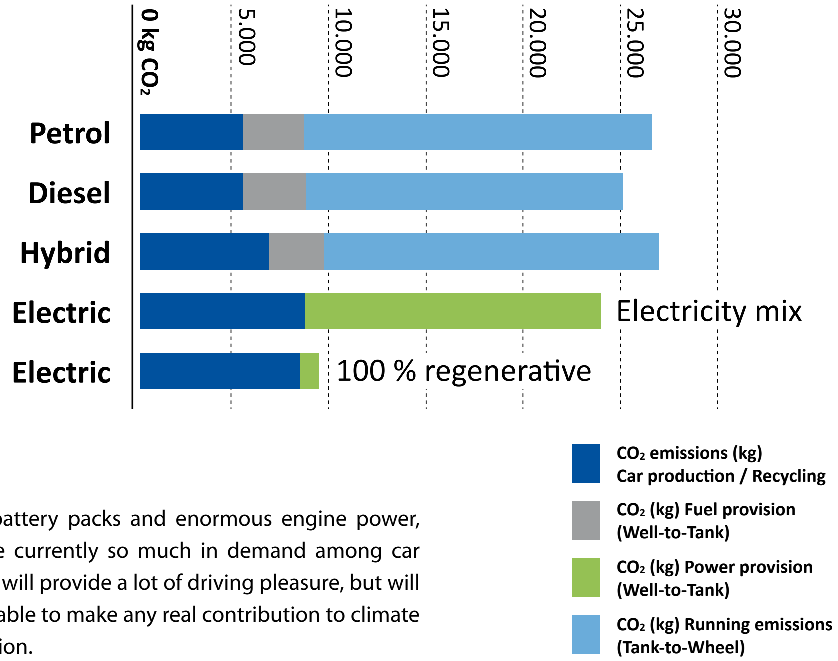


Fig. 3: Climate footprint of small cars with a mileage of around 150,000 kilometers (Image: © ADAC e.V., www.adac.de © 2018).[10]

1 W. Lee, et al.: Advances in the Cathode Materials for Making a Breakthrough in the Li Rechargeable Batteries. Angew. Chem. Int. Ed. (2019): DOI: 10.1002/anie.201902359.
2 On the construction and functioning of LIB, see the contribution by Prof. R. Moos, pp. 18-21.
3 The solvents are flammable and so represent a safety risk. Their replacement by solid ion-conducting materials is the subject of intensive research. In this regard, see the contributions by Prof. M. Thelakkat, pp. 26-29, and by Prof. R. Moos, pp. 18-21.
4 The Boston Consulting Group: Batteries for Electric Cars. Challenges, Opportunities, and the Outlook to 2020. BCG 2010.
5 Cf. also C. Liu, et al.: Understanding electrochemical potentials of cathode materials in rechargeable batteries. Mater. Today (2016), 19 (2), 109-123. DOI: 10.1016/j.mattod.2015.10.009.
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Michael Danzer

Battery modelling

Ways to understand and design electrochemical energy storage systems

Opening ceremony of the Bavarian Centre for Battery Technology on the Campus of the University of Bayreuth on September 6, 2018, from left to right: Prof. Dr.-Ing. Michael Danzer, Chair of Electrical Energy Systems (EES) and Head of BayBatt; Dr. Markus Zanner, Provost of the University of Bayreuth; Prof. Dr. Marion Kiechle, Bavarian State Minister for Science and the Arts (Photo: Peter Kolb).

When the Bavarian Centre for Battery Technology (BayBatt) was inaugurated on September 6, 2018, the symbolic starting signal was given by means of a battery. Bavarian Science Minister Prof. Dr. Marion Kiechle pulled a lever and pressed a metal stamp on the battery – and a sign immediately lit up signalling the official start of the new research centre on our Campus. However, for reasons of safety and appearance, we only used a model of a battery to close the electrical contact. If you looked closely, you could see why the model could never have worked as a battery: It was just a hollow metal cylinder with its poles at the same potential, and no electrical voltage could ever have been tapped. Nevertheless, many viewers believing the contraption to actually be a battery, inspected its design at great length.

What makes a model a model, and what defines a model in science?

The battery model of the opening ceremony was a representational model, an illustrative rendering, an image showing similarities in shape, texture, weight, and size to a real battery. Otherwise, it differed from the electrically active original primarily in its properties, its structure and, above all, its function.

Providing just the external similarities of the battery model, we deceived our guests, we more or less hoodwinked them. In science, however, models are there to achieve just the opposite; we want them to shed light on the darkness. Indeed, modelling plays a decisive role in the process of expanding scientific knowledge. Models serve to simplify and idealize complex structures, processes, and interrelationships, and thus make them accessible to our perception. By means of abstraction and reduction, analogy and construction, models are meant to help us better understand a more complex reality, and ultimately to arrive at a knowledge of the world, or at least at a deeper and more comprehensive understanding of a certain part of the world. Models are vehicles that enable us to explore real objects, properties, relationships, and contexts, and to make them technically usable.

One well-known objective model in science is the deoxyribonucleic acid (DNA) double helix, using which Francis Crick and James Watson discovered the molecular structure of genes. In 1962 they were honoured with the Nobel Prize for Medicine. One relevant example from the field of energy technology is the explanatory model of photovoltaics: If we describe light not as a wave but as a photon, and thus as a particle capable of lifting a bound electron from the valence band into the conduction band in a semiconductor, then we can readily understand how it is possible to pick up electric current at the terminals of a solar cell.

In science, there is actually a variety of goals towards which modelling is pursued:

- *Analysis models* are designed to elucidate material properties or the internal structures of processes.
- *Simulation models* are implemented in computers in order to investigate processes with the help of simulations instead of experiments.
- *Design or synthesis models* serve to accelerate pattern development (rapid prototyping), sensory monitoring, or the targeted influencing of technical systems with the aid of model-based control engineering methods..

Moreover, each scientific discipline has its own model systematics. It speaks its own language, with a vocabulary and grammar all of its own. In order to be able to cooperate interdisciplinarily between physics, chemistry, materials science, engineering and computer science, to look beyond one's own nose and to broaden one's knowledge horizon, mutual understanding and a mutual ability to speak (and sometimes even a translation) become necessary at the interfaces of the disciplines. On the Campus of the University of Bayreuth, such interdisciplinary cooperation has a tradition of more than four decades, and it will undoubtedly prove a great strength of the new Centre for Battery Technology.

AUTOR

Prof. Dr.-Ing. Michael Danzer is the Chair of Electrical Energy Systems (EES) and the Head of the Bavarian Centre for Battery Technology (BayBatt) at the University of Bayreuth.

Fig. 1: Model of a battery (Photo: Michael Danzer).

„Modelling at a research centre must follow a concerted approach that combines the specific models of the individual orders of magnitude and bridges scales."

Approaches to modelling for batteries, in fact, extend over many scales and orders of magnitude.

They range

- from the atom to the molecule to the particle (primary structure),
- from the electrode and the electrolyte to the electrode-electrolyte unit via interfaces (secondary structure),
- from the single cell to the cell compound (module) to the battery system,
- and from the battery system to integration into an energy system.

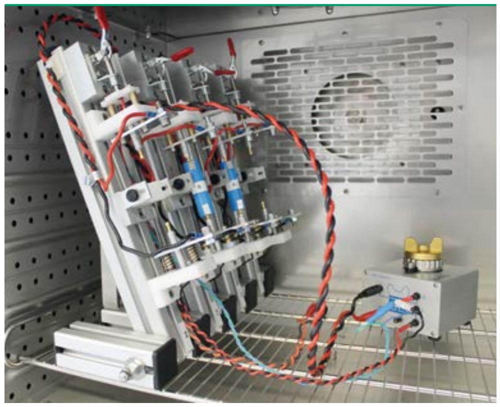

Fig. 2: Cell holder for an electrical test of experimental and round cells in a climatic chamber (Photo: Christian Wißler).

V_{cell}	terminal voltage
I_{cell}	terminal current
I_{mr}	main reaction current
I_{sr}	side reaction current
V_0	voltage source (electromotive force)
Z_i	complex internal resistance (impedance)
R_{sr}	resistance of side reaction

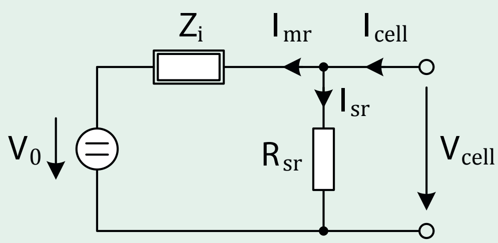

Fig. 3: The equivalent circuit diagram shows the terminal voltage of an energy storage device on the right of the model. The main terminal current contributes to energy storage, while secondary reaction currents lead to self-discharge or battery ageing. The structure of the model is transferable to many other technologies (Illustration: Michael Danzer).

Modelling in a research centre must therefore follow a concerted approach that both combines the specific models of the individual orders of magnitude and bridges scales (multiscale models). Meanwhile, goal-oriented models with clearly defined boundary conditions designed within the discipline's own boundaries must be expanded, while findings on a lower scale are to be made usable on the next higher scale, and requirements of the higher scale are to be transferred to the lower scale. Sometimes this will force scientists to leave their respective comfort zones and enter new territory.

Cornerstones of Modelling

The lithium-ion battery (LIB) so ubiquitous in science and technology today, is, in fact, a comparatively young technology that has been commercially available for less than 30 years. Sony first introduced the technology for portable electronics in the early 1990s. Since then, the march of lithium-ion batteries has been one incredible triumph, they now being found in everything from watches, smartphones, notebooks, cordless screwdrivers, electric vehicles, to large stationary storage devices. This rapid development has been accompanied and, to a large extent, made possible by analysis, simulation, and design models on the material and system level. Three cornerstones of modelling are worth highlighting here:

■ The function of lithium ion batteries is based on the intercalation of lithium ions into the lattice structure of a host material. Graphite is usually used as the active material for the negative electrode, although it is not stable due to the organic electrolytes used. A chemical reaction takes place that permanently binds lithium ions and thus reduces the capacity of the battery. In 1979 Emanuel Peled presented a model of a Solid Electrolyte Interphase (SEI), i.e. an intermediate phase or top layer between a solid and a liquid electrolyte.[1] In addition, he presented a mathematical model for the growth of the thickness d of the SEI over time t: $d = c \cdot \sqrt{t}$. For lithium-ion batteries, his SEI model explains that the active material is not in direct contact with the electrolyte and thus achieves considerable longevity. The equation above makes it possible to analyse and predict the capacity loss of an LIB.

■ One further milestone in the modelling of electrochemical processes and transport processes in batteries is the Newman model of 1993, also known as the theory of porous electrodes.[2] The key idea of this modelling approach is to calculate the physicochemical processes taking place in a battery, efficiently and spatially resolved, on the basis of their basic equations (first principle models). The complex geometry of a three-dimensional electrode is reduced to two (pseudo) dimensions by abstraction. One dimension is the surface normal of the electrode, the second the radius of a spherical particle. Using equations for migration, diffusion and charge transfer, the electrochemical behaviour of complex cell geometries can now be simulated using finite element methods (FEM). Here, the structure and morphology of the electrodes can be easily varied.

■ The state of charge (SOC) of a lithium-ion battery is not directly measurable – in contrast to

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2 M. Doyle, T. F. Fuller, J. Newman: Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/InsertionCell. Journal of the Electrochemical Society (1993), Vol. 140, No. 6, 1526-1533.
3 G. L. Plett: Extended Kalman filtering for battery management systems of LiPB-based HEV battery packs Part 2. Modelling and identification. Journal of Power Sources (2004), Vol. 134, 262-276.

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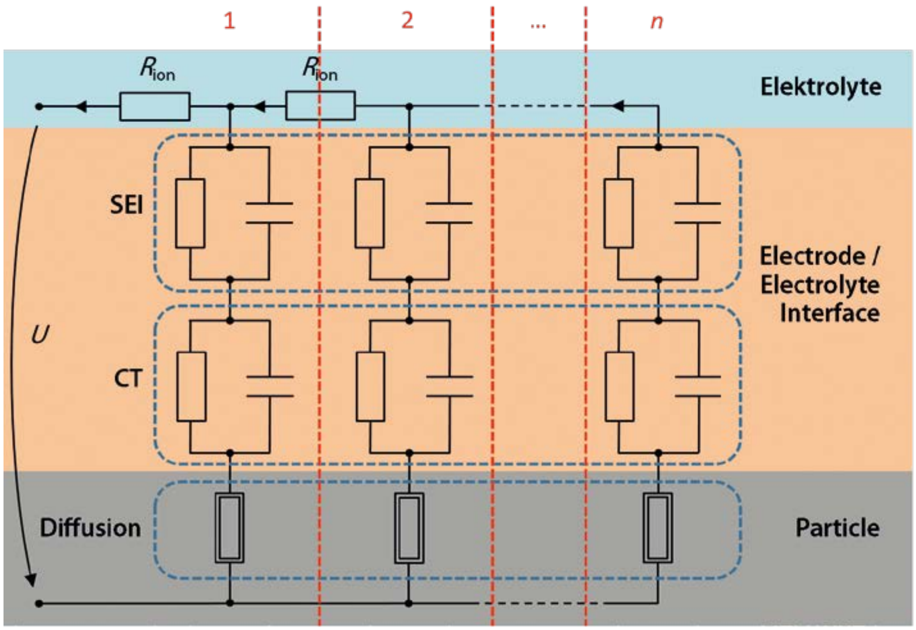
S. Schindler, M. A. Danzer: A novel mechanistic modelling framework for analysis of electrode balancing and degradation modes in commercial lithium-ion cells. Journal of Power Sources (2017), Vol. 343, 226-236. DOI: 10.1016/j.jpowsour.2017.01.026.

a lead-acid battery, whose state of charge can be determined by the acid concentration. In addition, the LIB technology lacks any overcharge tolerance, such as that of lead batteries. The state of charge of a lithium-ion battery must therefore be meticulously monitored. This means that the SOC must be determined continuously and precisely, and limit values must be strictly adhered to. Gregory Plett wrote a standard work on model-based state of charge estimation in 2004.[3] The design model for online diagnostics is an electrical equivalent circuit model of the input/output behaviour of the measurable variables of current and voltage at the terminals of the battery cell. The model can be parameterized by electrical tests on real cells, and has a high prediction accuracy. Estimation algorithms use this model description to precisely reconstruct the state of charge during operation from the measured variables in the application.



U Voltage
R_{ion} Ionic Resistance
SEI Solid Electrolyte Interphase
CT Charge Transfer

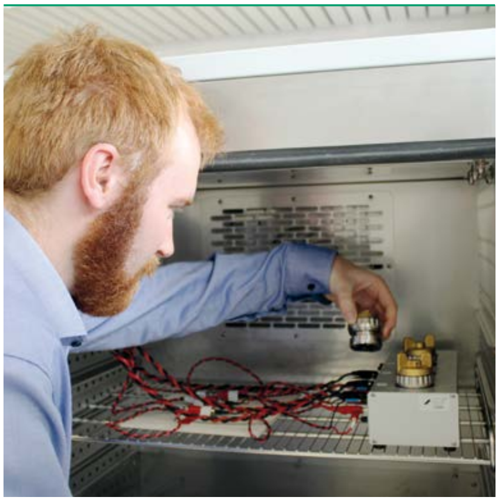
■ *Fig. 4: Extended, spatially resolved, electrochemical model of an electrode as an electrical network of electrical and ionic charge transport. Electrode processes take place in parallel branches, very much depending on local conditions and quantities (Illustration: Markus Hahn).*

Conclusion

To sum up, it is worth bearing in mind that: Models play a decisive role in the development of new storage concepts and the operation of battery systems. Through analysis models, we extend our understanding of the desired electrochemical processes, but also of the undesirable parasitic and even destructive reactions. Simulation models make it possible to intensively and extensively investigate storage concepts and cell designs without the need to produce cells at great expense. Design models can be used to develop model-based methods for battery management systems that ensure the efficient, long-lasting, and safe operation of batteries.

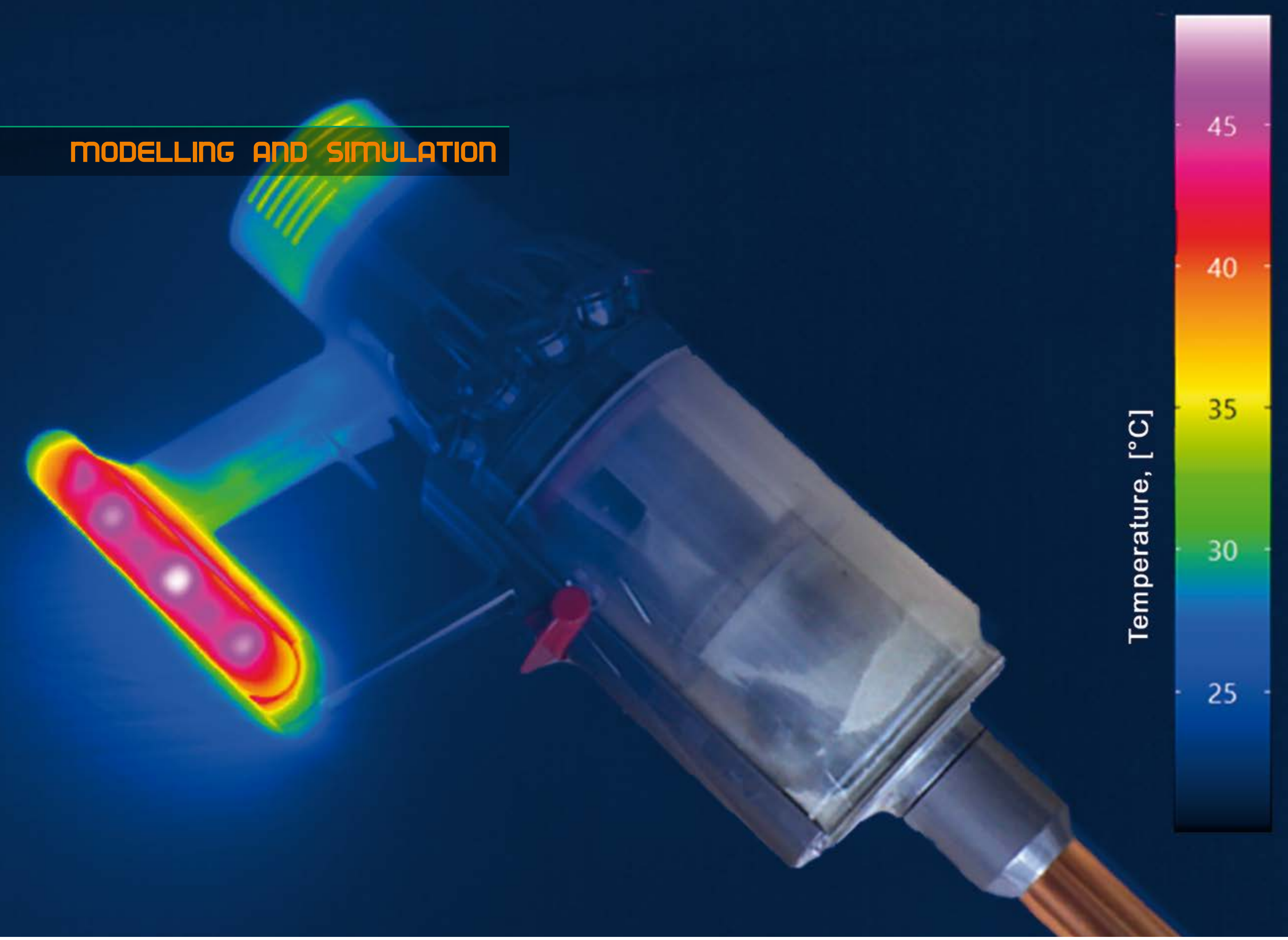
■ *Fig. 5 (left): Experimental cells for the investigation of battery electrodes with reference electrodes (Photo: Christian Wißler).*

■ *Fig. 6 (left): Insertion of an experimental cell into a cell holder (Photo: Christian Wißler).*



Battery modelling during studies

At the University of Bayreuth, students of materials science and energy technology are familiar with the various requirements and implications of modelling at different scales. In doing so, they learn to be able to communicate across the individual disciplinary boundaries. In the module „Modelling and Simulation of Electrochemical Storage (MSES)" different concepts of battery modelling are presented, which are then implemented by the students themselves in an intensive programming internship. The module is offered by the Chair of Electrical Energy Systems (EES), with support from the Chair of Physical Chemistry I.



Markus Retsch
Kai Herrmann
Flora Bitterlich

Heat management in batteries

Improving safety with thermal analysis and simulations

A thermal imaging camera uncovers the temperature differences that the head of a battery-powered hand vacuum cleaner exhibits after complete discharge (Photo: Markus Retsch).

Energy storage and power supply are becoming more and more important in our increasingly digital world. To this end, a wide range of energy storage technologies have emerged which differ greatly in terms of efficiency and performance, but also in terms of production costs and lifetime. Batteries are the most common form of mobile energy storage and selective energy release. The lithium-ion battery (LIB) stands out among the multitude of battery types. Compared to other rechargeable batteries (sodium-ion batteries or nickel metal hydride batteries), it has an increased energy density, and its performance remains practically the same even after several thousand charging and discharging cycles. However, LIBs also cause certain problems. For example, the Samsung Galaxy Note 7 had to be recalled in 2016 as reports of fires increased. This is just one case of LIBs in which a fire or even an explosion of the battery occurred due to poor thermal management in the battery.

Why is heat distribution within a battery so important? The charging and discharging of a battery is based on electrochemical processes, or to be more precise, a combination of reactions within the battery and charge transport in the form of lithium ions and electrons released in the process. Such processes are strongly temperature-dependent. In addition, heat is generated in each battery by the current flow (Joule heating). If unforeseen influences – for example an increased ambient temperature, mechanical damage, or aging – lead to a local temperature increase, this can trigger a large number of sometimes unstoppable follow-up reactions. In the best case, these follow-up reactions only reduce the functionality of the battery; in the worst case, they cause a fire.

Loss of control in the battery

How can the development of such thermal chain reactions be avoided? First of all, a precise understanding of the structure of a battery is necessary. A lithium-ion battery (Fig. 1) normally consists of a lithium compound as the cathode and a carbon-based anode, usually graphite. The electrodes are separated by a thin polymer membrane, the separator, to avoid a short circuit. This membrane is permeable for lithium ions. To facilitate the transport of the lithium ions, the battery is filled with a liquid electrolyte that coordinates the ions and ensures rapid charge transport. These are usually lithium salts dissolved in organic solvents. The function of the lithium-ion battery is mainly based on reversible reactions at the electrodes. Lithium ions are either stored or released again. The electrons generated are transferred to the outer circuit through an aluminium layer on the cathode and a copper layer on the anode. For most commercial applications, several such battery cells are joined together to form a battery module.

So where do the weaknesses in heat management lie? The battery generates heat through the current flow, both during the charging and discharging pro-

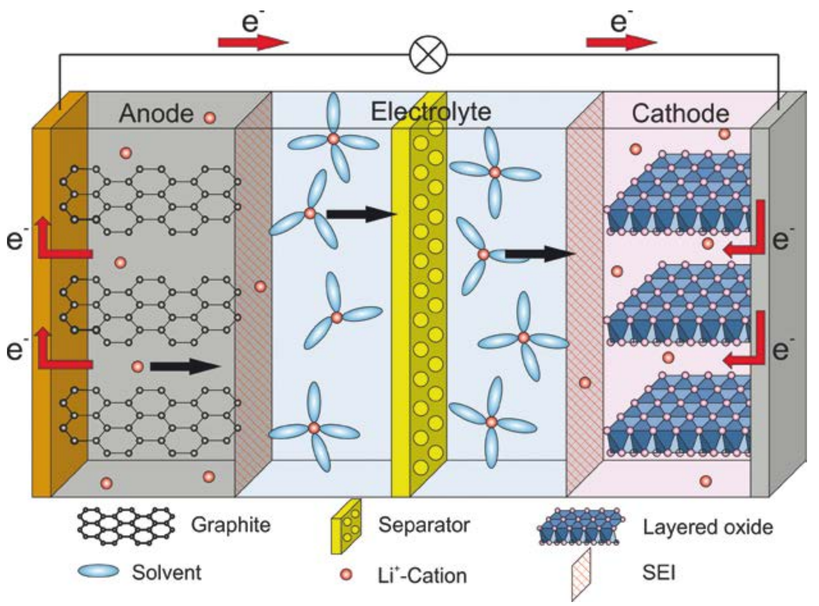


Fig. 1: The schematic structure of a Lithium-ion battery. The electron and ion flux are shown for the discharge process (Illustration: Markus Retsch / Kai Herrmann).

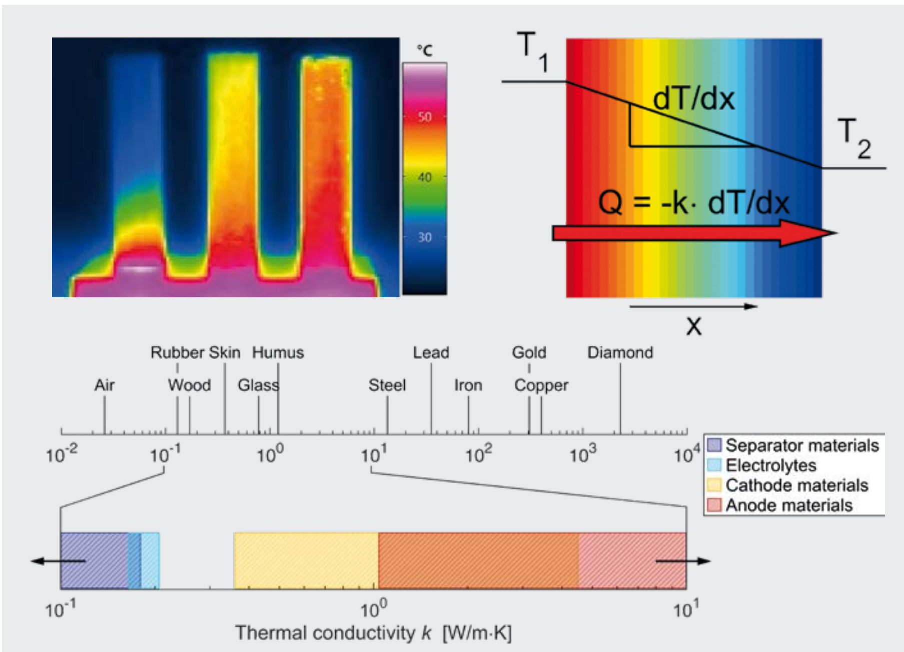


Fig. 2: Top left: Temperature distribution in rods made of different materials. Top right: The definition of the thermal conductivity via the temperature gradient according to Fourier. Bottom: The classification of the thermal conductivity of typical battery materials compared to other materials (Images: Kai Herrmann).

„Strategic temperature management requires, first and foremost, an understanding of the materials' thermal properties."

AUTHORS

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■ Flora Bitterlich (B.Sc.) is a master's student in the Physical Chemistry I Research Group.

cess. Additional heat is generated by the reactions taking place. In the normal state, this is not problematic. However, if the temperature gets out of control, a thermal chain reaction is triggered. This process can be divided into three stages:

- First, there is a local temperature increase. This can be triggered, for example, by mechanical damage or an internal short circuit. At this stage, the battery changes to an abnormal state, and the internal temperature begins to rise.
- This is when the overheating begins. The boundary layer between the anode and the electrolyte (SEI) begins to dissolve. As soon as the electrolyte is in direct contact with the anode, the lithium in the anode reacts with the organic solvents in the electrolyte. This releases highly flammable hydrocarbons, which increase both the pressure and the temperature in the battery. At around 130 degrees Celsius, the separator begins to melt. This leads to a short circuit between cathode and anode. Depending on the cathode material, additional oxygen can be released during its decomposition.
- This brings us to the third phase. A highly flammable mixture has accumulated in the battery at elevated temperature and pressure, which reacts and causes a fire or explosion.

In order to avoid a thermal chain reaction, temperature control during normal operation is crucial. This can be achieved externally by cooling the exterior of the entire battery module. The internal design of the individual battery cell can also help prevent local overheating. Possible approaches involve strategically designing interfaces between the battery components and employing an anisotropic battery structure to facilitate the dissipation of heat. In this context, the materials of the individual components and their thermal conductivities play a decisive role. At the same time, these components are made of very thin or non-uniformly structured materials. For this reason, strategic temperature management requires, first and foremost, an understanding of the materials' thermal properties. The various length scales and interfaces within a battery must be taken into account and balanced.

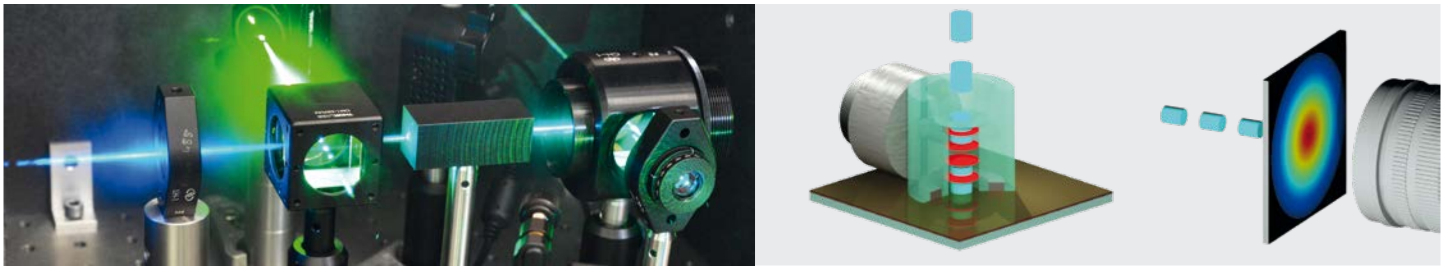
Thermal characterization

In order to classify and compare different materials in terms of their thermal properties, thermal conductivity is usually used as a parameter. Like electrical conductivity, this is a measure of how well a material conducts heat.

To quantify this property, Joseph Fourier formulated a law in 1822 which can be used for simple applications and for explanation in a one-dimensional form. It states that the local heat flux density **Q** is proportional to the temperature gradient $\frac{dT}{dx}$ in the direction of the heat flow. The constant of proportionality represents the thermal conductivity ***k***. Thermal conductivity can, for example, be represented by the temperature distribution along three rods of different materials with the aid of an infrared camera (Fig. 2). The strongest temperature gradient is exhibited by the polymer rod on the left side with the worst thermal conductivity.

The thermal conductivity of different materials extends over several orders of magnitude, with materials relevant for batteries covering only a small range. It is worth mentioning that graphite has a high thermal conductivity of several hundred watts per meter and Kelvin. Since graphite is a two-dimensional material, its thermal conductivity varies depending on the direction of the heat flow. If heat flows within the

■ *Fig. 3: Determining thermal conductivity via laser flash analysis (Photo: Markus Retsch).*



■ *Fig. 4: Spectroscopic methods enable scientists to determine thermal conductivity in thin (left) and anisotropic (middle and right) samples (Images: Kai Herrmann).*

two-dimensional surfaces, high thermal conductivity is present. However, if it flows perpendicular to it, the thermal conductivity is drastically reduced. This kind of directional dependence of the investigated property is known as anisotropy.

It is possible to characterize such anisotropic materials using the methods established at the chair of physical chemistry I at the University of Bayreuth. Thermal diffusivity is decisive in this context. It is closely linked to thermal conductivity and is a measure of how quickly temperature spreads within a given material. In order to determine thermal diffusivity over a wide temperature range, a light flash device is available that is capable of measuring at temperatures of up to 1,250 degrees Celsius (Fig. 3). The meas-urement is based on heating the lower side of a free-standing sample using a laser pulse, while the temperature arriving on the upper side is recorded time-dependently with the help of an infrared detector. Materials with high thickness and low diffusivity have a considerable time delay, whereas thin materials with high diffusivity have a minimal time delay.

The photo-acoustic method and lock-in thermography can be used to characterize anisotropic materials (Fig. 4). Both methods use a modulated laser as a periodic heat source. In the photo-acoustic measuring method, the heat generated primarily penetrates into the material vertically. In doing so, an acoustic signal is generated in a closed volume above the sample. In contrast, lock-in thermography is used to measure the thermal properties in the plane, i.e. parallel to the sample surface. The radial temperature profile created on the sample surface can be recorded with a high-resolution thermal imaging camera and then evaluated. By comparing the properties determined using both methods, it is possible to conclusively evaluate the anisotropy that is present. Since many battery systems are implemented in a layer structure, they also often exhibit anisotropic thermal properties.

However, the Bayreuth research group not only has the possibility to carry out experimental thermal characterization, but also to simulate a wide variety of problems. The software COMSOL® Multiphysics is used to simulate coupled physical processes. For example, the influence of forced convection cooling or the cooling capacity of a module can be estimated. It can also be used to make details visible that cannot be measured directly. Fig. 5, for instance, illustrates heat flow through a heterogeneous, particulate structure. The size ratio of the particles used has an enormous influence on the heat transport path.

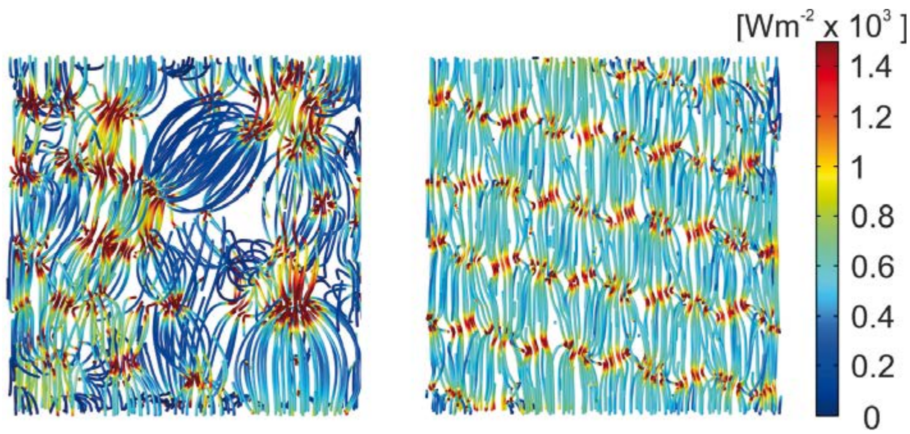
Future prospects

In order to increase battery safety via strategic design of the materials used, thermal characterization of the individual materials is indispensable. This is the only way to identify problem-solving approaches within the cell. In combination with improved simulations, this can open up new possibilities for material selection and cell construction for batteries that exhibit increased safety as power density increases.

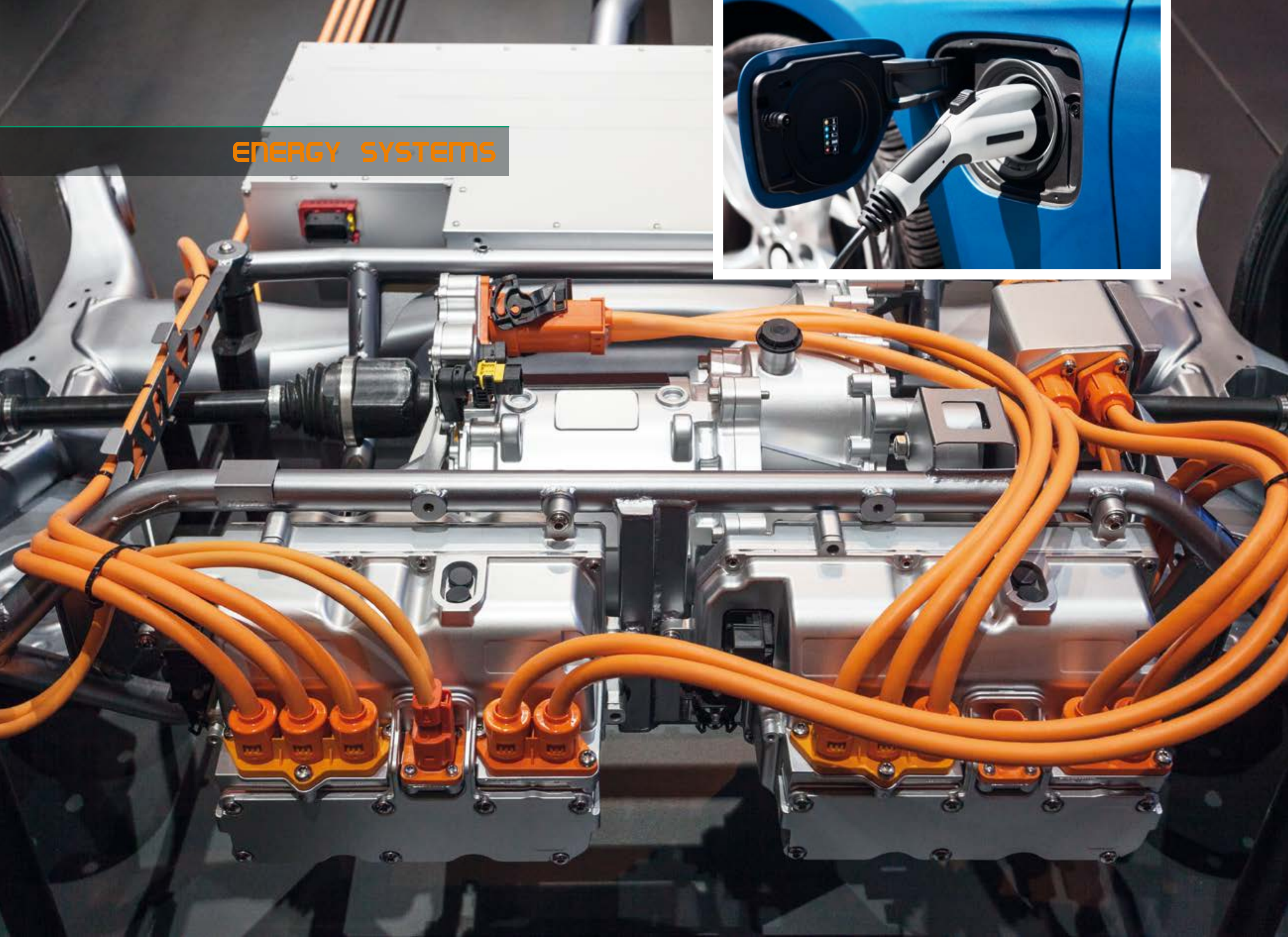
RECOMMENDED READING

F. A. Nutz et al.: Low Thermal Conductivity through Dense Particle Packings with Optimum Disorder. Advanced Materials (2018), Vol. 30, 14. DOI:10.1002/adma.201704910.

P. Ruckdeschel, A. Philipp and M. Retsch: Understanding Thermal Insulation in Porous, Particulate Materials. Adv. Funct. Mater., 2017, 27, DOI: 10.1002/adfm.201702256.



■ *Fig. 5: Computer-aided simulations make it possible to visualise how heat spreads in disordered and ordered materials (cf. F. A. Nutz, et al., see recommended reading) (Images: Markus Retsch).*



Mark-M. Bakran
Michael Gleißner
Teresa Bertelshofer

Batteries and electric drives

System considerations for e-mobility

Transmission of a plug-in hybrid vehicle (sst).
Small photo: Charging of a plug-in hybrid vehicle (sst).

For most people, the battery probably comes to mind as the most critical aspect of e-mobility. The battery determines the range, and to a large extent, the additional costs and the additional weight compared to an internal combustion vehicle. From the point of view of the vehicle's drive, however, the battery is only one of many components in the electric drive train. Taken as a system component, the battery has to contend with a completely different set of demands than, for example, those seen from the electrochemistry perspective.

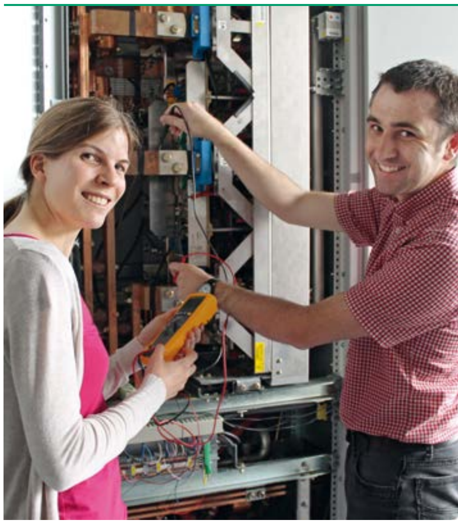
The task of vehicle system design is to consider all the conceivable system states of a vehicle, operating in different driving cycles, under different conditions within temperature ranges or loading regimes, for example, and to calculate the electrical and thermal behaviour in each case. On top of all that, an accurate prediction of the expected service life is required, too. The challenge here is that modelling must be carried out through several orders of magnitude in the time scale. The characterization of a battery cell is usually in terms of electrical frequency. System design, on the other hand, depends on a model that can be applied in terms of time. Moreover, this modelling must consider the electrical and thermal behaviour as interconnected.

The Chair of Mechatronics, a member of the Centre for Energy Technology (ZET) at the University of Bayreuth, looks at the battery from the perspective of power electronics. This is the intermediary between battery and drive motor for every electrically driven vehicle. This is where the adjustable voltages for the speed control of the machine are generated, but also the pulsed current, which loads the battery. Power electronics are thus decisive for battery load, for example, when providing high-frequency current; but at the same time, the voltage response of the battery is decisive for drive design, as well as for the torque that can be achieved, and the speed of the traction motor.

This special view of the battery leads to the insight that power electronics must use adapted electrical and thermal models of the battery, which can remain applicable to the special load profiles.

Electric drive train in a vehicle

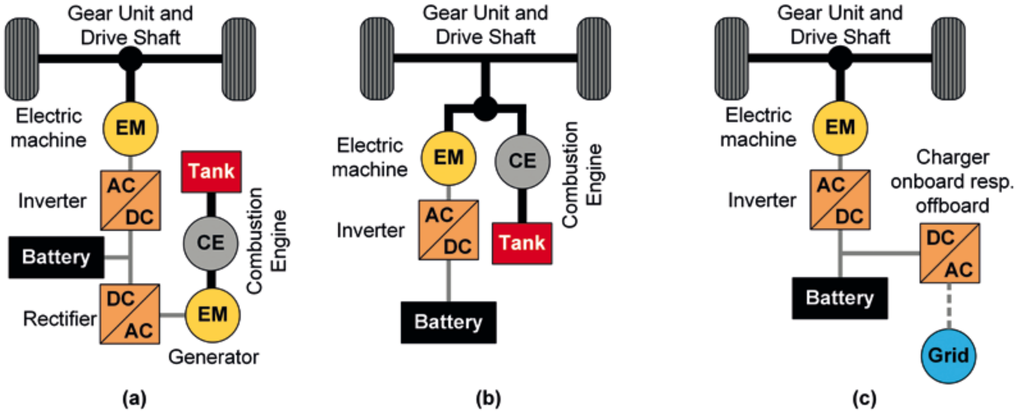
Purely electric vehicles (Battery Electric Vehicles, BEV) are operated solely with a battery. Hybrid vehicles (HEVs), on the other hand, have at least one other drive in addition to an electric motor. Whether a vehicle is designed as a mild, full or plug-in hybrid, or is indeed a purely electric vehicle, essentially determines the performance class of the electric drive, and also the energy of the battery to be installed, but invariably leads to a near identical electric drive structure (Fig. 2). And should the fuel cell one day be of interest as a supplier of energy, the electric drive structure will still look like that of a serial hybrid vehicle today.



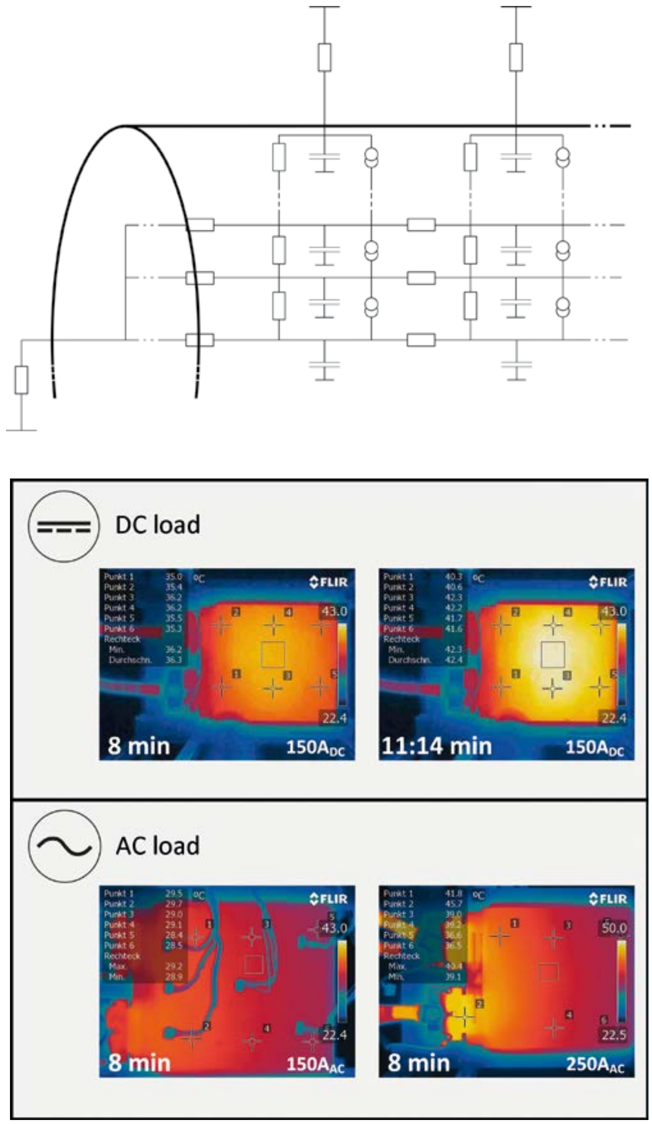
■ *Fig. 1: Dipl.-Ing. Teresa Bertelshofer and Dr.-Ing. Michael Gleißner measuring an inverter in the test hall of the Chair of Mechatronics (Photo: Christian Wißler).*

„Since the battery is the most expensive individual component in a battery-powered vehicle, measures to increase efficiency are highly worthwhile."

The available electrical voltage at the battery terminals is both a key factor and a problem, because the driver demands full performance even in cold and



■ *Fig. 2: Electric drive structure of a) Serial Hybrid Electric Vehicle, b) Parallel Hybrid Electric Vehicle, c) Battery Electric Vehicle (Illustration: Mark-M. Bakran / Michael Gleißner).*



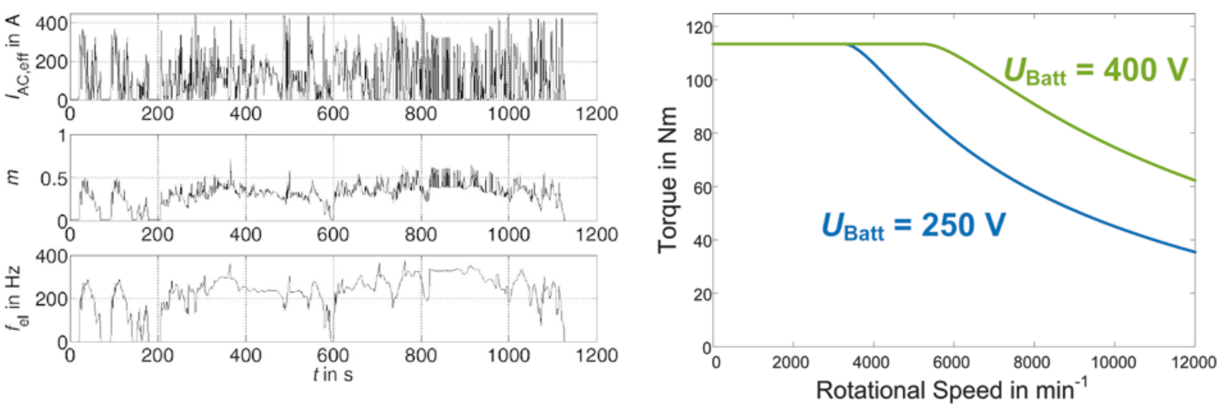
■ *Fig. 3: Thermal system modeling: a) Representative thermal model of a battery system, b) Measurements on a battery with AC and DC load (Illustrations and images: Mark-M. Bakran / Michael Gleißner).*

low batteries. System design therefore has to solve the problem that, on the one hand, maximum battery voltage represents the highest electrical load for the power electronics, while on the other, minimum battery voltage determines the performance that can be achieved. This brings us to a typical problem in the engineering sector, system optimization with many influencing variables and, at the end of the day, the goal of realizing a function as cost-effectively as possible. For instance, you have to answer the question: Should a cold battery be warmed for better performance, and – if so – should this be done externally or by actively loading the battery? A similar question applies to the other case, namely for the battery that is too warm: Should cooling be improved here, or the load reduced (Fig. 3)? And in each case it is important to consider what will be acceptable for the driver, and what they would see as a severe limitation. For example, they might feel restricted in their accustomed driving style if the vehicle did not accelerate as expected.

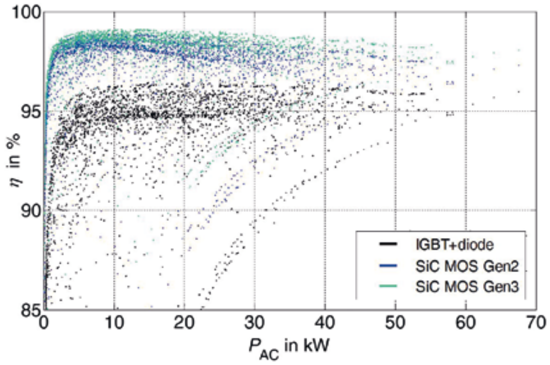
In fact, the real driving profile of an electric car differs significantly from the load on the battery, which is typically used by the cell manufacturer for characterization purposes. We encounter processes changing rapidly over time – Fig. 4 shows typical electrical influencing variables. It is clearly visible that the current load of the battery can be highly uneven. On the other hand, it can also be seen that the available drive torque is strongly influenced by the battery. This torque characteristic is at the same time the great strength of the electric car, because the full torque is constant and immediately available before maximum power is reached. This results in the impressive performance we see when an electric car leaves most more powerful vehicles with internal combustion engines standing at the traffic lights.

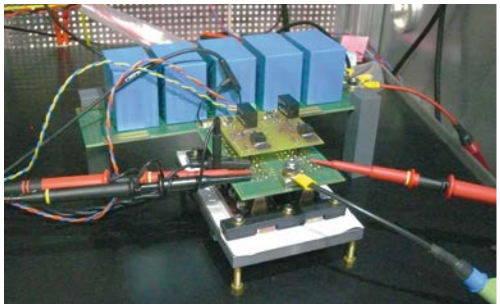
Optimization of power electronics for battery electric vehicles

Another fundamental topic of system design that includes the battery is efficiency. Even if the efficiency of an electric drive train is very high, losses naturally still occur. Here it is striking that the further



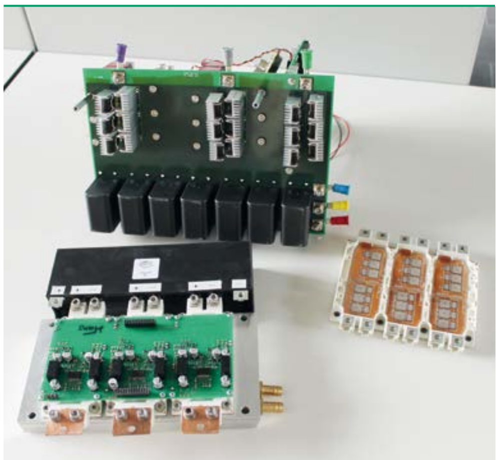
■ *Fig. 4: Influencing factors on battery design in electric vehicles. Current load in operational cycle (left), speed-torque characteristic curve of the driving motor (right) (Illustrations: Mark-M. Bakran / Michael Gleißner).*





■ *Fig. 5: Efficiency comparison of a conventional inverter and a silicon carbide inverter (left), characterization measuring station for a SiC semiconductor (right) (Illustration and photo: Mark-M. Bakran / Michael Gleißner).*

back in the drive train the losses occur, i.e. towards the drive motor, the more expensive they become. This is because the system components in front of each other have to provide additional power, which in turn results in losses. Since the battery is the most expensive individual component in a BEV, measures to increase efficiency are extremely worthwhile in this regard: for example, a three percent increase in efficiency in the drive reduces the cost of the battery by exactly three percent. The main focus of research in this area is currently on the use of new semiconductors in power electronics.



■ *Fig. 6: Small inverter for use in battery research (Photo: Christian Wißler).*

Here, the so-called wide-bandgap material silicon carbide promises significant advantages. „Wide-bandgap" refers to a larger band gap compared to normal silicon. This increases the load capacity of the component with voltage, which is why the components only have to be 1/10 as thick. These thinner components in turn enable a significant reduction in losses during power supply. The Department of Mechatronics at the University of Bayreuth is investigating such components, and is developing complete inverters for the drive. Here, real driving profiles can be used to demonstrate the extent of efficiency improvements (Fig. 5).

Fast charging of batteries in electric vehicles

Discussions about shorter charging times for electric cars are also a growing issue in the media. In this regard, charging capacities of well above 150 kilowatts are routinely bandied about. Even for the charging capacity of around 100 kilowatts that can be achieved today, the battery is already the limiting element in the system. For this reason, charging power must be greatly reduced at higher charge levels in order not to damage the battery.

For even greater performance, the additional challenge is that this can only be achieved at higher voltages. This means that the voltage must be increased from around 400 volts DC, as is typical these days, to 800 volts, in order to be able to carry the necessary current via the charging cable. Where a battery system today already requires a series connection of about 100 individual cells, this will then increase to 200. This will also increase the effort required to balance the charge differences in the individual battery cells, the cell symmetry, because every battery cell naturally has production-related tolerances. If the weakest cell is not to limit the overall performance, then balancing must be carried out with the aid of power electronics (Fig. 7a).

Here, too, the interplay of battery and system must be characterized very precisely, because too much balancing power increases the overall costs and reduces efficiency. On the other hand, the speccing of excessive levels of manufacturing quality increases

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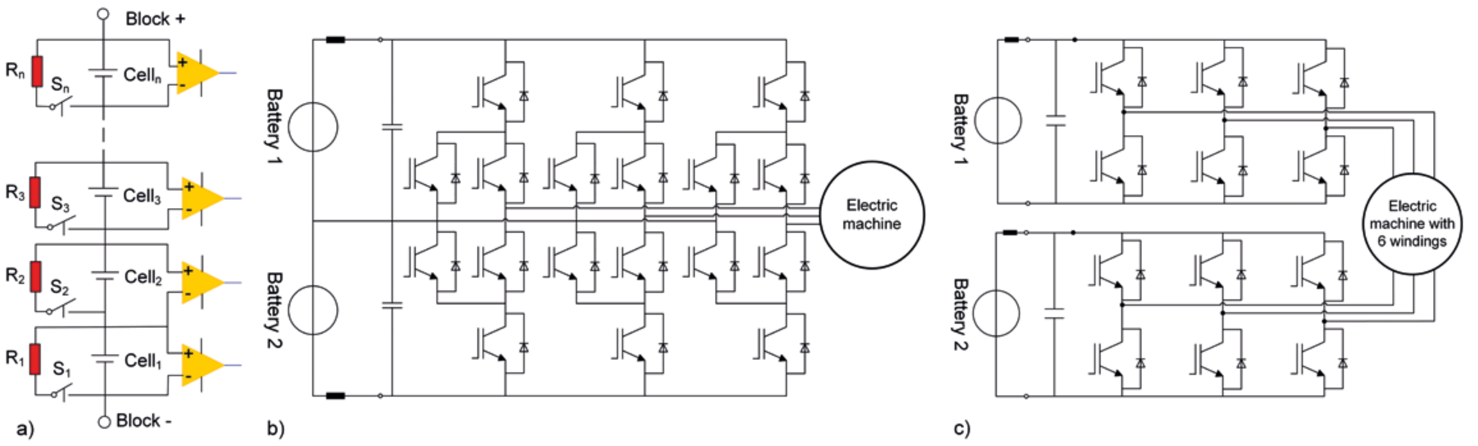


Fig. 7: *Diagram of the cell series circuit with balancing via resistors (a); diagram of a split battery with multi-level inverter (b) and with multi-phase motor (c) (Illustrations: Mark-M. Bakran / Michael Gleißner).*

the costs per cell. Again, an evaluation is only possible from a system perspective, by means of which it is possible to determine, for a given manufacturing tolerance, the exact balancing performance to be maintained. Also from the system perspective, this procedure must be compared with alternative approaches. In this case, for example, this would be the division of the complete battery into two partial batteries.

Such an approach is again only possible if the structure of the drive system is adapted accordingly. Again, there are two exemplary approaches:

- Either one uses adapted power electronics that are capable of feeding a motor from two partial batteries (Fig. 7b),
- or using a special electrical version of the motor that uses several winding systems (Fig. 7c).

In the first case, so-called 3-level or multi-level inverters are used, which offer additional potential for increasing efficiency. In the second case, a drive concept is achieved which is capable of maintaining driving operation even after a fault in a subsystem.

Summary

This exemplary presentation of topics relating to the electric drive system of a vehicle has shown that there is no component that does not have repercussions on the entire drive system, and that there is hardly a system decision that does not have a repercussion on the battery as a system component. An understanding of the battery from the system perspective is therefore the key to achieving the overall optimum. And everyone who drives an electrically powered vehicle in the future will be thankful for this optimum in the end.

Fig. 8: *The Chair of Mechatronics led by Prof. Dr.-Ing. Marc-M. Bakran gave support to the Elefant Racing team of Bayreuth University in 2019 again, in particular with regard to the construction of an electrically driven race car (Photo: © Elefant Racing).*

Philipp Wetzlar and Felix Krohn

Pole position thanks to electric drive technology

Fig. 1: *The racing car „FR 19 Loki" of the Elefant Racing Team 2019 (Photo: © Elefant Racing).*

Elefant Racing e.V., a student initiative at the University of Bayreuth, already has quite a tradition: since 2004, the University has been taking part in an annual worldwide racing series – the „Formula Student" – with racing cars built by its students. The team has often received international attention due to the success it has achieved in this area. There are currently almost 50 students from the fields of engineering, business administration, and computer science who are implementing their innovative technical ideas to compete against student teams from other universities in Germany and abroad.

In 2011, Elefant Racing was one of the first Formula Student teams to make the switch to electric drives. Since then, a new electric racing car has been built on Bayreuth's Campus every year. This has enabled our students to gain a considerable advantage with regard to knowledge and experience. One example is the battery packaging concept, which radically changed in 2019 due to the introduction of an all-wheel drive system: the previous two-part lithium polymer batteries were replaced by one large battery in the vehicle fuselage. This transition to a new battery concept not only further reduces weight but also increases safety. Furthermore, the cells were tested under racing conditions for the first time this year.

The racing car from Bayreuth weighs only 200 kilograms and can accelerate from 0 to 100 km/h in just 2.5 seconds. It is able to reach a top speed of 125 km/h.

Fig. 2: Installation of the battery in the racing car (Photo: © Elefant Racing).

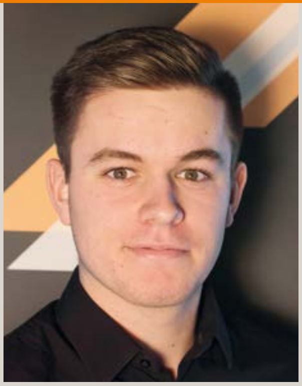
FACT SHEET

- Cells are divided into 6 „cell packs".
- 280 cells (pouch cells) 140S2P.
- 6.84 kilowatt hours.
- 420-588 volts.
- Discharge current >200 amps.
- Charging current ~100 amps.
- In the safety system, relays separate the positive pole from the negative pole of the battery. The status of the relays is monitored.
- Its own battery management system.
- IMD (insulation monitoring device) board for insulation monitoring between high and low voltage.
- The LV system is supplied via two isolated voltage transformers from the HV system.
- The battery is air-cooled by six integrated fans (~100W) and additionally secured by an automatic safety device which closes the additional ventilation slots in the battery box in the event of an error.

In 2019, the Elefant Racing team once again received support from renowned high-tech companies for both the construction and testing of its racing car. And without the close cooperation with the Mechatronics Research Group under the direction of Prof. Dr. Mark.-M. Bakran, the switch to all-wheel drive would not have been possible. Two members of the Bayreuth team wrote their master's theses in engineering on the wheel hub motors they had developed themselves to help make the drive system a reality.

It does not make sense to transfer the concept of the new electric racing car developed in Bayreuth to everyday automobiles since the battery is designed for racing and therefore has a very low storage capacity. However, a look back at the enormous technical advances made since the first Formula Student 15 years ago gives cause for optimism. Electric mobility definitely has a future, and Elefant Racing will continue to advance this field with creative design ideas.

AUTHORS



Felix Krohn, 1st Chairman of Elefant Racing e.V.

Philipp Wetzlar, 2nd Chairman of Elefant Racing e.V.

Dieter Brüggemann
Florian Heberle
Sebastian Kuboth

Smart Homes

Heat and electricity for our future homes

Vision of the future: The entire energy system of a smart home is controlled by remote control (sst).

With a view of the sunrise through blinds already open, the sound of your favourite music drifting in with the scent of freshly brewed coffee – this is how you can imagine waking up in a „Smart Home" in the future. In addition to these conveniences, intelligent systems should above all provide a more efficient energy supply and load control for our residential buildings. To this end, for instance, electricity consumption from washing machines, freezers, and other household appliances can be timed to coincide with peak production in the public grid. In addition, the extent to which private battery storage can relieve the energy grid is currently being investigated. An important goal here is to increase the service life of batteries, reduce their costs, and thus achieve economical operation.

The economic efficiency of battery storage systems

In private households today, rechargeable secondary batteries, known as accumulators, are still being used primarily in combination with photovoltaic systems. Instead of feeding the self-generated solar power into the public grid, in order to purchase it again from there later for about three times the price, it is temporarily stored in a battery and later called up to supply the household. This increased home consumption thus improves economic efficiency. A further advantage results from the fact that, at high PV output, no more than 70 percent of the maximum system output is usually fed into the public grid as contractually agreed. By using a battery, the surplus current is stored instead of „regulating" the system output - that is, reducing it so that it's capacity is not fully utilised.

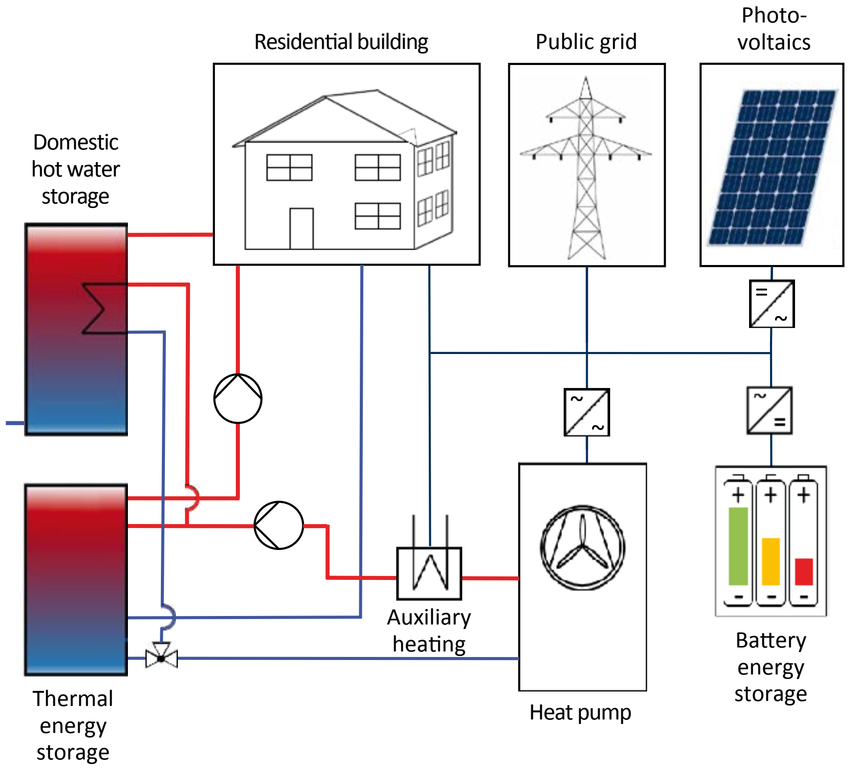


Fig. 1: Schematic structure of a modern energy system in residential buildings (Illustration: Sebastian Kuboth).

These days, remuneration for photovoltaic electricity fed into the public grid is falling steadily. In July 2018, for example, the average EEG remuneration for the commissioning of a roof-mounted system with a maximum peak output of 10 kilowatts was still 12.2 cents per kilowatt hour. In the meantime, however, this figure has fallen further, amounting to only 10.6 cents per kilowatt hour in July 2019. A further decline in remuneration is to be expected in the future. It is therefore becoming increasingly attractive to combine a domestic PV system with an electrical energy storage device.

Fig. 2: Charging an electric car in the garage. The charging station runs on recycled EV batteries (sst).

Fig. 3: *Volumetric flow sensor of the pilot plant for heat pumps (Photo: Christian Wißler).*

However, despite steadily falling prices, investments in electrical energy storage systems keeping self-generated solar power on tap for private consumption are still associated with considerable costs. Consequently, the capacity is often not sufficient to completely store excess energy on sunny days. For this reason, the Centre for Energy Technology (ZET) at the University of Bayreuth is investigating innovative concepts to combine the direct storage of electricity in batteries with the conversion of electrical energy into other forms of usable energy. It should be borne in mind that a large part of the energy required by private households takes the form of heat. This is why the integrated systems for residential buildings, as researched at ZET, are particularly concerned with combining battery technologies with „Power to Heat" technologies, i.e. the efficient conversion of electrical energy into thermal energy.

Batteries and air source heat pumps increase the self-sufficiency of residential buildings

An efficient method of converting electrical energy into heat is the use of heat pumps. In addition to electrical operating power required, these draw heat from the air, the water, or the soil of the surrounding environment. Thus, over an average year, they can often provide four times the electrical energy actually used as heat. For thermodynamic reasons, this ratio, the coefficient of performance, is mainly determined by the temperatures of the outside air (heat source) and the heating water (heat sink): The smaller the temperature difference between the heating water and the heat source, the more efficient the heat pump can be. However, especially with air-to-water heat pumps, the temperature of the ambient air can change by up to 20 degrees Celsius within 24 hours. A standard heat pump control system is normally not able to react sufficiently well to these fluctuations. Therefore, a heating curve, preconfigured for a particular building, and dependent on the outside temperature, is usually used. With this type of control, the heat pump must generate more heat the colder the ambient air becomes. However, this has a negative effect on the performance factor and on home consumption of solar power.

Integrated energy systems: Flexible through model predictive control

Today, the combination of heat pumps and batteries means that the energy self-sufficiency of residential buildings – i.e. the most complete possible self-sufficiency in heat and electricity – is within reach. For these integrated energy systems to work both

RECOMMENDED READING

S. Kuboth, A. König-Haagen, F. Heberle, D. Brüggemann: Model predictive control of air-to-water heat pump heating systems with thermal energy storage. Proceedings of the 13th International Renewable Energy Storage Conference and Exhibition (IRES 2019). Düsseldorf, 2019.

S. Kuboth, F. Heberle, A. König-Haagen, D. Brüggemann: Economic model predictive control of combined thermal and electric residential building energy systems. Applied Energy (2019), Vol. 240, 372-385. DOI: 10.1016/j.apenergy.2019.01.097.

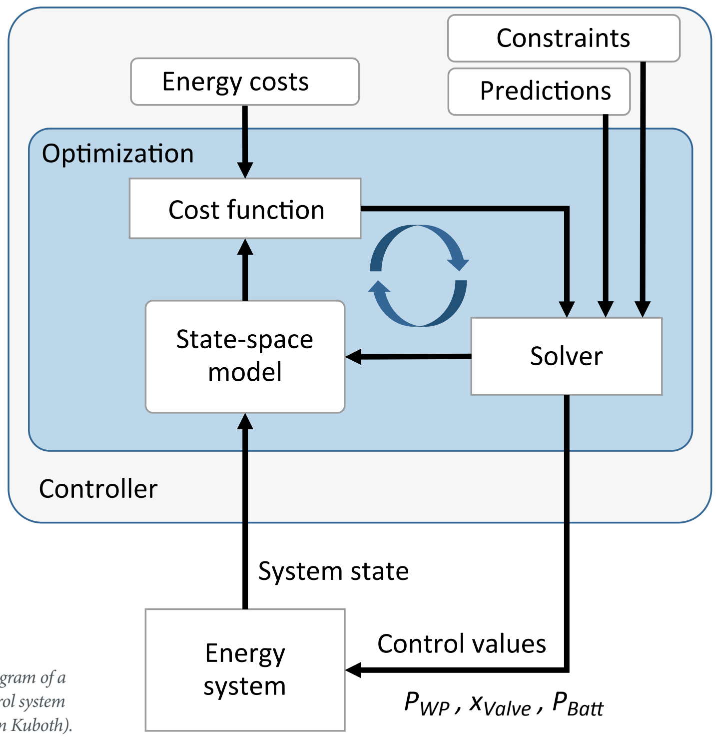
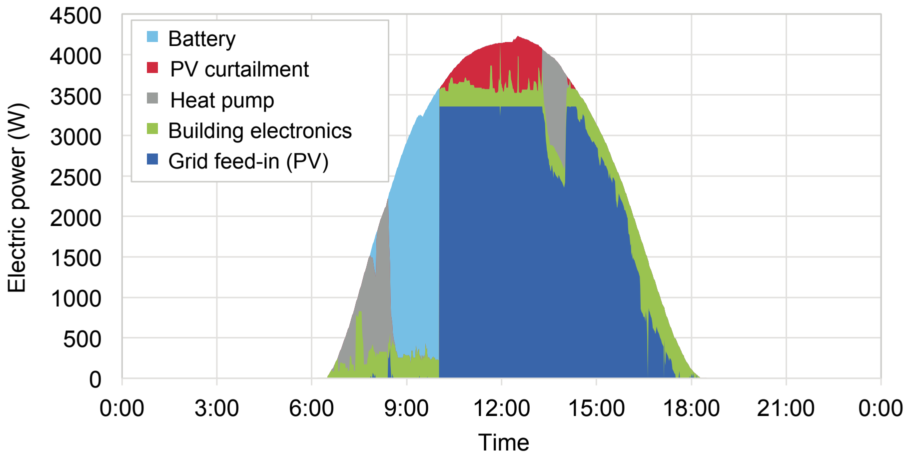


Fig. 4: *Function diagram of a model predictive control system (Illustration: Sebastian Kuboth).*

energy-efficiently and economically, they should be able to adapt as flexibly as possible to changing external influences. A particularly promising approach is „model predictive regulation". With the aim of exploiting the advantages of this method, the Chair of Engineering Thermodynamics and Transport Processes is developing and testing concepts for integrated building energy systems. The challenge is to anticipate the diversity of influencing factors and physical relationships. In addition to energy efficiency and cost-effectiveness, comfort is another important criterion for residents - for example, sufficient, but not too high, room and service water temperatures.

The basis for the model predictive control of smart homes is a 24-hour forecast of the weather at the building's location. From this, the expected energy demand and the quantities of solar power generated can be derived. On the basis of this prediction, short-term future scenarios are calculated and evaluated with a cost function, so that it is possible to specifically optimize plant operations using mathematical algorithms. Weather data – such as outside temperature and global radiation – are predicted by neural networks (a kind of artificial intelligence) among other things, meaning loads such as hot water consumption can be predicted. By repeating the control process several times, a stable controller is obtained which even reacts to unexpected weather changes or consumption. At any time, the latter is able to weigh up against each other the storage of electrical energy in the battery and the storage of thermal energy as possible options, and coordinate the two. The future of the smart home therefore lies in the flexible coordination of various subsystems for energy supply.



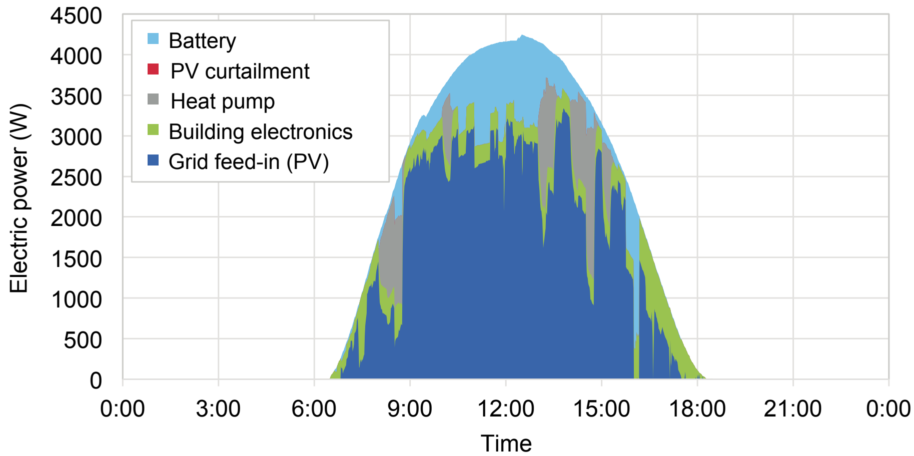


*Fig. 5: **Above:** Typical daily profile of the output of a photovoltaic system, and of the use of electrical energy. **Below:** Daily profile of the output of a photovoltaic system. Model-predictive control flexibly determines how the solar power generated is used (Illustrations: Sebastian Kuboth).*

Smart home systems in simulation: decreasing costs, longer battery life

In order to develop and optimize integrated energy systems for smart homes, it is important to understand the different scenarios resulting from changing times of day and weather conditions. Simulations are suitable for detailed investigations of these scenarios. For this reason, the Bayreuth engineers have created a dynamic simulation model based on physical models and empirical correlations derived from them. The results have been impressive: Energy costs can be significantly reduced in a modern detached house with underfloor heating, a medium-sized PV system with a peak output of 4.8 kilowatts, and lithium-ion battery storage with a

Research training group „Energy self-sufficient buildings"

The Universities of Bayreuth and Bamberg and the Universities of Applied Sciences of Coburg and Hof have joined forces in the TechnologieAllianzOberfranken (TAO). The Centre for Energy Technology (ZET) of the University of Bayreuth forms the core of the joint research training group „Energy self-sufficient buildings". The research work of the doctoral candidates concerns in particular the provision and storage of energy for buildings. In this context, a concept for model predictive control tailored to today's demands is currently being developed.

AUTHORS

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capacity of four kilowatt hours. Compared to a standard control system, the model predictive control system enables an annual reduction in energy costs of 16.2 percent.

The cost savings are made up of several factors:

- The capacity of the PV system can be used at any time, and does not have to be shut down. There are therefore no curtailment losses.
- Electricity consumption by the heat pump is reduced by 11 percent.
- The amount of solar electricity used for private consumption will increase by 63 percent.

In addition, there is a further financial advantage: the use of an electric auxiliary heater can be largely dispensed with. In addition, the predictive mode of operation also increases user comfort.

Because home consumption of the solar power generated increases, the battery is used less for temporary energy storage. The question therefore arises as to whether the coupling of battery and heat pump makes sense at all. The Bayreuth research has shown that this is indeed the case. Compared to an energy system in which these components are used separately, it results in higher overall home consumption and thus a higher degree of self-sufficiency. In addition, the service life of the battery is extended. One reason for this is that its average state of charge drops. Normally, this is done without reducing the number of charge/discharge cycles or the total energy stored and discharged. Here it is important that the energy produced in the morning on sunny days is fed into the public grid below the feed-in limit, so that the battery is only partially operating during this time, or not at all. It is then fully loaded during the midday and afternoon hours. In the final balance of loading and discharge, there is no difference to the reference case in which the battery is continuously deployed for storage and supply at maximum capacity. If the performance-dependent efficiency of the battery inverter and the battery itself are known, it is possible to specifically increase the efficiency of the battery system by a targeted reduction of charging and discharging.

From simulation to pilot plant

Investigations in a test facility at the Center for Energy Technology (ZET) have confirmed the simulation results. This system couples real heat pumps, storage tanks and hydraulics with a simulated building and a simulated PV system. In „hardware-in-the-loop" tests, electrical energy consumption was reduced by almost 20 percent and heat pump operation by around 30 percent. The test plant was compared

■ *Fig. 6 (middle): Dr.-Ing. Florian Heberle and Sebastian Kuboth M.Sc. control the pilot plant for heat pumps at the Center of Energy Technology (ZET) at the University of Bayreuth (Photo: Christian Wißler).*

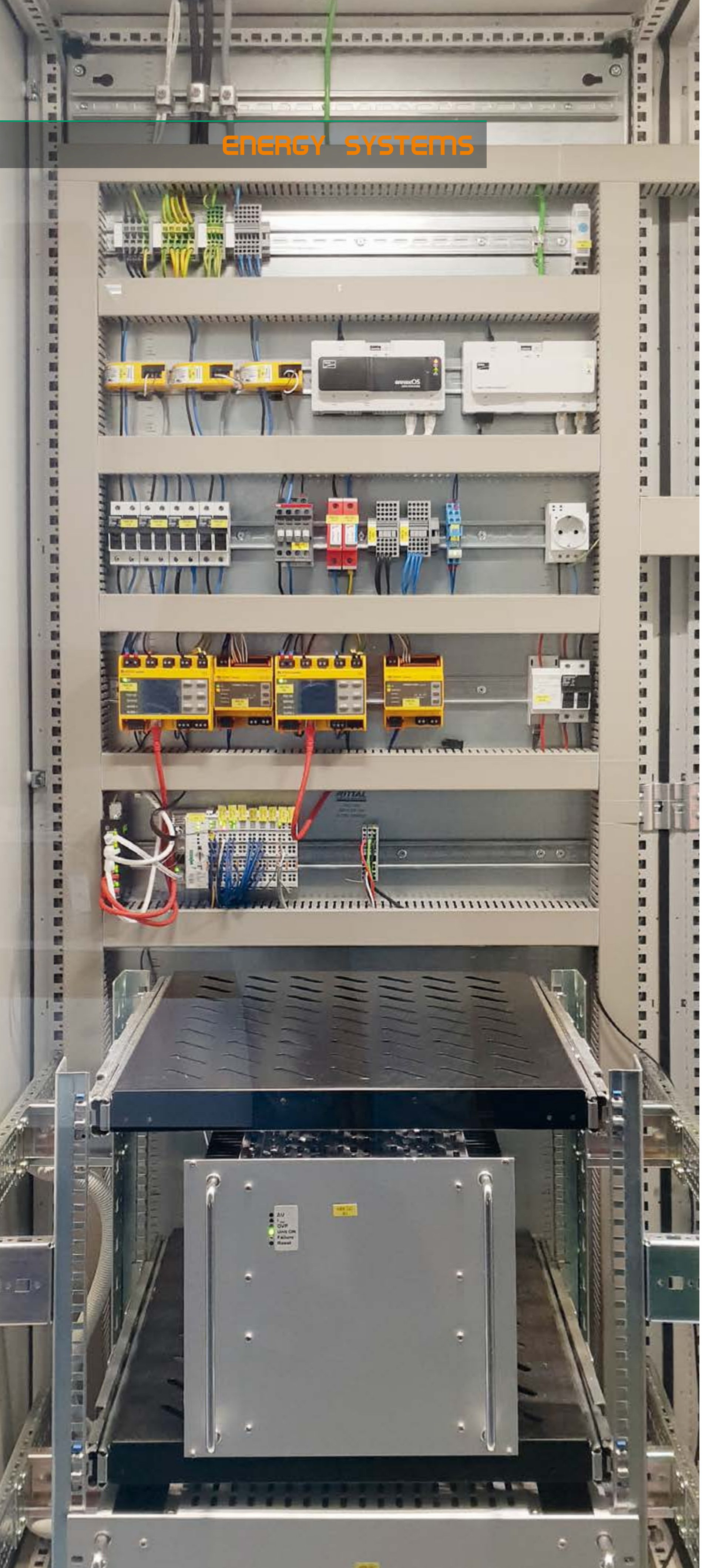
over several days with a reference plant of the same design with a standard control system.

The Bayreuth research work on integrated energy systems thus makes an important contribution to the challenge of turning your house into a „smart home" – with the benefits of lower costs, greater self-sufficiency, reduced energy consumption and a longer service life for system components such as batteries and heat pumps. The flexible and intelligent control concepts developed for this purpose could even be transferred to other energy systems by adapting them accordingly. They could be used, for example, in industrial plants and municipal facilities.

■ *Fig. 7: Heat pump used in the ZET for the investigation of energy systems in residential buildings (Photo: Christian Wißler).*

■ *Fig. 8: Plate heat exchanger that dissipates precisely calculated amounts of heat to the cooling network of the University of Bayreuth (Photo: Christian Wißler).*

„The combination of heat pumps and batteries means that the energy self-sufficiency of residential buildings is within reach."



Gerhard Fischerauer
Tobias Kull

Industrial and municipal plants

Energy-optimised operation aided by intelligent battery control

Intelligent energy node (IEN) / Module for uninterruptable power supply (UPS) at Richter R&W Steuerungstechnik in Ahorntal (Photo: Bernd Zeilmann).

These days, there are numerous energy systems available that are more or less well characterized as such, but whose functional interaction in a heterogeneously integrated overall system has yet to be brought up to the state of the art. In building services engineering, for example, heating control and ventilation can be possibly engaged in a perpetual „fight" against each other. Or photovoltaic (PV) systems are switched off because there is no storage facility available to accept energy from them at that moment.

The Centre for Energy Technology (ZET), in cooperation with several companies, above all Richter R&W Steuerungstechnik, is working on solution strategies for the efficient provision, distribution, and storage of energy in industrial and municipal facilities. The work is funded by the Federal Ministry of Economics and Energy. An improvement in the overall behaviour of a system consisting of energy sources and consumers can be achieved by controlling the coupling between the system's individual parts by means of a superordinate control device. In fact, the generation, interpretation, and use of condensed information leads to almost intelligent system behaviour. When various system components are networked and controlled in private homes, the term „smart home" is commonly used today (see pp. 48 to 53). Meanwhile, similarly coordinating production or supply facilities is generally referred to as a „Smart Energy System". Its control device is referred to here as a „Smart Controller" or as an „Intelligent Energy Node (IEN)".

Energy system control in industrial and municipal sectors

A higher-level control system can influence the energy costs of a larger system in a variety of ways, for example by

- taking into account forward-looking analyses such as weather forecasts, consumption, and tariff data from intelligent measuring systems (smart meter data), or vehicle fleet data,
- controlling the supply of energy from different energy sources, and the demand of energy to storage facilities and consumers,
- or avoiding transformation losses between network levels.

In the industrial and municipal sector, however, additional requirements must be considered when installing an IEN compared to applications in private households. To begin with, the integration of an IEN into existing systems requires compatibility with standard industrial hardware. Typically, programmable logic controllers (PLCs) are used for this purpose. This IT environment, however, does not provide the same resources and programming languages as normal PCs.

Questions of functional safety (risks to the environment from the system) and security (risk to the system from the outside) also play a much more important role than in private households. If a private

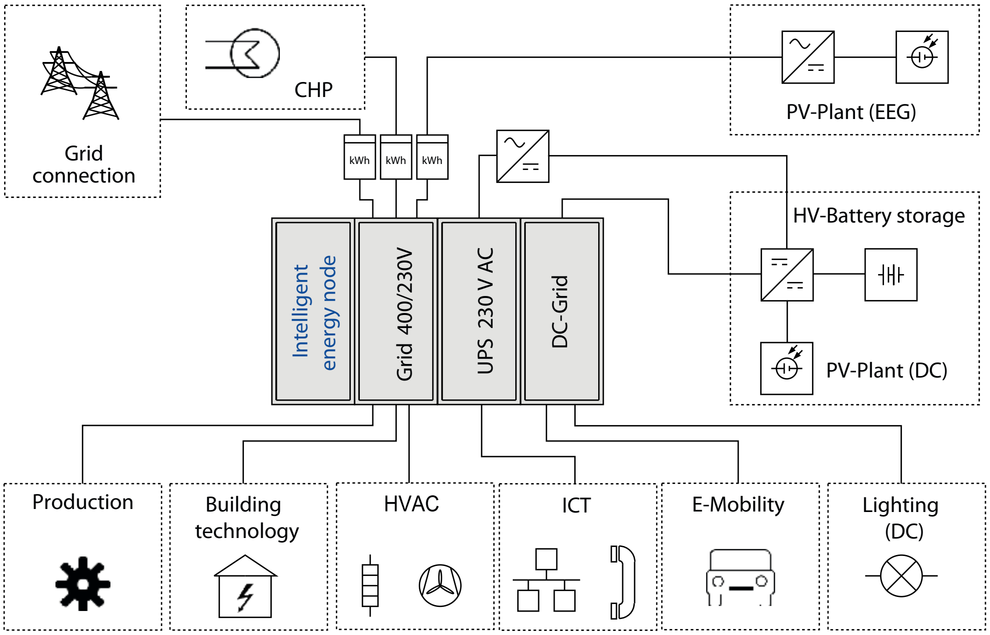


Fig. 1: Block diagram of the real energy system in the pilot plant (Illustration: Tobias Kull / Richter R&W Steuerungstechnik).

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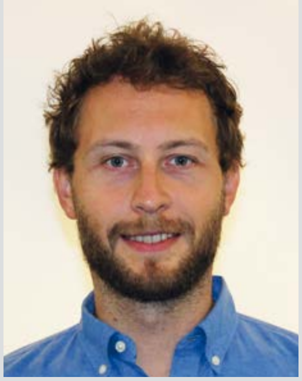

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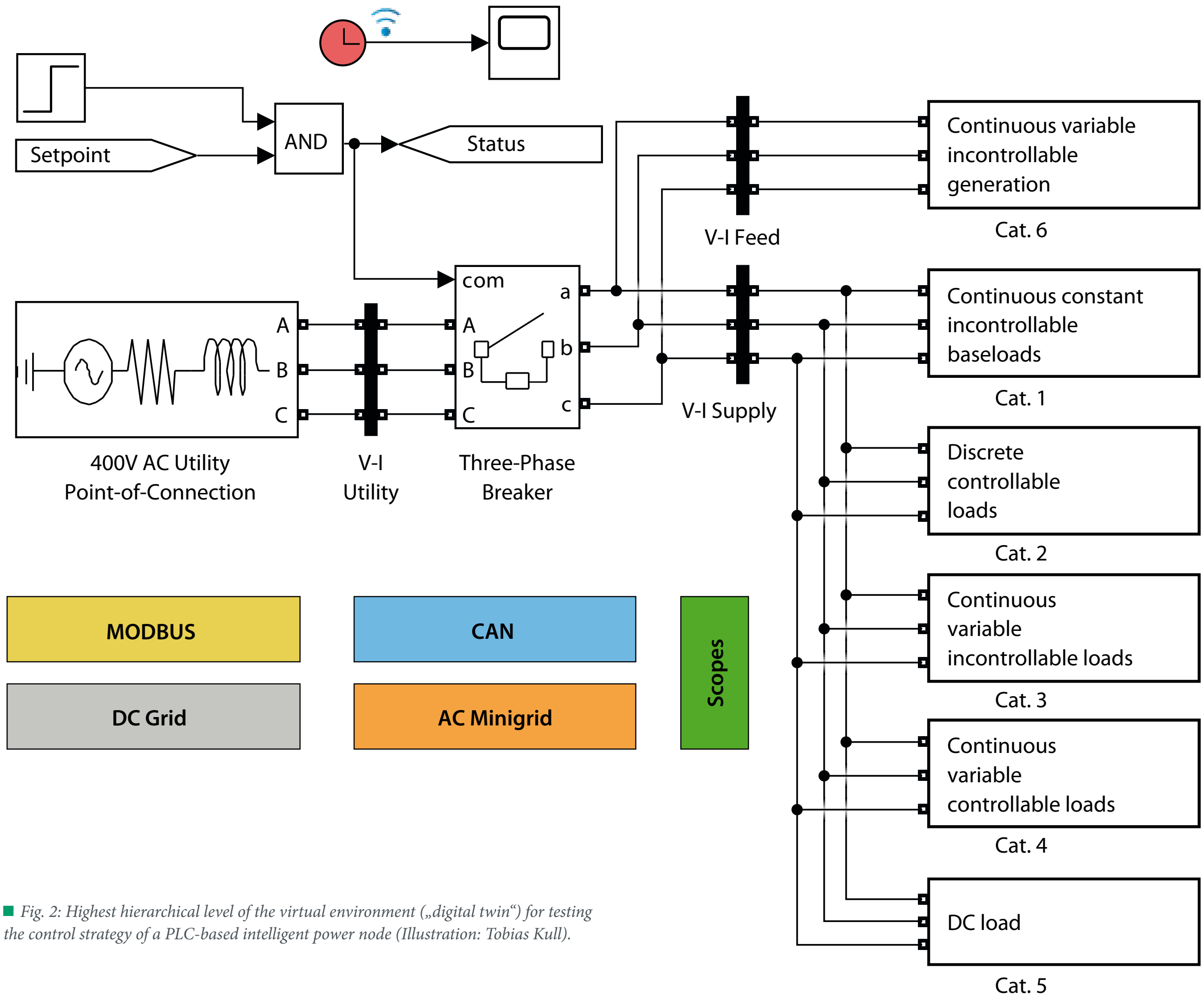


Fig. 2: Highest hierarchical level of the virtual environment („digital twin") for testing the control strategy of a PLC-based intelligent power node (Illustration: Tobias Kull).

PC is paralyzed by a Microsoft update or by malware, it is mainly just annoying. On the other hand, if the control of a sewage treatment plant is blocked and, in the worst case, incompletely treated wastewater is discharged into natural waters, the consequences can be disastrous. For this reason, the PLCs used are Linux-based and not directly connected to the Internet.

Methodology of virtual commissioning

From a safety and security point of view, a newly developed intelligent power node cannot be tested in a real application environment. Rather, the IEN must be presented with an imitation of the world in which it will later be embedded. Components of this world are, for example, a photovoltaic system, a battery storage system, or a consumer. The IEN hardware is thus embedded into a test environment that includes all system parts to be controlled and represents a „digital twin" of the later real application environment. This is also referred to as a hardware-in-the-loop concept. In order to rule out errors in technical communication, the IEN must interact with the digital twin via industry-typical peripherals and interfaces.

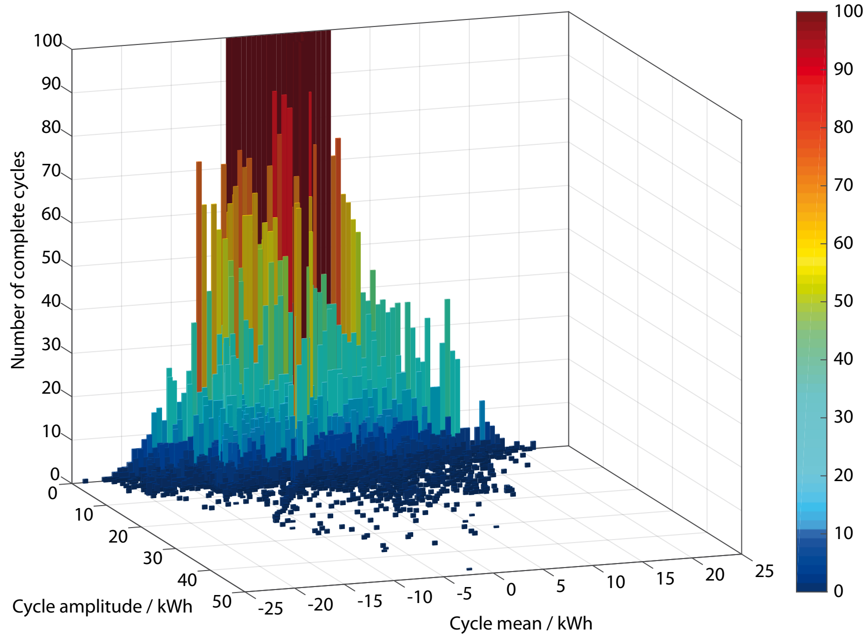
At the Center for Energy Technology of the University of Bayreuth, a laboratory environment was set up in which a PLC-based intelligent energy node interacted with a PC via industrial bus systems (Modbus TCP and CAN). Here the digital twin of the application environment was implemented in the Matlab/Simulink programme, which is frequently used by engineers. In this way, it is possible to input control commands from the control algorithm on the IEN into the PC („*Feed Consumer A from the battery stor-*

RECOMMENDED READING

T. Kull, B. Zeilmann, G. Fischerauer: Hardware-in-the-loop Test Concept for an Energy-optimized Process Control, in: R. Tutsch, A. Schütze (ed.): Tagungsband 20. GMA/ITG-Fachtagung Sensoren und Messsysteme 2019. Wunstorf 2019, S. 789-793. DOI: 10.5162/sensoren2019/P3.8.

age and disconnect Consumer B from the mains"), to calculate the reactions of the energy system model to these control commands („Battery is discharged"), and to report back to the IEN the calculated or actually measured reactions to its commands.

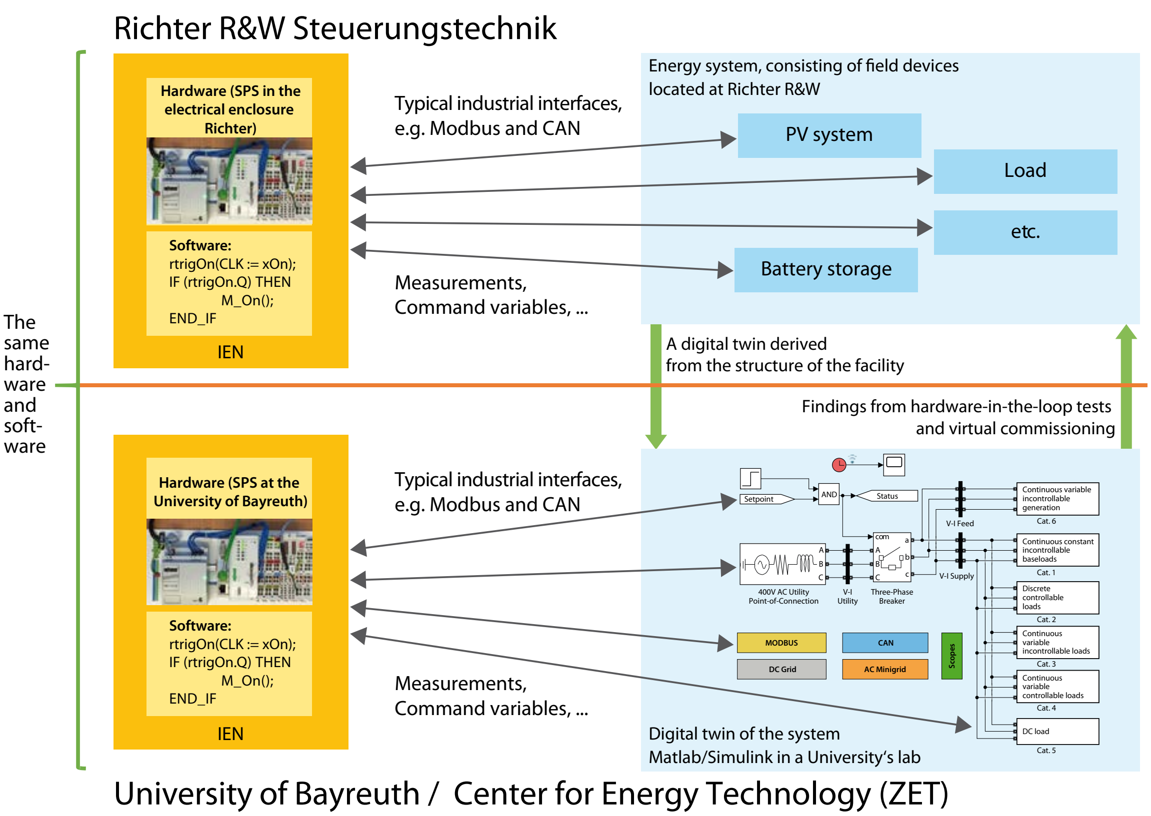
Consequently, it becomes feasible to test the basic function of an IEN algorithm and detect any errors. One of the biggest advantages is that it can be tested on an accelerated time scale compared to the real world. Imagine, for instance, if the functionality of the IEN in summer (heat, a lot of PV power) and in winter (cold, little PV power) could only be tested in a real system. Apart from the safety issues, such tests would take months or years. On the other hand, the method of virtual commissioning makes it possible to go through different performance scenarios, and the behaviour of an IEN algorithm in a matter of days.



■ *Fig. 3: The Rainflow histogram shows the charge/discharge of the battery storage in the reference system for the period from August 18, 2018 to January 16, 2019. The number of closed cycles is plotted as a function of power fluctuation and the mean state of charge, and is truncated up to 100 for illustrative reasons. Obviously, cycles with low power fluctuation and low state of charge variation dominate here. With this information, the battery storage can be optimally dimensioned (Image: Tobias Kull).*

System design based on previous data

An IEN must adapt its control strategy to the details of the energy system it manages. In the case of larger and heterogeneous systems, an inventory of time-dependent energy consumption is the starting point for any control strategy, and also of any system expansion, with PV systems or battery storage, for instance. As part of its cooperation with Richter R&W Steuerungstechnik, ZET has at its disposal a reference system that enables an inventory to be made



■ *Fig. 4: The real energy system of Richter Steuerungstechnik R&W and the ‚digital twin' on the Campus of the University of Bayreuth (Illustration: Tobias Kull / Christian Göppner).*

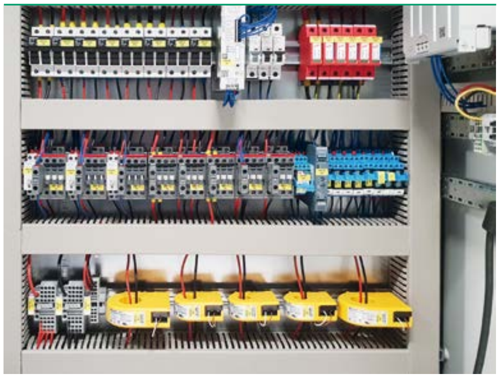


Fig. 5: IEN / DC-module (DC-grid) (Photo: Bernd Zeilmann).

Fig. 6: Residual current monitoring in the DC-module (Photo: Bernd Zeilmann).

at any given time thanks to all the necessary data having been collected since August 2018. Specifically, the output powers of two PV systems, the power drawn from the grid and the sum of the consumer loads are recorded. As expected, additional battery store would help reduce energy costs because it could absorb temporary excess PV power.

However, even the question of the optimal size of the battery is far from trivial. A battery with large capacity would be expensive, but would go through only a few complete charge/discharge cycles per unit time and therefore last longer (each battery only lasting a certain number of cycles). A small battery would be less expensive, but would be charged and discharged more often and therefore age faster.

The period over which the current costs of a battery storage system amortize depends to a large extent on the way in which it is used and the respective financial conditions, such as the feed-in tariff for PV output. In the case of the reference system, a small battery under favourable market conditions can pay for itself after five years, but a large battery under unfavourable market conditions only after 33 years. At present, therefore, only small storage units can be justified from an economic point of view. Only by using it for multiple tasks, like emergency power supply, peak load avoidance and grid-connected flexibility services accompanied by load flexibilisation (if these are remunerated), can the investment in a battery storage system pay for itself in shorter periods of time.

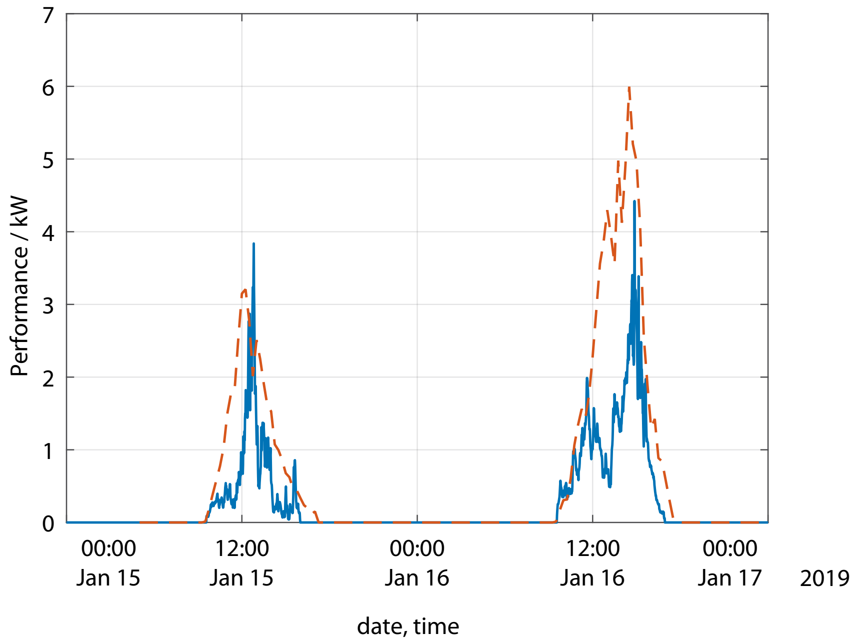
Fig. 7: Bernd Zeilmann, managing director of Richter R&W Steuerungstechnik, Tobias Kull M.Sc., and Prof. Dr.-Ing. Gerhard Fischerauer at Richter's production facilities (Photo: Christian Wißler).

Feedback control on the basis of real-time and future measurement data

An IEN developed with the methodology of virtual commissioning must be provided with information on the status of its energy sources and consumers both in the development and test phase and later in the real application environment. As with any control loop, measuring instruments are used for this purpose, especially power measuring instruments. It is typical for professional applications that there are no uniform interfaces and data formats, but that one must connect very heterogeneous data sources with each other. The current work at the Chair of Measurement and Control Systems at the University of Bayreuth is cutting edge in Germany, in that it includes technology still in the development phase, and thus in a constant state of change. Examples include communication with smart meter gateways and charging stations for electric vehicles.

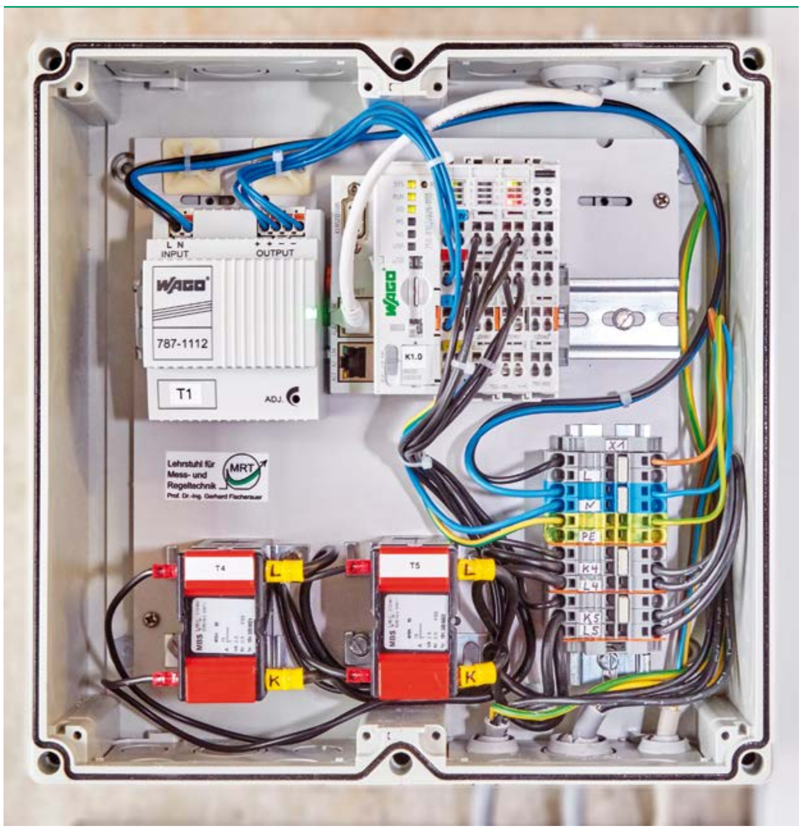
Energy systems with PV systems and battery storage have one special feature in that the behaviour of the overall system can be optimised by predicting the measured values of PV output power. If the sun is going to shine tomorrow, you can discharge the battery now and recharge it tomorrow, but if it is set to rain, you can conserve the battery and switch off less important consumers instead. Of course, the PV output of tomorrow cannot actually be measured.

„Energy systems with PV systems and battery storage have one special feature in that the behaviour of the overall system can be optimised by predicting the measured values of PV output power."



■ *Fig. 8: Measured (blue curve) or predicted (red curve) output power of a real photovoltaic system. Forecast with a horizon of 45 hours, based on the weather forecast model of the German Meteorological Service (DWD), the characteristics of the PV system and the PV model library PVLIB Python (Image: Tobias Kull).*

■ *Fig. 9: Measurement data acquisition on a photovoltaic system (Photo: Tobias Kull).*



However, it can be estimated by using weather forecasts and the characteristics of the PV system as a basis. This does not work perfectly (even weather forecasts are wrong), but quite well. In fact, if predicted PV outputs are incorporated into energy system management („model predictive control"), the statistical average results are better than if future weather conditions are disregarded. One of the challenges solved by ZET was that while weather forecasts can be conveniently obtained online, for reasons of security, the IEN must not be directly connected to the Internet.

The primary advantage of integrating battery storage systems into energy systems is that a higher proportion of the energy generated by the PV system is consumed by the user. Forecast-based charging also makes a significant contribution to solving the problem of daytime-dependent load on electricity grids. On the basis of these forecasts, the peak output of the PV systems in the grid can be collected in battery storage at midday. This relieves the load on the networks by reducing the amount of electricity fed into the grid. In summary, the integration of intelligently controlled battery storage could be said to be an imperative.

Bernd Koch
Marco Krasser

Shaping our energy future together

How regional partners are driving the energy transition forward

View of the city centre of Wunsiedel (Aerial photograph: Franz X. Bogner).

SWW Wunsiedel GmbH, the municipal utility in the Upper Franconian town of Wunsiedel, certainly has an ambitious goal: by 2030, together with partners from industry and science, they aim to create an independent supply area based on renewable energies. Important steps have already been taken on this path towards a regional and sustainable energy supply: Since 2011, the city has managed to save 144,000 tonnes of CO_2, and, in addition to feeding green electricity into its own grid, sell surpluses on the energy market. The basis for a set of innovative projects all geared towards the common goal of a sustainable energy future, is the corporate strategy developed in 2003, which was published in 2008/2009 as a roadmap and vision under the title „WUNsiedler Weg – Energie".

The strategy focuses on five core areas in which these forward-looking ventures are to be implemented by 2030:

- Use of renewable energies
- Construction of energy storage facilities
- Digital networking
- Increasing energy efficiency
- Innovative concepts for mobility

In addition, the use of suitable market models will be discussed. In order to guarantee cross-sector and networked solutions, the development of strategies was setup to avoid singular and silo-like project approach right from the beginning.

Moreover, communications will become increasingly important in the future as the digitisation of energy infrastructure continues apace. SWW Wunsiedel GmbH has therefore been building a comprehensive fibre optic network since 2011.

The energy storage device SIESTORAGE – Pilot project for a technology partnership

Since 2015, SWW Wunsiedel GmbH has been supported by Siemens AG in implementing its vision. In 2016, the two companies not only signed the contract for SIESTORAGE – currently the largest battery storage system in the municipal network – but also announced the start of a technology partnership. In addition to the large-scale lithium-ion storage unit rated at 8.4 megawatts and 10.05 megawatt hours, the partnership has resulted in the design and implementation of numerous other projects since then. The focus is and always has been on viable projects that fit into the context of the „WUNsiedler Weg – Energie". Cross-sector approaches in the fields of energy, heating and mobility play an essential role in this.

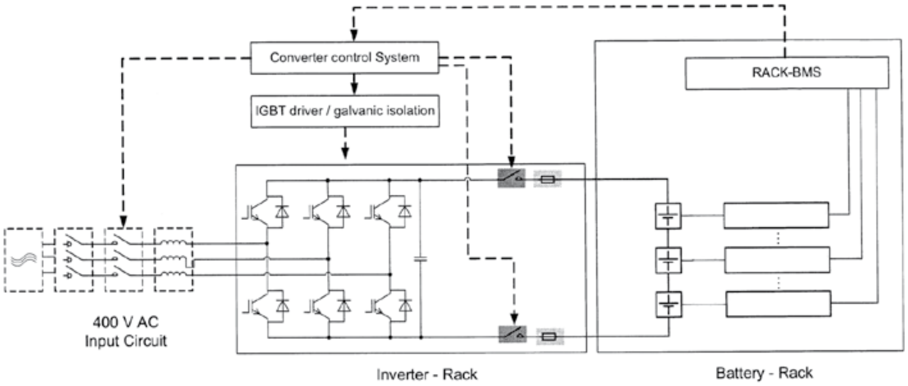
Fig. 1: Battery container of the SIESTORAGE modular energy storage system (Photo: © Siemens AG).

The „House of the Energy Future", opened in 2018, has contributed significantly to the success story of the festival and energy city of Wunsiedel. Here the local population, interested people from neighbouring regions, and representatives from politics, business, and science have the opportunity to discover more about the vision of SWW Wunsiedel GmbH and the city of Wunsiedel. Visitors can also better understand the interaction of the projects already implemented, contributing to an increase in public acceptance. Using an IT application based on *Siemens MindSphere*, the „Showroom" presents a digital map of the network and infrastructure, and illustrates the relationships between the various networks (400 and 20,000 volt power grids, heating network and gas network). Moreover, different network states can be simulated across various sectors on the basis of stored scenarios. For example, the effects that an expansion in the number of electric vehicles will have on the power grid can be made visible.

The „WUNsiedler Weg – Energie" offers great potential for further shaping our energy future. The most recent project is a power-to-gas plant. In cooperation with SWW Wunsiedel GmbH, Gasversorgung Wunsiedel, Wunsiedel district administration, and municipal representatives from politics and industry, laid the foundation stone for the supra-regional „Hydrogen Initiative Wunsiedel" on 21 May 2019.

Primary control power – the basis of a win-win cooperation

The Siemens SIESTORAGE storage facility is the largest joint venture to date. The cooperation model, which is based on a special leasing contract (manag-



■ *Fig. 2: Schematic diagram of the battery storage structure (Illustration: © Siemens AG).*

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■ Marco Krasser is Managing Director of SWW Wunsiedel GmbH.

ed service), is financed by revenues derived from primary control service. Given its on-demand status and immediate activation, this is the most demanding form of control power in terms of quality assurance. It is, however, critical because only as much energy may be fed into the grid as is simultaneously taken out of it. Only in this way can a stable frequency of 50 Hertz be guaranteed in the German power grid. Primary control power (PRL) – also known as primary reserve – has the task of balancing out fluctuations between the feeding in and tapping of electrical energy in the shortest possible time. To avoid power outages, the production of energy must be commensurately increased (positive PRL) or decreased (negative PRL) within 30 seconds.[1]

PRL is a service provided by the German transmission system operators (TSOs) and has been put out to public tender since 2001. Since 2007, the invitation to tender has been issued via the Internet platform „regelleistung.net", which also provides information on the legal and regulatory framework.[2] Together with PRL, secondary control power and minute reserve power are also put out to tender, these being intended to compensate for fluctuations in the electricity grid after a longer lead time of five and 15 minutes respectively. In fact, the PRL markets of Germany, Belgium, the Netherlands, France, Switzerland, and Austria are internationally linked, and market a total of around 1,470 megawatts of PRL (status: January 2019). Meanwhile, the PRL requirement for Germany is around 603 megawatts (2017)[3], and PRL exports are permitted on condition that they do not exceed 30 percent of country-specific PRL demand.[4]

In order to be allowed to participate in the PRL control services market, providers must first pass a technical and organisational examination. As part of this pre-qualification, the responsible TSO evaluates both the generation units and the controllable consumer loads. These requirements were updated in 2019.[5] In general, the performance of the full PRL service over a period of 15 minutes must be proven for prequalification. For battery storage systems in Germany, the transmission system operators have called for a 15-minute increase in capacity provision (in total: 30 minutes). However, the Federal Network Agency rejected this on 2 May 2019, thus aligning the German grid with the competitive conditions in the interconnected European grid.

Energy storage as the technological heart of stable energy supply

Highly dynamic, modular energy storage systems, such as SIESTORAGE in Wunsiedel, have significant advantages in the provision of primary control power. They enable providers to make use of various degrees of operational freedom, and thus a cost-optimised mode of operation. These include especially

- the optional over-fulfilment of PRL of the required proportional frequency response by up to 120 percent,
- the utilisation of the dead band of ±10 millihertz around the nominal frequency of 50 hertz,
- loading/unloading operations using other technical units
- and, last but not least, the ability to deliver PRL faster than in the 30 seconds stipulated.

With these advantages, and the possibility of pooling smaller units, but (since July 2019) also by converting the weekly tender to a daily one, competition in the standard services market will be further strengthened. This creates an important basis for the integration of additional quantities of renewable energy into the electricity grid.

The modular energy storage system from Siemens is accompanying the city of Wunsiedel on its journey to becoming an independent supply area by ensuring stable and reliable power supply. It integrates renewable energies and optimises the use of fossil electricity generation for a modern, environmentally friendly grid. SIESTORAGE combines state-of-the-art power electronics for grid applications with high-

„Decentralized energy systems and digital networking are cornerstones of future-proof business models."

performance lithium-ion batteries. And thanks to its modular design, the SIESTORAGE system can be adapted to specific requirements. It enables a wide range of applications for distribution networks, infrastructure, buildings, and industry.

Interdisciplinarity and innovation

The key points of the „WUNsiedler Weg - Energie" fit perfectly with the objectives of the Siemens Group Decentralized Energy Systems (DES) based in Nuremberg. This interdisciplinary group deals with solutions in four areas:

- Hybrid power plants
- Sustainable district development
- Peak load management
- Self-consumption optimization

In power categories ranging from 100 kilowatts to 100 megawatts, the DES team is always looking for solutions that contain a high proportion of regenerative capacity, while never losing sight of cost-effectiveness - because energy must remain affordable. In the area of hybrid power plants, for example, the department is working on combinations of wind turbines, batteries and electrolysis. In the area of district development, the focus is on sustainable energy supply with electricity and heat. The various building blocks must be related to each other and integrated, such as heat pumps, photovoltaic systems, electric home storage units or wall boxes for charging electric vehicles. Optimized grid load and self-sufficiency are very much the hot topics in the industry. The focus here is on secure supply at a good cost, and of course also on safeguarding the production process, which itself usually requires electricity, heat and often gas. These days, modern emergency power concepts are major pieces in the puzzle.

Conclusion and outlook

In summary, the model region Wunsiedel can be described as a good example of the proactive use of sector coupling, i.e. for the integration and networking of various elements in the energy system in favour of renewable energies. Decentralized energy systems and digital networking are therefore the cornerstones of sustainable business models that are successful both commercially and ecologically. „The person that brings together all the various forms of energy will be more flexible and will be able to profit from the market," explains Andreas Schmuderer, Head of Sales Consulting Decentralized Energy Systems at Siemens Germany.

The technology partnership between SWW Wunsiedel GmbH and Siemens AG is to be supplemented in future by the interdisciplinary Bavarian Centre for Battery Technology (BayBatt) at the University of Bayreuth. The cooperation between university research, technology concerns, and communities opens up new perspectives for the optimization and improvement of the storage technologies used, not least with regard to cell ageing. In addition, further possible applications for high-tech storage systems are to be explored. Together, the partners involved are seeking to ensure that the vision of an independent regional energy supply will soon be a reality.

A modular energy storage system

The system installed in Wunsiedel consists of:

- three 40" containers with lithium ion cells
- a 40" container with inverters, mains connection and control system
- a concrete station with transformers and medium-voltage switchgear

The following core components work together here:

- **Medium voltage:** Switchgear with eight medium-voltage switchgear panels serves to connect to the 20 kV customer network for charging and discharging the battery storage unit.
- **Transformers:** Four converter cast resin transformers 20/0.4 kV rated at 2,000 kilovolt amperes are each used to adjust the voltage between the customer's grid and the battery storage unit.
- **Conductor rail:** Energy is transported between the battery storage facility and the precast concrete station via four 3,700 ampere conductor rails.
- **Three battery containers:** These containers are each equipped with 504 battery modules housed in 36 cabinets. Each battery cabinet has a capacity of approx. 91 kilowatt hours.
- **An inverter container:** This includes control and regulation cabinets, twelve converter cabinets and four mains connection cabinets.

Fig. 3: Transformer (Photo: © Siemens AG).

1 Cf. Consentec GmbH: Beschreibung von Regelleistungskonzepten und Regelleistungsmarkt. Studie im Auftrag der deutschen Übertragungsnetzbetreiber. Aachen 2014.
2 Cf. www.regelleistung.net/ext/download/eckpunktePRL
3 Bundesnetzagentur für Elektrizität, Gas, Bundeskartellamt Telekommunikation, Post und Eisenbahnen / Bundeskartellamt: Monitoringbericht 2018. Elektrizitätsmarkt – D – Systemdienstleistungen. Bonn 2019.
4 Cf. www.regelleistung.net/ext/static/prl
5 Prequalification procedure for control reserve providers (FCR, aFRR, mFRR) in Germany („PQ-Conditions"), status: 23 May 2019.

Gilbert Fridgen
Leon Haupt

Batteries as key technology

Interdisciplinary battery research for a more sustainable electricity sector

Futuristic representation of an energy park that integrates the generation of renewable energies and energy storage through batteries (sst).

The nuclear catastrophe in Fukushima in 2011 turned out to be the moment that galvanized the political will in Germany to transform its energy system based on conventional generation. The coal phase-out agreed in January 2019 is a further irreversible step on the road to an electricity supply dominated by renewable energies. Wind and solar energy, in particular, play an important role in replacing conventional power plant types. This trend is particularly evident in the electricity sector: in 2018, the share of electricity produced from renewable sources reached a record high of 32.3 percent for Europe.[1] Tendency rising.

However, it is specifically wind power and photovoltaics (PV), the new hopes of the energy transition, that are causing the grid operators the most headaches – in many respects: The high volatility in electricity generation from wind and sun, combined with

■ *Fig. 1: Electric high-voltage pylon (sst).*

uncertainty about short-term weather fluctuations, are leading to serious system instability. In order to keep an electricity grid stable, the amount of electricity fed into the grid must at all times correspond to the amount purchased or consumed. Previously, volatility on the electricity consumption side was countered by reducing and increasing electricity generation, which was usually generated by conventional power plants (coal, gas, etc.). However, renewable energies, which are to gradually replace fossil-fired power plants, can only be regulated to a limited extent, and are heavily constrained in balancing short-term fluctuations in consumption. Moreover, the generation of PV electricity, which due to the physics of sunlight has a production peak at midday, only partly coincides with the maximum consumption loads in the early morning and evening.

In addition, power grid bottlenecks occur when, for example, strong winds blow over the North Sea, and only a small amount of the electricity generated can be used locally. Much of this electricity will then have to be transported from northern Germany to the industrial centres in the south and along the Rhine. In addition to the daily fluctuations, there are also seasonal fluctuations, and the risk of dark doldrums. This is a weather phenomenon that can last for several days, in which a combination of weak winds and a lack of solar radiation pushes the electricity grids and the security of supply to the limit of its capabilities.

Electrochemical storage systems as the building blocks of a solution

Existing hydro pumped storage plants are already compensating for these fluctuations, but cannot absorb the new demand for energy storage. This is due on the one hand to the rapid expansion of plants for the generation of renewable energies, and on the other hand to the fact that the potential of pumped storage power plants in Europe is limited. In this situation, battery storage systems can make a difference in solving this problem by

- compensating for grid bottlenecks within milliseconds,
- shifting surplus electricity generated by PV systems during the day to evening peak periods
- and even mitigating seasonal production bottlenecks caused by dark doldrums.

Battery storage systems are attractive for almost all fields of application in the electricity sector: They can be made to measure, can charge or discharge a lot of energy in a short time and are able to provide large amounts of energy over long periods of time.

Battery storage as a key technology in electric vehicles

Besides lead (Pb) and nickel-metal hydride (NiMh), lithium is particularly important among battery

1 Cf. Agora Energiewende: The European Energy Transition 2030: The Big Picture. Ten Priorities for the next European Commission to meet the EU's 2030 targets and accelerate towards 2050. Berlin 2019; plus press release by Agora Energiewende: The Big Picture of a European Energy Transition 2030", 6. March 2019, www.agora-energiewende.de.

2 Here it is important to differentiate between the subcategories of lithium technologies. These include nickel-manganese-cobalt-oxide (NMC), lithium-manganese-oxide (LMO), lithium-nickel-cobalt-aluminium-oxide (NCA), lithium-iron-phosphate (LFP), and lithium-titanate (LTO).

materials providing the basis for battery storage.[2] A major advantage of lithium-ion batteries is their relatively high gravimetric energy density compared to other non-fossil technologies. This describes how much energy per kilogram of mass can be stored in the battery. Current technological developments are accompanied by increasing demand from the electric vehicle industry. It is constantly on the lookout for efficient methods to increase the range of its electric cars, while at the same time limiting their weight and running costs, all towards the goal of safely navigating the paradigm shift towards electric driving.

We are currently experiencing a demand pull in which research and development activity is being induced by customer demand. This „market pull" is being answered with an extremely fast growing production capacity for lithium-based batteries. Chinese and American battery cell manufacturers alone plan to expand their output by almost 400 percent to more than one terawatt hour (TWh) of storage capacity by 2030. This is a manifestation of a development that will make batteries a key technology in the 21st century and, as expected, further reduce battery production costs.

■ *Fig. 2: BBattery system in an energy park (sst).*

■ *Fig. 3: E-mobility on the Campus of the University of Bayreuth (Photo: Christian Wißler).*

Versatile application for stationary power storage systems

Falling battery prices are also affecting the market for stationary battery storage systems. In order to conduct battery projects in an economically viable manner, however, business models are needed that intelligently bundle several applications through so-called „stacking", and thus make use of different sources of income. As things stand, at present there are basically four ways of exploiting the flexibility provided by battery storage systems:

- **Market service:** Arbitrage trading on the electricity, day-ahead and intraday markets has priority in market service operations. Here the battery charges in time intervals marked by low prices, and discharges when the power shortage is large, and therefore the prices are highest.
- **System serviceability:** In system service operation, the battery participates in the control power market and maintains capacity to stabilize the power grid. Depending on the dimensions and reaction time of the system, the primary, secondary or minute control power markets can be supplied here.
- **Grid serviceability:** While system service operation is aimed at stabilizing the electricity grid at the national and European level, battery serviceability has a different focus: Here the local distribution grid and local services, such as local congestion management, are in the fore. The latter is becoming increasingly important in the context of the progressive expansion of decentralised renewable energies, and the increasing acceptance of electric vehicles, as line bottlenecks in the distribution network are likely to occur more frequently. The provision of battery flexibility represents an alternative to the previous and expensive policy of grid expansion.
- **Self-optimization:** In fact, batteries are even playing an increasingly important role in optimizing one's own energy management in order to reduce electricity costs. This applies both to industries and municipal facilities as well as to homes (smart homes). A reduction in costs can be achieved by increasing self-supply from local renewable energies, by reducing the annual peak load, or by exploiting volatile electricity prices. Indeed, intelligent battery storage systems promise protection from increasingly fluctuating electricity prices.

Obstacles to stationary storage systems in business and regulation

However, in order to get the amount of electricity storage required for the energy transition onto the grid, a significant expansion drive is still required. This will not easily happen owing to the difficult economics of current battery storage projects. Basically, the reasons for this can be divided into endogenous (technology-dependent) and exogenous (market, regulatory and social) factors:

Endogenous factors are technology-dependent barriers that can be reduced or eliminated mainly through research and development aimed at better battery technologies. The necessary research and development steps pertain to battery cell costs and efficiency, service life, cyclic degradation rate, self-discharge, resource criticalness, and recyclability, among other things. On the other hand, there are also *exogenous* hurdles that are shaped by market, regulatory, and social factors. In Germany, economic attractiveness is curbed mainly by the following framework conditions:

„A development that will make batteries a key technology of the 21st century.“

- Daily price fluctuations on the electricity market only have a limited impact on consumers. The high proportion of fixed costs (electricity taxes, grid charges, EEG levy, etc.) levels out price fluctuations, weakens the financial incentives for marketable operation, and thus lowers the profit margin of the battery.
- The special role of the battery as a consumer and time-delayed generator has not yet been fully reflected in the regulatory system. This leads to double taxation: both charging and discharging trigger corresponding taxes. This makes market-, system- and network-relevant applications more difficult, and reduces the potential yield of a battery project.
- Meanwhile, the lack of remuneration mechanisms for network serviceability impairs the planning of battery projects. However, networked home storage can play a critical role in the local management of network congestion, reducing the need for network expansion investment. However, the savings achieved are difficult to quantify and there is currently no uniform remuneration scheme.

Holistic view of the value chain of batteries

To unleash the full potential of battery solutions, an integrated view of endogenous and exogenous factors is required. The Bavarian Centre for Battery Technology (BayBatt) bundles the necessary competencies at the University of Bayreuth and caters to the whole value chain of batteries with its research. On the one hand, research is being carried out into new material combinations and manufacturing processes that will improve the cycle stability, efficiency and scalability of production; while on the other hand, new application solutions are being developed that improve the economics, for example, through self-learning battery and energy management systems. Meanwhile, household storage units networked together in a „swarm" are currently being evaluated. Other research and development topics at BayBatt include cross-sector concepts such as the active integration of electric cars into the power grid (Vehicle-To-Grid) and the stationary reuse of discarded electric car batteries (Second Life Battery Storage).

Information systems as a value-adding interface between market and technology

Information Systems combines the market view with technological aspects and thus makes a decisive contribution to interdisciplinary research within the BayBatt framework. The research team for information systems and sustainable IT management in Bayreuth focuses on data-driven models, the digital networking of batteries, and the analysis of the economic efficiency of battery storage systems deployed in various roles.

In order for battery operation to be optimized from an economic point of view, a variety of factors are relevant and ultimately decisive:

- the modelling of the battery storage,
- the consideration of technical restrictions, e.g. performance limits, ageing, state of charge,
- abstraction of the technically complex characteristics of the battery storage device,
- the consideration of the dependencies between different application cases resulting from stacking,
- the inclusion of individual application patterns, for example of households and industrial load curves.

The Bayreuth research team focuses not only on the intelligent modelling of individual accumulators, but also on the control and coordination of a large number of batteries in a swarm. In this context, interesting technical and economic perspectives are being offered by so-called virtual batteries, which consist of a district storage facility, decentralised PV home storage facilities and mobile storage facilities in the form of electric vehicles. The central control of these virtual systems could well make a significant contribution to the security of supply of the electricity system.

The bottom line

The Bavarian Centre for Battery Technology brings together research expertise on battery storage in a multi- and interdisciplinary network on the Campus of the University of Bayreuth. In close consultation with industry, it addresses the emerging technological and market challenges in order to further improve the technology and economy of storage systems, and thereby further promote the integration of renewable energies.

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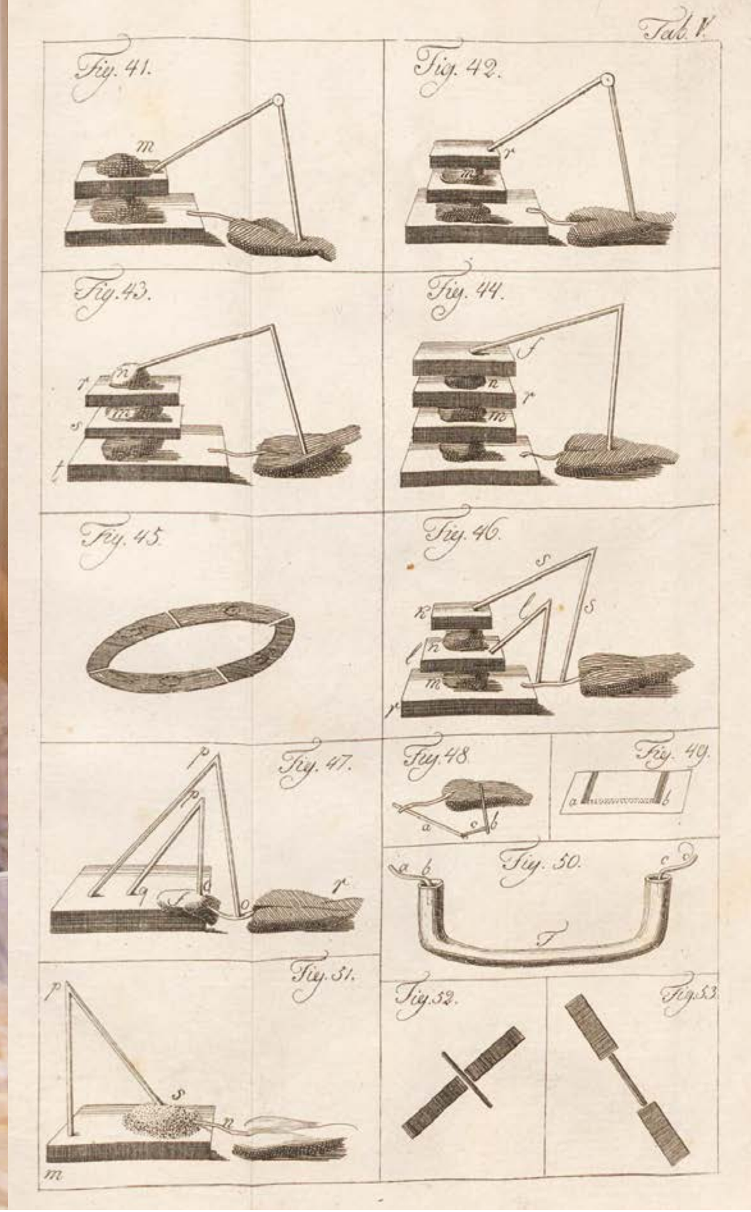

■ Christian Wissler

Humboldt and Volta

From Galvani's experiments to the invention of the battery

■ *Left: The column battery, which was constructed by Alessandro Volta in 1800, in the Museum Tempio Voltiano in Como, Italy (Photo: wikimedia commons, GuidoB, CC-BY-SA-3.0-migrated). Right:Copperplate (Figs. 21 - 30) from Vol. 1 of Humboldt's „Versuche über die gereizte Muskel- und Nervenfaser", published in 1797. Humboldt's experimental arrangement still lacks an important construction principle for the construction of a column battery (cf. p. 71). (Illustration: Bavarian State Library / Munich Digitisation Centre: Digital Library).*

It is above all because of the many years he spent on scientific journeys, especially to Central and South America and later to Russia, that Alexander von Humboldt is cherished not only in the scientific community, but also more broadly around the world, as an epitome of globally-oriented natural, climate, and environmental research. Far less well known, however, is the fact that as a young man he lived in Franconia. In fact, from 1792 to 1797, he was responsible for mining here, and at the same time conducted intensive scientific studies. He was particularly interested in the experiments of Luigi Galvani, Professor of Anatomy at the University of Bologna. In 1791 Galvani had published a treatise entitled „De viribus electricitatis in motu musculari“ in which he believed he could prove the existence of an „animal electricity“. Experiments on frogs had led him to believe that animal organisms contained an „electrical fluidum“. This explained why animal muscles began to twitch when they came into contact with hooks and rods made of different metals at the same time. The idea that there was such a thing as „animal electricity“ was actually not new, but had been repeatedly reinforced by observations of unusual fish species in the 18th century. Galvani, however, sought to extend the theory to encompass the animal world as a whole, including humans.

When Humboldt heard about this in 1792, his curiosity was immediately aroused. In the following years, he undertook about 4,000 experiments on about 3,000 animals in order to gain a more precise understanding of the phenomena described by Galvani, and a wealth of new data material. Frogs, fish, rats and toads were the preferred objects of his experiments. Moreover, he did not shy away from extremely painful experiments on himself to create galvanic effects on his own body with metallic objects. Humboldt published a treatise of almost 1,000 pages on the design of these experiments and their results in 1797 and 1798 in two consecutive volumes: *Versuche über die gereizte Muskel- und Nervenfaser sowie Vermuthungen über den chemischen Process des Lebens in der Thier- und Pflanzenwelt* („Experiments on stimulated muscle and nerve fibres, as well as speculations about the chemical process of life in the animal and plant kingdoms“). Measurements and subjective perceptions, descriptions of experimental set-ups, often rather groping considerations in interpreting the results, fundamental reflections, and a wealth of references to other authors are all gloriously interwoven with each other. The texts, supplemented by engraved plates, reflect the profile of a researcher who observes in detail and is deeply fascinated by the objects of his studies, but who never gives up the methodical control of his experiments.

Electricity in the living world?

Experiments and exhibitions on electrical phenomena had been fashionable in Europe since the end of the 17th Century. Electrostatic generators and Leiden bottles were used to create spectacular effects, which exerted a great fascination precisely because the underlying physical and chemical relationships were so far from being understood. Electricity, its manifestations in nature, and its production by technical means was therefore a „hot topic“ when the young Humboldt discovered it for himself. But there was another reason why he was captivated by Galvani's studies. Scientific debate in the 18th century was much inspired by the question of the extent to which visible processes in the living world could be explained solely by physical or chemical mechanisms. Could there also be something like a „life force“ that penetrated all living organisms and thereby connected humans, animals, and plants?

„Loosening the Gordian knot of the life process ...“

Humboldt had already taken a liking to this idea early on.[1] He developed it in poetic form in the story *Die Lebenskraft oder der rhodische Genius* („The Life Force or the Rhodian Genius“), which appeared in 1795. His scientific work was also influenced by his interest in the unity of animate nature – for example, when he spoke out in a debate with the physiologist Samuel Thomas Sömmering against making sharp distinctions between animal and plant organisms. Galvani's studies on the „electrical fluidum“ now seemed to open up a field of research that promised to empirically substantiate or even verify the idea of a „life force“.[2]

Humboldt follows this intellectual thread when he explains the results of his experiments in the first volume of his „Versuche“: The muscle contractions triggered by different metals are „actual effects of vitality“, the „stimulus“ lies „in the excitable organs themselves“ and is therefore not carried into the organs by the metals.[3] Up to this point, he is in agreement with Galvani. He maintains a distance, however, with regard to the use of the term „animal electricity“. He does not want to equate the „gal-

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RECOMMENDED READING

F. Holl, E. Schulz-Lüpertz: „Ich habe so große Pläne dort geschmiedet ... Alexander von Humboldt in Franken. Gunzenhausen 2012.

S. Finger, M. Piccolino: Alexander von Humboldt: Galvanism, Animal Electricity, and Self-Experimentation. Journal of the history of the neurosciences (2013), 22. Part 1: 225-260; Part 2: 327-352.

Fig. 1: Luigi Galvani (1737 – 1798), oil painting by an unknown artist from the Museo di Palazzi Poggi, Bologna (Foto: wikimedia commons, PD-Art (PD-old-100)).

Fig. 2: Statue of Alessandro Volta (1745-1827) in Como (Photo: wikimedia commons, Ramessos).

vanic fluidum", as he prefers to call Galvanis „electricum fluidum", with electricity, as was known to flow through metallic conductors. For Humboldt, it had not yet been proven that there was a universal phenomenon called „electricity" overarching both animate and inanimate nature. On the contrary, he believed he had found evidence in his own experiments that the fluid Galvani cited to explain those muscle contractions could be distinguished from electricity in metallic conductors.[4]

Empiricism instead of speculation

This caution against hasty explanations grows in the course of his studies. In the second volume of his „Versuche" Humboldt says goodbye to monocausal explanations which attribute the phenomena observed in animal and self-experimentation to the action of a „life force". The idea that everything living represents a complex functional unit now leads to a paradigm of research, which in principle, proceeds from a multitude of factors all contributing to scientific understanding: „In a living organ everything is living. The vital functions therefore do not depend on individual substances, but on the interaction of them all. We must not select individual substances and ascribe to them what is the common result of the whole mixture." And elsewhere he distances himself from calling something „a force in its own right, when it is perhaps only brought about by the interaction of material forces about which have been known for a long time." As long as the possibility persist for these forces to sufficently natural life functions, research should not seek „refuge" in the assumption of a separate life force whose existence is unproven.[5] The heuristic principle Humboldt formulates here seems to echo the principle attributed to the scholastic William of Ockham, which had gained new significance in the theory of science in the 19th Century: „Entia non sunt multiplicanda necessitatem."[6]

Such restraint was not to be taken for granted, as a glance at the development of the history of ideas in Germany shows. The Romantic poets, for example, were fascinated by electrical phenomena and created imaginative relationships to psychological experiences and social interactions. Speculative natural philosophy and metaphysics increasingly moved away from empirical research. Thus Hegel finally explained: „Electricity is the pure purpose of the form that liberates itself from it; the form that begins to abolish its indifference; for electricity is the immediate emergence or the being that does not yet come from the form, nor is it conditioned by it – or not yet the dissolution of the form itself, but the superficial process in which differences leave their form, but keep it as their condition, and are not yet independent of it."[7] The bridges to an observing and measuring form of natural research had long since been torn down.

From Franconia to Northern Italy

A pioneering form of science committed to empiricism, and uncaged by conceptual systems, however, remained Humboldt's elixir of life. Therefore he was able to argue constructively with scientists representing other positions, and to deal calmly with his own erroneous assumptions. He proved this not least in his relationship with Alessandro Volta, Professor of Experimental Physics at the University of Pavia. Volta had initially embraced Galvani's assumption of an „animal electricity", even regarding it as one of the greatest discoveries of all time.[8] But a short time later, without denying the presence of electricity in some fish species, he decided to take a diametrically opposite position. He argued that frogs' legs, which began to twitch in contact with various metals, did not do so because they contained an inherent „electrical fluid" at all. Rather, their movements were triggered from the outside by an electrical voltage when a connection between different metals was established via the muscle tissue. Humboldt resisted following this view which later proved to be true – even when he visited his Italian colleague at Lake Como in 1795 and both experimented with frogs. He was still too fascinated by the idea of "soon loosening the Gordian knot of the life process".[9]

Fig. 3: Alexander von Humboldt (1769-1859), 1807 portrayed in pencil and ink by Frédéric Christophe de Houdetot. Scan of the original from the Conseil d'État's library, Paris, France (Image: wikimedia commons, PD-scan (PD-old-100)).

The world‘s first battery

Volta used the knowledge he had gained in his experiments for a groundbreaking design. He placed damp sheets of fabric, cardboard, or leather between zinc and copper discs; a combination which today would be called „galvanic elements". The sheets soaked in acid constituted an electrolyte, and the metal discs acted as electrodes, so that a voltage arose.[10] By stacking these elements on top of each other in a column, Volta generated a combined total voltage sufficient to create an electric circuit. In a famous letter from 1800 to the President of the Royal Society in London, Sir Joseph Banks, Volta gave a detailed account of his invention. His column battery proved to be a technical sensation. While previous electrostatic generators could only generate electricity by friction for a few seconds, there was now for the first time an instrument with which an electric circuit could be maintained on a chemical basis over a longer period of time.

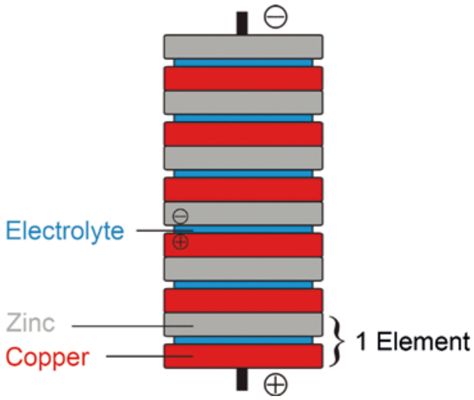


Fig. 4: *The construction principle of the „Voltaic Column" (Illustration: wikimedia commons, Nick B., CC-BY-SA-3.0-migrated).*

Humboldt did not hesitate to acknowledge the success of his colleague. At the same time, he noticed that some of his earlier experimental set-ups were quite similar to experiments Volta had undertaken to construct his battery: „I had been preoccupied with the phenomena of galvanic electricity for years with the enthusiasm that drives to research, but which impedes the correct understanding of what is being researched; by placing metal discs on top of each other and bringing pieces of muscle tissue or other substances in between, I had unconsciously built up real columns (...)", he noted in retrospect.[11]

However, they were not „real columns" in the sense of Volta's battery. As Humboldt's description and the associated copper engravings (see p. 68) show, an important construction principle was missing: In the column battery, the galvanic elements must be stacked in such a way that different metals lie directly on top of each other. This is the only way to escalate the voltage generated in the cells. Would Humboldt have found this decisive step in the construction of the battery if he had followed Volta's views in 1795?

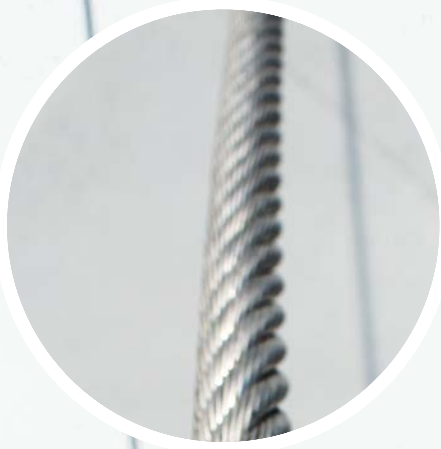
On the way to electrophysiology

In 1805 Humboldt met Volta again. Indeed, Volta's influence contributed to Humboldt's scientific evaluation of his travels to South and Central America, where he finally abandoned the idea that the electric current in metallic conductors – which Volta could now generate with his battery – was something quite different from the galvanic effects observed on animal organisms. The results he had obtained from studies on tropical electric eels confirmed his view that „electricity and galvanic effect are one in essence."[12] With these studies, Humboldt made pioneering contributions to a field of research that only began to establish itself in the middle of the 19th century, and in doing so, also threw new light on Galvani's studies: experimental electrophysiology. For a long time, it had remained unaffected by the rapid advances in battery technology. But in recent times, especially in the development of the pacemaker, both fields of research have come together.

Fig. 5: *Alexander von Humboldt and Aimé Bonpland on the Orinoco, painting by Eduard Ender, 1856 (Image: wikimedia commons, PD-Art (PD-old-70)).*

1 Cf. also A. Mook: Die freie Entwicklung innerlicher Kraft. Die Grenzen der Anthropologie in den frühen Schriften der Brüder von Humboldt. Göttingen 2012, bes. 77-100.
2 Moreover, Galvani‘s studies on „animal electricity" seemed to open up the possibility of approaching the old question of whether and how the soul can act on the body "in a new and experimentally verifiable way"; B. Specht: Physik als Kunst. Die Poetisierung der Elektrizität um 1800. Berlin – New York 2010, 82.
3 F. A. von Humboldt: Experiments on stimulated muscle and nerve fibres, as well as speculations on the chemical process of life in the animal and plant kingdoms Bd. 1-2. Posen, Berlin 1797-1798, Bd. 1, 397 and 379.
4 S. Finger, M. Piccolino (2013): see recommended reading 249ff.
5 Quotation and remark 3, Bd. 2, 63; 433; 432.
6 „Entities must not be multiplied beyond what is necessary (for an explanation)."
7 G.W.F. Hegel: System der Philosophie. Zweiter Teil: Die Naturphilosophie, § 323, Zusatz. Sämtl. Werke Bd. 9. In der Ausg. von H. Glöckner, Stuttgart 1958, 369.
8 Like remark 4, 240.
9 Letter to J. C. Freiesleben, 9 Feb. 1796. Quoted and evidenced in F. Holl, E. Schulz-Lüpertz (2012), see recommended reading, 101.
10 Volta and the physicist Christoph Heinrich Pfaff were the first to put different metals in a row, which is today called the electrochemical voltage series.
11 Alexander von Humboldt's Reise in die Aequinoctialgegenden des neuen Continents. In deutscher Bearb. von Hermann Hauff. Stuttgart 1859, 402.
12 Like remark 8, 408. „Humboldt himself, convinced by Volta, now concedes to the identity of electricity and Galvanic action ...", Soemmering notes after 1805. Quoted and evidenced in W. F. Kümmel: Alexander von Humboldt und Soemmering: Das galvanische Phänomen und das Problem des Lebendigen, in: G. Mann, F. Dumont (eds.): Samuel Thomas Soemmering und die Gelehrten der Goethezeit. Stuttgart – New York, 1985, 73-88, here 85.

Quotations translated by Ralph Reindler.



Steel cables in the sunlight

In the inner courtyard of the Geosciences building, on its north wall, sunlight falls on a six-metre-high, 18-metre-wide installation by the Bavarian artist Alf Schuler. *Seilverspannung* ("Cable Bracing") from 1977 was one of the first works of art to be installed on the Campus of Bayreuth University, which opened in 1975. In the sunshine, the stainless steel wire ropes give rise to delightful plays of light and shadow that change throughout the day. They are fastened to the ground with steel eyelets at 1.20 metre intervals, which correspond to the position of the lower joints on the white wall.

Alf Schuler was born in 1945 in Anzenbach/Berchtesgaden. He received his artistic education at the Werkkunstschule Aachen, and at the Academy of Fine Arts Nuremberg as a pupil of Gerhard Wendland . He soon achieved international fame with sculptures, drawings, floor works, and wall pieces. His work continues to develop the „Minimal Art" movement that emerged in the USA after the Second World War. Installations made of ropes, iron pipes, and other industrially manufactured materials make physical phenomena, such as gravity and tension, visible and tangible. In 1977 Alf Schuler was awarded the City of Nuremberg Prize and in 1981 the Böttcherstraße Art Prize in Bremen. In 1989 he was appointed professor for fine arts at the Kunsthochschule Kassel.