



SPEKTRUM

The Science Magazine of the University of Bayreuth ■ Volume 16 ■ Issue 1 ■ September 2020

UTILIZATION FOR ENERGY

Hydrogen as energy carrier

PAGES 6-15

STORAGE MATERIALS

From space travel to everyday transport

PAGES 44-47

SUSTAINABLE PRODUCTION

Spider silk for the *Energiewende*

PAGES 62-67

FOCUS

Hydrogen

Dear Readers,



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

The Covid19 pandemic and its as yet unforeseeable consequences is reinforcing a trend that has been in evidence for quite some time. The public, the media, and politicians are increasingly seeing research as a resource for solving challenges, not so much of individual parts of the economy or society, but of our civilisation as a whole.

This includes the question of how we are to guarantee the supply of energy in the context of climate protection, resource conservation, economic prosperity, and demographic change. The University of Bayreuth has firmly established the focus area of "Energy Research and Energy Technology" on its campus to combine research and teaching. Here, the Centre for Energy Technology (ZET) bundles current cross-faculty research issues, such as the coupling of different sectors of the energy industry or concepts of energy self-sufficiency, while the Bavarian Centre for Battery Technology (BayBatt) is concerned with broad, interdisciplinary research into battery storage systems.

In this innovative environment, our campus is meanwhile home to engineering, materials science, and

chemical research work concentrating specifically on hydrogen: one, possibly even *the* energy source of the 21st century. The focus is on the production, storage, and energetic use of "green" hydrogen, especially utilizing fuel cell technology. The present issue of SPEKTRUM aims to give you a taste of this dynamic research activity. Quite often, it is promising young scholars who are deeply involved, who are busy implementing their own research ideas in a master's or doctoral thesis, and taking advantage of access to state-of-the-art laboratories for that purpose. Particularly for "hydrogen" as a significant topic of the future, our principle holds true: That studying and research go together at the University of Bayreuth.

Yours faithfully,



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:

- 2/2019: Africa
- 1/2019: Batteries
- 2/2018: War
- 1/2018: Planet Earth
- 2/2017: Sustainability
- 1/2017: Governance
- 2/2016: Molecular Bioscience
- 1/2016: Innovation
- 2/2015: Digitization

- www.uni-bayreuth.de/de/universitaet/presse/spektrum

Half a decade ago, the United Nations officially launched 2030 Agenda for Sustainable Development. It called on industrialized, emerging, and developing countries to work in key areas of politics, business, and society to implement the UN's Millennium Development Goals. These goals include climate protection, but also access for all to affordable, reliable, sustainable, and modern energy. No question – in order to achieve these goals, it is necessary to reduce the use of carbon-based energy sources, and to promote decentralized forms of energy production more than in the past. This means, however, that the production of hydrogen from renewable energy sources, as well as its storage and use for energy purposes, is becoming increasingly important.

Meanwhile, it has become difficult even for recognized experts in the field to keep track of all the developments in these extraordinarily dynamic areas. Indeed, the practical challenges that are being worked on in various scientific and technical disciplines are widely divergent. Universities and research institutes, municipal administrations, and a large number of research-based companies are now involved in paving the way to powerful and economi-

cally viable energy systems on the basis of "green hydrogen".

The new issue of our scientific magazine SPEKTRUM gives you an insight into this broad range of topics with a set of fascinating, selected examples. At the same time, it showcases the diversity of scientific expertise on our campus. For more than four decades now, the close networking of research structures and our interdisciplinary approach to economic and social issues of the future have proven their worth. You can be sure the University of Bayreuth will commit itself just as wholeheartedly to innovative and sustainable solutions in the field of hydrogen as well.

Yours faithfully,



*Prof. Dr. Thomas Scheibel
Vice President for Internationalisation,
Equal Opportunities & Diversity
at the University of Bayreuth*



■ Prof. Dr. Thomas Scheibel is the Chair of Biomaterials 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

Printing:

bonitasprint gmbh, Würzburg

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.

All contributions are free for publication provided sources are cited and specimen copies forwarded.

■ Cover figure: 3D model of the hydrogen molecule H₂, below: Absorption spectrum of hydrogen (sst).

■ Fig. left: The sculpture "you are free" by Robert Kessler in front of the building Natural Sciences III on the campus of the University of Bayreuth (Photo: Christian Wißler).

Hydrogen

- 2 **Welcome**
Prof. Dr. Stefan Leible
President of the University of Bayreuth
- 3 **Editorial**
Prof. Dr. Thomas Scheibel
Vice President for Internationalisation,
Equal Opportunities & Diversity
at the University of Bayreuth
- 4 **Contents**

Utilization for energy

- 6 **Hydrogen as energy carrier**
Storage and transport of energy
by pure and bound H₂
- 16 **Power-to-gas as a key technology**
Networking the electricity and
gas sectors for a sustainable
energy industry
- 22 **Powering into the future
with hydrogen**
*Interview with Dr. Peter Hoffmann and
Norbert Lechner, TenneT TSO GmbH*



Liquid fuels can be produced from hydrogen and carbon dioxide by Fischer-Tropsch synthesis (Photo: A. Reul).



A Bayreuth research team is working on the optimization of a new generation of fuel cells (Photo: C. Wißler).

- 26 **On our way to post-fossil
energy supply**
Innovative research on fuel cells in
the ForOxiE² research network
- 32 **The secret of the HT-PEM fuel cell**
Phosphoric acid replaces water



Demanding material tests promote the technical and economic attractiveness of solid fuel cells (Photo: C. Wißler).

- 38 **Far from old hat:
Alkaline fuel cells**
- 40 **Material development,
design, viability**
The KOSOS project optimizes
stack technology



Storage materials

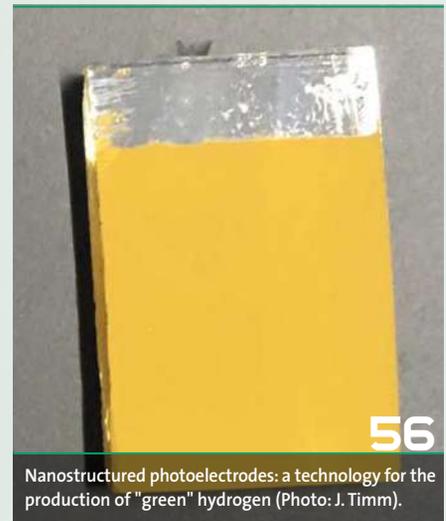
- 44 **From space travel to
everyday transport**
Hydrogen as a fuel for
new energy systems
- 48 **Ultralight construction materials
for hydrogen tanks**
New plastics reinforce the
efficiency of hydrogen-powered
fuel cells



Fiber-plastic composites increase the energy efficiency of hydrogen-powered cars (Photo: Grzegorz Czapski / shutterstock.com).



■ Interdisciplinary and innovative also in energy research:
The campus of the University of Bayreuth (Photo: UBT).



56

Nanostructured photoelectrodes: a technology for the production of "green" hydrogen (Photo: J. Timm).

Sustainable production

- 56 Harvesting hydrogen with sunlight**
Photoelectrochemical water splitting with nanostructured semiconductor electrodes
- 62 Spider silk for the *Energiewende***
Photocatalytic hydrogen production with novel hybrid systems

- 68 Sustainability₃**
Chemical reactions for the production of hydrogen
- 71 A model of Sustainability₃**
Hydrogen storage with a powerful catalyst



54

The district of Wunsiedel i. Fichtelgebirge is developing into a model region for a decarbonized energy supply (Photo: F. X. Bogner).

Regional Cooperation

- 54 Decarbonisation by hydrogen**
Questions to Peter Berek, District Administrator of the District of Wunsiedel i. Fichtelgebirge
- 55 Prospects for research & practice**



62

A novel hybrid material for electrolysis: Photocatalysts based on spider silk (Photo: C. Wißler).



■ Andreas Jess

Hydrogen as energy carrier

Storage and transport of energy by pure and bound H₂

■ Measurement of the input volume flow of a Fischer-Tropsch reactor, right in the picture: Alexander Herbers, research associate at the Chemical Engineering research group (Photo: Andreas Reul).

In 2019, the contribution of wind power and photovoltaic systems to net electricity consumption in Germany was 28 percent. Renewable energy sources as a whole – i.e. including biomass and hydropower plants – accounted for as much as 39 percent of this (Table 1). For the further expansion of renewable energies, however, the fluctuating electricity production from sun and wind must be used more efficiently. Moreover, renewable energies are seldom generated close to the consumer. This calls for innovative solutions for both the storage and transport of energy, in particular, electricity from wind farms in northern Germany and from the North Sea to southern Germany. This is because 54 percent of the installed capacity of German wind turbines is located in Lower Saxony, Brandenburg, Schleswig-Holstein, and the North Sea (Table 2). The same applies to solar power generated primarily in the south and transported to the north, given that 40 percent of photovoltaic power is installed in Bavaria and Baden-Württemberg alone.

However, it raises the question of how the necessary transport of regenerative energies is to be realised. Electrical networks with sufficient capacity are not yet available, new high-voltage overhead lines are meeting with public protest ("monster corridors"), and the laying and maintenance of underground cables are much more complex and expensive.

One promising alternative is the use of surplus electrical energy to produce hydrogen (H₂) through the electrolysis of water. H₂ can be stored and transported as a compressed gas or in liquid form and used for many types of energy conversion, such as reconversion into electricity or in fuel cell vehicles. The injection of hydrogen into the natural gas grid – and thus its transport and storage in an existing supply system – is also currently permitted up to an H₂ content of five percent. However, hydrogen can also be used to produce synthetic natural gas (SNG, methane) and liquid fuels by chemical conversion with CO₂.

Hydrogen: Basic substance of chemistry and energy supply

It is a little known fact that hydrogen has been a basic component of the chemical industry and energy supply for many decades (Table 3). Worldwide, about 100 million tonnes of H₂ are produced annually. In terms of energy, this is roughly equivalent to Germany's primary energy requirements. However, only two percent of H₂ is

Energy source	Share of net electricity generation (total 556 TWh)	Share of CO ₂ emissions due to electricity generation (total 219 million tonnes)
Conventional energy sources (fossil fuels, nuclear power)		
lignite	18.5 %	52.1 %
hard coal	9.5 %	19.6 %
natural gas	14.9 %	15.1 %
nuclear power	12.2 %	–
other (particularly oil and waste)	6.1 %	13.2 %
total conventional	61.3 %	100 %
Renewable energy		
wind (1/5 offshore, 4/5 onshore)	20.5 %	–
photovoltaic	7.7 %	–
biomass	7.2 %	–
hydropower	3.2 %	–
total renewable	38.7 %	–

Federal state	Share of installed capacity of PV units (total 45.2 MW)
Bavaria	27.7 %
Baden-Wuerttemberg	12.9 %
North Rhine-Westphalia	10.9 %
Lower Saxony	8.7 %
Brandenburg	8.2 %
other federal states	31.6 %
Federal state / offshore	Share of installed capacity of wind energy units (total 61.4 MW)
Lower Saxony	18.8 %
offshore (North Sea)	12.5 %
Brandenburg	11.7 %
Schleswig-Holstein	11.1 %
North Rhine-Westphalia	9.6 %
Saxony-Anhalt	8.5 %
other federal states	27.8 %

■ Table 1: Net electricity generation (= gross electricity generation by power plants for public electricity supply and industrial power plants minus own power plant requirements and line losses) by energy source and CO₂ emissions of electricity generation in Germany 2019 (Source: Umweltbundesamt: Climate Change, Strommix 2019).

■ Table 2: Installed capacity of photovoltaic systems and wind turbines by federal state 2018 (www.statista.de).

obtained in pure form by electrolysis, but mostly as a by-product of the coupled production of chlorine and caustic soda by chlor-alkali electrolysis ($\text{NaCl} + \text{H}_2\text{O} \rightarrow 0,5 \text{Cl}_2 + \text{NaOH} + 0,5 \text{H}_2$). Water electrolysis ($\text{H}_2\text{O} \rightarrow \text{H}_2 + 0,5 \text{O}_2$), which has been the focus of attention in recent years for the utilization of excess electricity, only accounted for 0.1 percent of global H_2 production in 2014. Currently, 58 percent of H_2 is produced in the form of synthesis gas – a mixture of CO and H_2 – from natural gas, heavy oil, and coal. 40 percent of it occurs as a by-product in oil refineries, in the petrochemical industry, or in the coal and steel industry as a component of coke oven gas. If pure hydrogen is required, it is separated from the H_2 -laden gases of these processes. Ultimately, however, H_2 is still hardly ever used in its pure form, for example, as a fuel, but mainly in a bound form, for example

as a basic chemical substance such as ammonia or methanol, or as a fuel such as desulfurized gasoline, jet fuel (aircraft turbine fuel), and diesel oil¹ (Table 3).

Storage and transport of energy: Hydrogen vs other energy sources

If one compares the various gaseous and liquid fuels and energy storage systems, such as batteries, with regard to the energy stored or storable in them, two parameters must be taken into account: Depending on whether the energy is related to the weight or the volume of the energy source, the terms gravimetric or volumetric storage density come into play. At 33 kWh per kilogram (lower heating value, LHV)², hydrogen has an outstandingly high gravimetric stor-

Differing without disagreeing: Why data on the share of renewable energy in electricity generation varies so much

Everyone knows "gross" and "net" when it comes to money - but what do these designations mean in terms of electricity generation? Gross electricity generation is the total amount of electrical energy produced, for example, by a country in a certain period of time. But this is not the net electricity that comes out of the socket. Net electricity generation is obtained by subtracting from the gross value line losses and the power plants' own electricity requirements.

But that is only one reason why the figures often differ. It also depends on whether one considers only public electricity supply or total electricity generation, which also includes industrial power plants. As these often run on fossil fuels (especially natural gas), this not only influences the

total amount of energy, but also shifts the exact share of renewable energy, i.e. wind, water, sun, and biomass, which are of particular interest in the *Energiewende* ("energy turnaround"). Finally, such values naturally also depend on the period under consideration, and on whether or not it was particularly windy and sunny. The mean value over one year is usually the most meaningful measure.

The following example shows how differently the share of renewable energy in German electricity generation can be reported. Total net and gross electricity generation (i.e. including industrial power plants) are still quite similar at just under 39 and 40 percent respectively. If, on the other hand, net electricity for public supply only



Photo: sst

is considered, the annual average share for the same reference year (2019) is over 46 percent, and for the month of March as high as 54 percent. So the figures are all different, but none of them wrong - you just have to know what they are telling you.

Share of renewable energies in German electricity generation 2019

Period	Net electricity for public supply		Total net electricity *	Gross electricity Total *
	March 2019	2019	2019	2019
Electricity generation in TWh	48 [1]	514 [1]	556 [2]	606 [3]
Share of renewable energy **	54.1 %	46.4 %	38.7 %	40.0 %

* Power generation by power plants for public supply and by industrial power plants.

** Wind power, hydropower, photovoltaics, biomass.

Sources:

[1] Fraunhofer ISE: Monatliche Stromerzeugung in Deutschland in 2020. www.energy-charts.de/energy_de.htm

[2] Umweltbundesamt: Climate Change, Entwicklung der spezifischen Kohlendioxid-Emissionen des deutschen Strommix in den Jahren 1990-2019. Dessau-Roßlau 2020.

[3] Agora Energiewende: Die Energiewende im Stromsektor: Stand der Dinge 2019. Rückblick auf die wesentlichen Entwicklungen sowie Ausblick auf 2020. Berlin 2020.

age density (Table 4). For comparison, the storage density of petrol and diesel oil is "only" around 12 kWh per kilogram, that of natural gas 14 kWh, and that of a lithium-ion battery as little as 0.2 kWh per kilogram. However, the volumetric storage density of H₂ under ambient conditions is abysmal. At a pressure of 1 bar and a temperature of 20 degrees Celsius, a litre of H₂ contains just 0.003 kWh of energy (LHV), compared to 9 kWh of a litre of gasoline or diesel oil. However, through compression to pressures of up to 700 bar or by liquefaction (at minus 253 degrees Celsius), the volumetric storage density of H₂ can be increased to values of 1.3 or 2.3 kWh per litre respectively. It is then three to four times greater than that of a lithium-ion battery, but still about 80 percent less than that of diesel oil. In addition, the compression and liquefaction of H₂ is associated with considerable energy input amounting to 10 percent (compression, 700 bar) and 30 percent (liquefaction) of its calorific value.

At 200 bar, natural gas reaches the volumetric storage density of liquid hydrogen and, at a gas pipeline pressure of 100 bar, almost that of highly compressed hydrogen (700 bar). Similar values are also achieved by LOHC systems (Liquid Organic Hydrogen Carrier), in which H₂ is chemically bonded and stored without pressure by hydrogenation of aromatic hydrocarbons. The high volumetric storage density of hydrocarbons is also shown by the fact that compared

Raw material	Share in H ₂ production and technology
natural gas	28.7 % synthesis gas (steam reforming)
crude oil	17.3 % synthesis gas (heavy oil gasification)
	17.7 % Oil refinery by-product (petroleum production; fuel reformer)
	6.6 % Petrochemical by-product (olefin production)
	41.6 % in total
coal	11.5 % synthesis gas (coal gasification)
	16.2 % coke oven gas (furnace coke production)
	27.7 % in total
water	1.9 % by-product of Cl ₂ /NaOH production (electrolysis)
	0.1 % Wasserelektrolyse
	2.0 % in total
total	100 % = 96 million t H₂ = 275 million t crude oil equivalent
H₂ consumption according to product or industry (rounded percentages)	
chemical industry	
ammonia	32 %
methanol	14 %
other chemical products (acetic acid, oxo-alcohols ...)	5 %
energy supply	
crude oil refinery	28 %
fuels from coal / natural gas (Fischer-Tropsch synthesis)	5 %
coke/steel (coke oven gas)	16 %

■ Table 3: Global Production of Hydrogen 2014 (Jess and Wasserscheid, 2020).

Substance	Storage density (lower heating value)		Density in kg/litre	H ₂ content	
	kWh/Litre	kWh/kg		kg H ₂ /litre	kg H ₂ /kg
diesel oil	9.5	11.5	0.83	0.12	0.14
petroleum	8.5	11.5	0.74	0.11	0.14
methanol	4.4	5.5	0.79	0.10	0.13
natural gas (CH ₄) 20 °C, 200 bar	2.3	14	0.16	0.041	0.25
natural gas (CH ₄) 20 °C, 100 bar	1.1	14	0.08	0.020	0.25
H ₂ -253°C, liquid	2.3	33	0.071	0.071	1
LOHC (Perhydrodibenzyltoluol)	1.9	2.1	0.94	0.058	0.062
H ₂ 20°C, 700 bar	1.3	33	0.039	0.039	1
H ₂ 20°C, 100 bar	0.25	33	0.0077	0.0077	1
H ₂ 20 °C, 1 bar	0.003	33	0.00009	0.00009	1
Li-Ionen-Battery	0.5	0.2	2.5	-	-

■ Table 4: Gravimetric and volumetric storage density of fuels and energy storage systems (LOHC – liquid organic hydrogen carrier, Li-ion batteries). (Source: various references, inter alia Jess and Wasserscheid, 2020, see recommended reading).

to pure hydrogen, even more H₂ can be contained in one litre: 0.12 kilograms of H₂ for diesel oil and 0.041 kilograms of H₂ for methane (200 bar), compared to 0.039 kilograms for 700 bar compressed hydrogen and 0.071 kilograms for liquid H₂.

"The fuels produced via the Fischer-Tropsch synthesis could therefore be used in the transport sector, for heat generation in households, and in the chemical industry. They would consequently replace crude oil and natural gas, which currently have to be imported, in the main, into Germany and many other countries."

■ Table 5: Costs and performance (energy flows) of the transport of energy sources by ship, pipeline, and high-voltage line (Jess and Wasserscheid, 2020).

A look at capacity calculated in gigawatts (GW) (1 gigajoule per second = 1 GW) and the specific

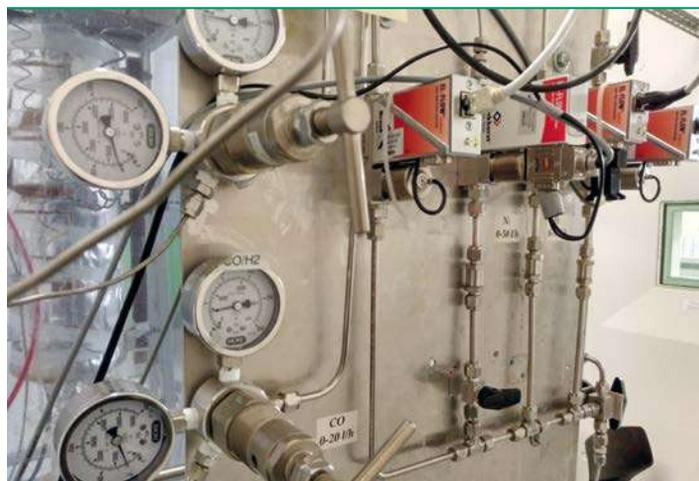
Transport system	Energy source	Conditions	Performance in GW	Transport costs in US \$ per 1,000 km per GJ (Share of Energy price)
tanker	crude oil	capacity: 300,000 t speed: 20 km/h distance: 3,000 km	23	0.04 (0.4 %)
	natural gas (liquid)	capacity: 125,000 m ³ speed: 20 km/h distance: 3,000 km	5	0.6 (6 %)
pipeline	crude oil	diameter: 0.9 m speed: 2 m/s	50	0.06 (0.6 %)
	natural gas	diameter: 0.9 m pressure: 90 bar speed: 10 m/s	20	0.2 (2 %)
	hydrogen	diameter: 0.9 m pressure: 30 bar speed: 15 m/s	3	2.3 (23 %)
high-voltage line	alternating current	overhead line 380 kV/8 A	3	1.4 (6 %)
		overhead line 220 kV/3.5 A	0.8	2.8 (11 %)
	direct current	overhead line 600 kV/5 A	3	0.8 (3 %)
		underground cable 600 kV/5 A	3	4 (16 %)

Assumptions: Oil price USD 60 per barrel (159 litres) = USD 10 per GJ; natural gas and H₂ price USD 10 per GJ; electricity price USD 25 per GJ (= EUR 0.08 per kWh; industrial price in Germany 2018 excluding taxes).

costs of energy transport using various energy sources by ship, pipeline, and high-voltage line is also very instructive (Table 5). The highest energy transport capacity can be achieved with liquid hydrocarbons such as crude oil, 23 GW per oil tanker and 50 GW per pipeline. A natural gas pipeline comes in at a similar value (20 GW). Hydrogen pipelines currently operate at pressures of up to 30 bar, which makes a capacity of 3 GW possible. However, pressures of up to 100 bar and thus 10 GW are quite conceivable. By way of illustration: 10 GW corresponds to the electrical output of 10 large coal-fired power plants or 1,000 large wind turbines.

In contrast, the power output of electricity transported through high-voltage lines is much lower (0.8 to 3 GW). This also shows the advantage of energy transport by means of gaseous and liquid hydrocarbons and, as the case may be, even via H₂. In terms of transport costs, gaseous and liquid hydrocarbons such as natural gas and crude oil, and their transport by tankers and pipelines, also perform significantly better than a hydrogen pipeline or high-voltage lines (Table 5). For example, the transport costs for an oil pipeline are only 0.06 US dollars per 1,000 kilometres and per gigajoule (GJ). In 2019, the oil price averaged USD 60 per barrel (= 159 litres), which is equivalent to USD 10 per GJ. In relation to the price of energy, this means that transport costs by oil pipeline are only 0.6 percent per 1,000 kilometres. For a natural gas pipeline (1,000 kilometres), this constitutes 2 percent, which is considerably less than for a 30-bar hydrogen pipeline at 23 percent. Even if 100-bar hydrogen pipelines were built, the figure of 7 percent would be significantly higher than for natural gas. This is because the volumetric energy density of hydrogen at 100 bar (and 20 degrees Celsius) is almost 80 percent lower than that of natural gas under these conditions (Table 4).

Assuming an electricity price of 25 US dollars per GJ (8 US cents per kWh), which is two and a half times higher than the price of oil, the cost of transporting electricity through high-voltage direct-current lines (600 kV) per 1,000 kilometres is between 3 (overhead line) and 16 percent (underground cable) of the price of the electricity transported. With the alternating current overhead lines still in use today, this figure is 6 to 11 percent. The transport of electricity is therefore more expensive in comparison to hydrocarbons (natural gas, crude oil), but especially with a high-voltage direct current overhead line, it is still cheaper than transporting hydrogen through a pipeline.



It should also be noted that the transport of liquid fuels consumes very little energy: ³ An oil tanker consumes 0.06 GJ per tonne of oil over a distance of 1,000 kilometres; and since one tonne of oil corresponds to an energy of 42 GJ (LHV), this would be only 0.14 percent of the energy content of the transported oil. In the case of pipeline transport, the figure is 0.5 percent (primary energy); while the energy losses of high-voltage direct current transmission over 1,000 kilometres are significantly higher at around 5 percent.

Hydrocarbons, produced from regenerative hydrogen and CO₂

Compared to hydrogen or batteries, gaseous and liquid hydrocarbons not only have a high volumetric storage density (Table 4), but also have other advantages: Synthetic natural gas (methane) and up to 5 percent pure hydrogen can be fed into the German natural gas grid and stored in large quantities in underground natural gas storage facilities. Currently, salt-cavern and aquifer storage facilities with a total working volume of 24 billion standard cubic metres are in operation in Germany. This corresponds to a quarter of the annual natural gas consumption of Germany (Table 6).

The CO₂ required for hydrogen methanation could come from biogas plants or from industrial processes, whether from power plants or the steel, cement, and chemical industries. CO₂ from these industrial processes, which are indispensable at least in the medium term, could be used to produce gaseous or liquid fuels.⁴ In simple terms, this means that, ideally, power plants, currently based on fossil raw materials

such as coal and natural gas, which are responsible for about 50 percent of total global CO₂ emissions, could be redesigned to be "CO₂ neutral". The extraction of CO₂ from industrial waste gases is all the more interesting in this context because it is currently not yet possible to extract CO₂ directly from air in a profitable way. At present, in June 2020, CO₂ is present in the atmosphere in a very low concentration of 0.041 percent (= 410 parts per million, ppm). For comparison, before industrialization, the CO₂ concentration was 280 ppm, which represents an increase of 46 percent. The majority of climate experts consider a further increase in the CO₂ content to be very problematic in view of global warming. According to the estimates of the Intergovernmental Panel on Climate Change (IPCC), for example, a concentration of 500 ppm is expected to increase the global mean temperature by two degrees Celsius compared to the pre-industrial era (today it stands at one degree). For a technically efficient and economical separation of CO₂ from the air, however, this low concentration is currently still a very big hurdle.

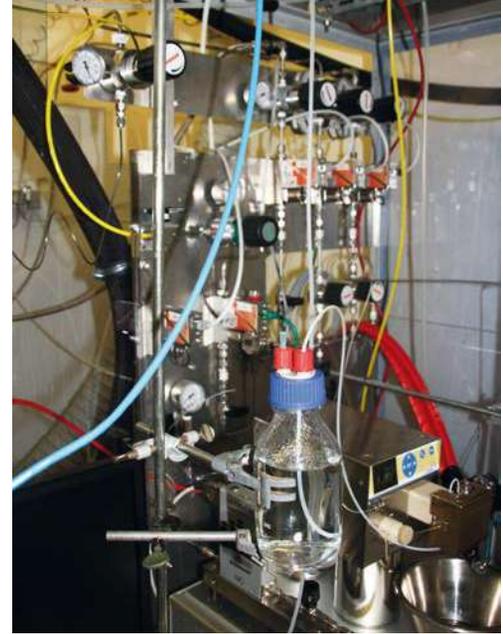
■ Fig. 1 (left): Gas supply of a Fischer-Tropsch reactor (Photo: Andreas Reul).

■ Fig. 2 (right): Heated exhaust pipes for sampling Fischer-Tropsch products (Photo: Andreas Reul).

■ Table 6: Characteristics of German gas storage (Status: end of 2018, Source: Erdöl Erdgas Kohle (2019) 135, 415-420).

TABLE 6		
Work volume of German natural gas storage	unit	
	billion m ³ (standard conditions)	GWh
aquifer reservoirs	9.1	88,900
salt-cavern reservoirs	15.2	148,500
total	24.3	237,400
for comparison: natural gas consumption	97 billion m ³ /year = 947,700 GWh/year	

■ Fig. 3: Gas and liquid addition by means of mass flow controller and evaporator unit for Fischer-Tropsch synthesis (Photo: Christian Wiffler).



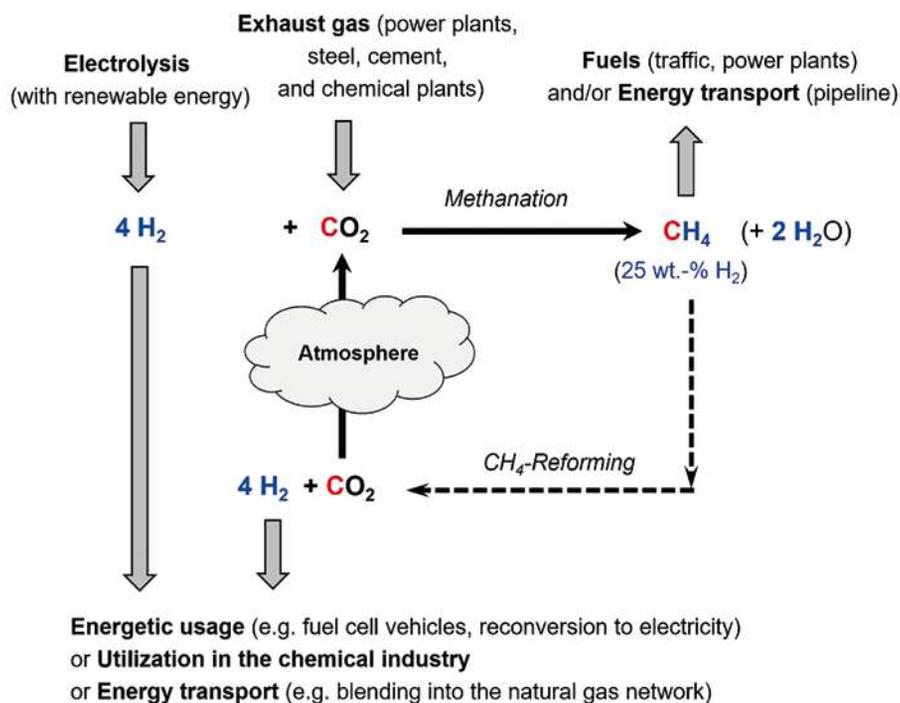
Via Fischer-Tropsch synthesis, synthetic and hence highly pure liquid fuels can be produced from H₂ and CO₂ for aviation (jet fuel) and ocean-going vessels (diesel oil) – i.e. for areas in which the use of hydrogen and battery electric drives is currently unrealistic. The use of battery and H₂ fuel cell systems for the propulsion of non-nuclear submarines, such as in the German Federal Navy, which is often brought up in this area, is a very specialized exception and cannot be transferred to civil shipping. Furthermore, liquid hydrocarbons do not require special storage or transport containers, and their application potential is great. Moreover, existing infrastructure in the transport sector and in the chemical industry is still based almost exclusively on petroleum-based fuels. Thus, in shipping and road transport and in aviation, gasoline, diesel oil, and jet fuel are the main fuels used. In the chemical industry outside of the USA and China, on the other hand, mainly light gasoline (naphtha) is used for the production of basic chemical substances such as ethylene or propene. In the USA, ethane, which is a by-product of the extraction of so-called "wet" shale gas, is also currently used as a raw material, while China is increasingly relying on coal as a raw material.

The fuels produced via the Fischer-Tropsch synthesis could therefore be used in the transport sector, for heat generation in households, and in the chemical industry. They would consequently replace crude oil

and natural gas, which currently have to be imported, in the main, into Germany and many other countries. Although the CO₂ produced in the many small units comprising aircraft, ships, cars, and heating systems would be released into the atmosphere, CO₂ emissions could still be reduced by a total of 50 percent. In addition, research is now working towards significantly reducing the pollutant emissions from the combustion of petrol, diesel, and jet fuel in engines and turbines. It is quite realistic to expect that H₂ and CO₂ could be turned into fuels that emit fewer pollutants than today's petroleum-based fuels.

And there is one other advantage: Wind power and photovoltaic plants often generate electricity that is not directly needed. This could be used for electrolytic hydrogen production and thus (also) for the synthetic production of gaseous or liquid fuels.

■ Fig. 4: Power-to-gas technology (CO₂/CH₄-cycle) for chemical storage of H₂ (Illustration: Andreas Jess).



The overall chemical process: the example of power-to-gas technology

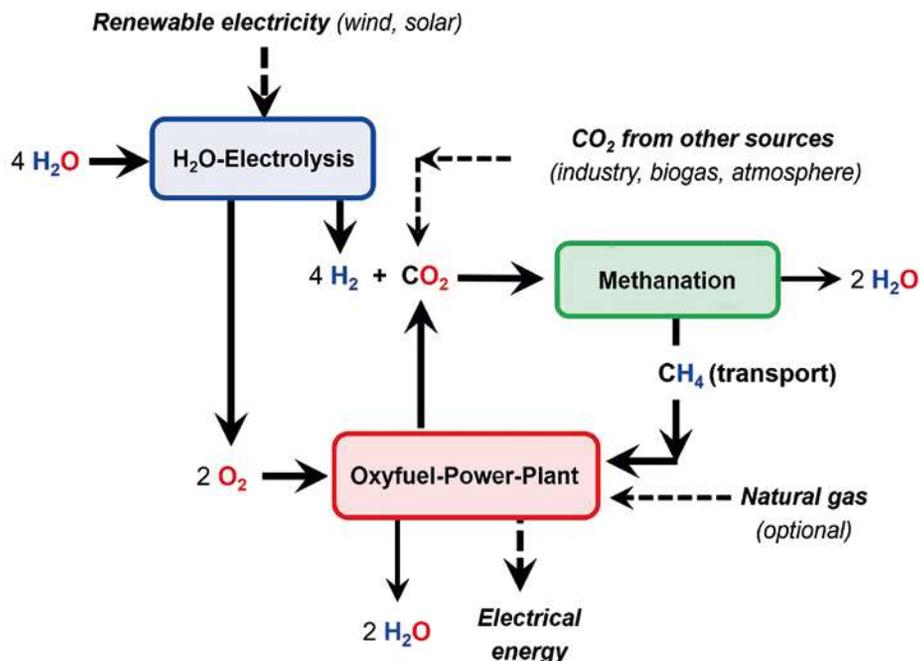
The entire chemical process is explained here using the example of methanation, i.e. the production of synthetic natural gas (SNG) (Fig. 4). This is also referred to as power-to-gas technology (PtG).⁵

There are two process stages to be distinguished:

1. Initially, hydrogen and oxygen are produced by water electrolysis:

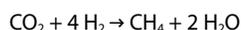


Electrical energy that is generated in excess by wind power or photovoltaic systems at a certain time and/or location is used.



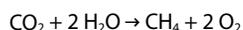
■ Fig 5: Power-to-gas technology combined with Oxyfuel powerplant (Illustration: Andreas Jess).

2. Hydrogen can be used *directly* as a fuel, as a chemical raw material, for energy transport, and energy storage, for example by adding it to the natural gas grid. It can also be converted into methane (CH₄, SNG) in a second process stage with CO₂, which is obtained from industrial waste gases (and in the distant future perhaps from the air) with the aid of catalysts (nickel):

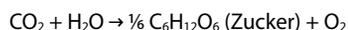


The reverse reaction of methanation, i.e. the renewed formation of H₂ from the methane produced, is possible, but is technically quite complex, especially for smaller applications. It is only a practicable option in special cases, in order to provide consumers at another location, such as a chemical company, with pure hydrogen from the methane – which is relatively easy to transport (pipeline) compared to hydrogen.

The sum of the two process stages results in the overall reaction:



This reaction has an analogy in nature: In photosynthesis, carbon dioxide and water are also used as synthesis components:



There, however, sugar is the target product, while the concept presented here is concerned with the production of hydrocarbons.

A particularly attractive option is the coupling of PtG technology with an oxyfuel power plant (Fig. 5). In this case, the highly-pure oxygen produced during electrolysis is most useful. Here, the synthetic natural



■ Fig. 6: Adjusting the pressure in the Fischer-Tropsch reactor (Photo: Christian Wiffler).

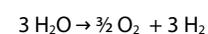
gas (SNG) can be burned in oxygen and not in air as is common today. After condensation of the water vapour, practically pure CO₂ is produced without any further separation measures required, which in turn is ready for methanation. Fossil natural gas can also be used as an option; for in Germany – when the phase-out of nuclear energy is completed in 2022 and coal-fired electricity is no longer generated from 2038 – it is predicted that regenerative electricity generation will have to be supplemented by conventional or oxyfuel natural gas power plants for a long time to come. With an efficiency of 50 percent, these are more efficient than lignite and hard coal-fired power plants (about 38 percent). In addition, natural gas power plants emit 0.4 kilograms of CO₂ per kWh of electricity generation, which is significantly less

CO₂ than coal-fired power plants (about 1 kilogram of CO₂ per kWh). What is certain, is the more SNG is generated and used for electricity generation, heat supply (households, industry), and transport (natural gas vehicles), the lower the overall CO₂ emissions will be.

When coupling PtG technology with an oxyfuel power plant, it would make sense to incorporate both hydrogen production and methanation into synthetic natural gas at the one location, if possible, in order to avoid the relatively complex and expensive transport of hydrogen (Table 5). In individual cases, therefore, the SNG produced must be transported by pipeline to a remote oxyfuel power plant and, conversely, the CO₂ produced must be transported back to the methanation plant.

From a technical point of view, transporting carbon dioxide through a pipeline is unproblematic; in fact, it has been operating successfully in North America since the 1970s. Currently, 50 CO₂ pipelines of a total length of 7,000 kilometres are in operation there. These were mainly installed to achieve better oil yield by injecting CO₂ into oil fields. The transport costs are also manageable: They amount to between 10 and 15 US dollars per 1,000 kilometres and tonne of CO₂.⁶ Transportation is therefore similarly inexpensive to natural gas, at USD 10 per 1,000 kilometres and ton of CH₄ (USD 0.2 per 1,000 kilometres and GJ, Table 5). Combustion of one tonne of CH₄ produces 2.75 tonnes of CO₂, resulting in total costs for outward and return transport of 40 to 50 US dollars per 1,000 kilometres and tonne of CH₄. This is equivalent to 10 percent of the energy price of the natural gas transported. In Germany, on the other hand, transport distances much shorter than 1,000 kilometres between a CH₄ power plant and a wind power or photovoltaic plant, i.e. the place of electrolysis and methanation, would be expected. The relative costs will therefore be in the single-digit percentage range.

Finally, it should be mentioned again that liquid fuels can also be produced from H₂ and CO₂ by Fischer-Tropsch synthesis in a similar process:



"-CH₂-" here stands for a chain link (methylene group) in long-chain hydrocarbons, such as marine

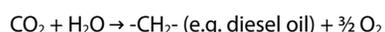
■ Fig. 7: Test facility for Fischer-Tropsch synthesis (Photo: Andreas Jess).





■ Fig. 8: View of the Faculty of Engineering Science at the University of Bayreuth (Photo: UBT).

diesel oil or aviation fuel. In sum, this results in the overall reaction:



Research aims at the University of Bayreuth

To produce gaseous or liquid fuels from regenerative hydrogen and CO₂, a multi-stage process is necessary (Fig. 4 and 5). To analyze this process and to optimize it in its technical as well as economic aspects, is the goal of current research of the Chair of Chemical Engineering, which is a member of the Centre for Energy Technology (ZET) at the University of Bayreuth. A laboratory facility operated at ZET is used for fundamental investigations to optimize Fischer-Tropsch synthesis (Fig. 7).

The research work here is partly embedded in joint projects in which engineering scientists from the

University of Bayreuth work closely together with partners from science and industry:

- A sector coupling of electricity and gas is being investigated in cooperation with the Chair of Thermodynamics and Transport Processes and the Tennet corporation.⁷
- In the PlasmaFuel project funded by the German Federal Ministry of Economics and Energy, the Chair of Chemical Engineering, the University of Stuttgart, and two industrial companies are researching the development of a novel process for the production of pollutant-free marine diesel.
- Fundamental investigations on the Fischer-Tropsch synthesis are being carried out in two projects funded by the German Research Foundation (DFG) and in cooperation with the company Evonik.

AUTHOR



■ Prof. Dr.-Ing. Andreas Jess is the Chair of Chemical Engineering (CVT) at the University of Bayreuth.

RECOMMENDED READING

A. Jess, P. Wasserscheid: Chemical Technology: From Principles to Processes. Wiley VCH, 2nd edition, 2020.

P. Kaiser, R. Unde, C. Kern, A. Jess: Production of liquid hydrocarbons with CO₂ as carbon source based on reverse water-gas shift and Fischer-Tropsch synthesis. Chem. Ing. Techn. (2013), 85, 489-499. DOI: 10.1002/cite.201200179.

M. Molina Martinez, C. Kern, A. Jess: Catalytic hydrogenation of carbon dioxide to methane in wall-cooled fixed bed reactors. Chem. Eng. Techn. (2016), 39, 2404-2415. DOI: 10.1002/ceat.201500614.

- 1 The so-called hydrodesulfurization leads to the conversion of organic sulfur compounds into hydrogen sulfide which is easily separated and further converted into elementary sulfur (used by the chemical industry, e.g. for production of sulfuric acid), and to hydrogenated hydrocarbons. Thus, a certain part of the hydrogen remains in the desulfurized fuel.
- 2 The lower heating value, LHV, is the amount of heat, related to a specific amount of fuel (for example, one kilogram), that is released during the complete combustion of a fuel if there is no condensation of water vapour. The higher heating value, HHV, correspondingly, is the energy when the combustion exhaust gas is cooled (to 25 degrees Celsius) and the water vapour condenses. HHV is therefore greater than the LHV by the value of the heat of condensation. For example, the HHV of H₂ is 39 kWh per kilogram, which is around 20 percent higher than LHV. For natural gas, the difference is 11 percent, while for gasoline and diesel oil it is around eight percent. Since "only" the LHV is used in most combustion processes, these are the values listed and compared here.
- 3 C.f. A. Jess, P. Wasserscheid: Chemical Technology. From Principles to Products. Wiley VCH, 2020.
- 4 C. Kern, P. Kaiser, R. Unde, C. von Olshausen, A. Jess: Considerations concerning the energy demand and mix for global welfare and stable ecosystems. Chem. Ing. Techn. (2011), 83, 1777-1791. DOI: 10.1002/cite.201100066.
- 5 The quite analogous process of generating liquid hydrocarbons (PtLiquid) has been described in detail in: A. Jess: Flüssige Kraftstoffe aus CO₂ und regenerativem Strom. Ein zukunftsweisender Forschungsansatz zur Sicherung der Energieversorgung. SPEKTRUM – das Wissenschaftsmagazin der Universität Bayreuth (2014/2), 22-25.
- 6 R. Doctor et al.: Transport of CO₂, in: IPCC Special Report on Carbon Dioxide Capture and Storage. Cambridge 2005. <https://archive.ipcc.ch/report/srccs/>
- 7 See the article on pp. 16-21 of this issue of SPEKTRUM.



■ Dieter Brüggemann
Andreas Jess
Christoph Linhardt

Power-to-gas as a key technology

Networking the electricity and gas sectors for a sustainable energy industry

■ *Concept of hydrogen storage from renewable sources – wind turbines and photo-voltaics. Hydrogen may be fed into the natural gas grid subject to conditions (sst).*

The German energy system is undergoing fundamental change. In addition to the gradual phase-out of nuclear energy by 2022 and coal-fired power generation by 2038, a far-reaching decarbonisation of other sectors (industry, transport, heating, etc.) is being undertaken in order to set course for a sustainable and secure energy future.

The Renewable Energy Sources Act

The use of renewable energies in the German energy industry was first legally regulated in 1990 by the Electricity Feeding Act. Electricity supply companies were obliged to pay for electricity that was not generated from conventional fossil fuels. After the expansion in the use of renewable energy, especially in the form of wind power plants, and the Kyoto Protocol of 1997, which aimed to reduce global greenhouse gas emissions, changing circumstances in the market and on the political level made it necessary to revise the law to enable the continued commercial operation of wind power and solar plants. The Renewable Energy Sources Act (EEG) of 2000 postulated, among other things, a doubling of the share of renewable energies by 2010, an obligation to purchase and remunerate, and the setting of a minimum remuneration.

After numerous further developments and amendments, the EEG is "the central steering instrument for the expansion of renewable energies. The aim of the EEG is to restructure the energy supply system, and to increase the share of renewable energies in the electricity supply to at least 80 percent by 2050. The expansion of renewable energies is particularly in the interest of climate and environmental protection, to develop a sustainable energy future. In addition, the economic costs of energy supply are to be reduced, fossil energy resources are to be conserved, and technological development in the field of renewable energies is to be promoted" (Federal Ministry of Economics and Energy, 2020).¹

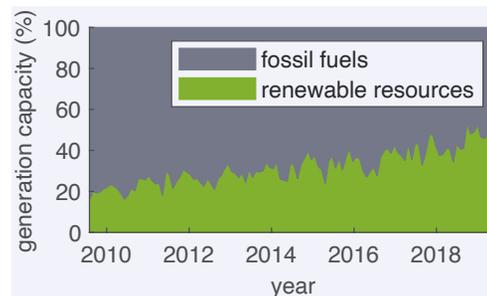
Increased use of renewable energy sources

Developments at the political level and in the German energy industry over the last decade have led to an increase in installed capacity in the wind and solar energy sector. They have thus enabled a significant increase in the share of renewable energy in the German power grid. In fact, the share of renewably

generated electrical energy in the grid has increased from around 20 percent in 2010 to up to 50 percent on a monthly average for 2019 (Fig. 1). The installed capacity for electricity generation from renewable energy sources (wind, solar, biomass, hydropower) reached almost 120 gigawatts (GW) at the beginning

"Power-to-gas technology enables sector coupling: the connection of the electricity grid with the gas grid for the storage and transport of energy."

of 2020, representing 57 percent of total installed capacity. However, when it comes to ensuring security of supply, the fluctuating nature of electricity generation from renewable energy sources must be taken into account. Thus, in times of high in-feed of wind energy and solar radiation, it would be possible to cover demand across all of Germany in theory; but if there is a lack of wind and solar radiation, in the extreme case a "dark doldrum", conventional gas, coal, or nuclear power plants must step into the breach. Short-term fluctuations in generation capacity also lead to increased control costs for transmission system operators.



■ Fig. 1: Electricity production in Germany - monthly mean values (Fraunhofer ISE, 2020).

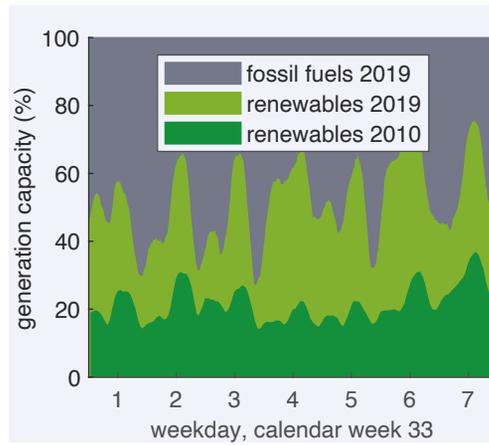
The effect of the current expansion of energy from renewable source on electricity generation becomes particularly clear when shorter periods of generation capacity are considered. Fig. 2 illustrates this by comparing one week in August in the years 2010 and 2019. The share of renewable electricity in 2019 was on average more than twice as high as in 2010. This resulted in a much more dynamic situation, with the renewable share of electricity production fluctuating between 30 and 70 percent. Conventional power plants had to compensate for these fluctuations.

Moreover, the increase in the share of energy from renewable sources in electricity generation has re-

quired further technical and economic innovation, in particular:

- improved forecasting models for renewable electricity generation,
- an accelerated expansion of the network for transporting energy from the site-based generation plants to the energy-intensive conurbations in Germany,
- a flexibilization of consumption structures in industry.

■ Fig. 2: Electricity production in Germany – daily values (Fraunhofer ISE, 2020).



For some time now, the focus has been on energy storage systems that make it possible to separate the generation and consumption of electricity. This decoupling represents a sensible and efficient way of integrating volatile energy sources. It will play an important role in the German energy industry in the future.

Change in the energy industry: Power-to-gas technology

In order to successfully convert the traditional supply of energy from fossil fuels to flexible and renewable energy sources on a large scale, short and medium-term supply gaps must be taken into account. For technical reasons, electricity cannot be stored directly on the grid. Consequently, solutions have to be developed to ensure security of supply in the future with an even higher share of renewable energies. In addition to known energy storage systems, such as batteries and pumped-storage power plants, which are only feasible to a limited extent in Germany, power-to-gas technology is becoming the main focus for storage in the medium-term. It enables so-called sector coupling: the connection of the electricity grid with the gas grid for the storage and transport of energy.

This opens up a wide range of potential applications. These include, firstly, the storage of electrical energy in the form of hydrogen or methane (obtained by converting H₂ with CO₂), the use of the storage gas as chemical feed stocks and, if required, its feeding back into gas power plants. Beyond that, many other energy requirements could be met with "green" energy. These include, for example,

- industrial applications that rely on natural gas, oxygen, or hydrogen,
- gas-fired boilers for domestic heating,
- gas engines for difficult to electrify areas in the transport sector and H₂ powered vehicles.

■ Fig. 3: Power-to-gas plant with biological methanation in Allendorf/Hessen. In the electrolyzer, excess electricity is converted into hydrogen (Photo: Viessmann Werke).



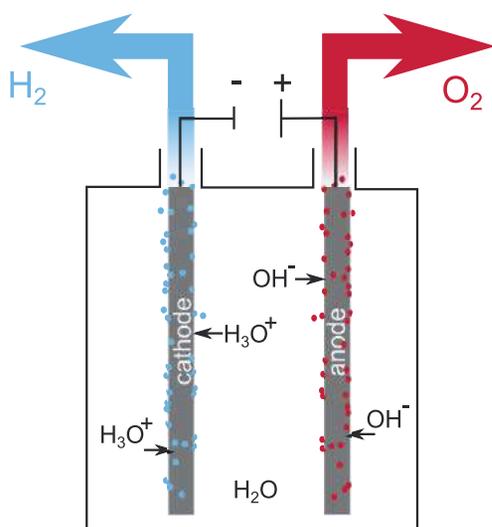
All these areas would be completely or partially decarbonized by power-to-gas technology, and thus become climate-neutral or more climate-friendly.

In power-to-gas technology, excess electrical current is first used in electrolyzers to split water into hydrogen and oxygen ($H_2O \rightarrow H_2 + 0,5 O_2$). With the aid of a carbon source such as CO_2 , hydrogen can then be converted into methane, the main component of natural gas, by the Sabatier reaction ($4 H_2 + CO_2 \rightarrow CH_4 + 2 H_2O$). The methane (synthetic natural gas, SNG) can then either be fed into the natural gas grid or made available for other applications. Feeding hydrogen into the gas grid is currently subject to restrictions, mainly in order not to significantly change the combustion properties of the H_2 natural gas mixture compared to "normal" natural gas. Depending on the application, permissible H_2 concentrations in natural gas range between one and ten percent. Here, there is still a need for development work and regulatory adjustments.

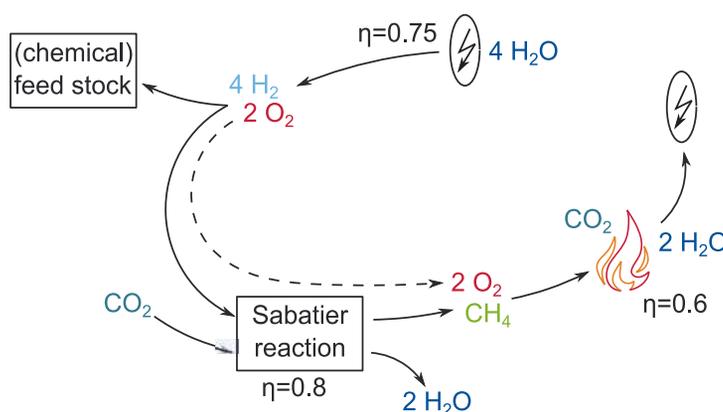
Water splitting by electrolysis today is mainly carried out using three different technical processes:

- Alkaline electrolysis (AEL)
- Membrane electrolysis (Proton exchange membrane, PEM)
- High temperature electrolysis (Solid oxide electrolyser cell, SOEC)

Depending on the electrode and electrolyte materials used, the partial reactions differ on the anode and cathode side. In all three cases the transported



■ Fig. 4: Schematic representation of the processes in an electrolyser (Illustration: Christoph Linhardt).



■ Fig. 5: Power-to-gas process with reverse power generation and optimization of efficiency (Illustration: Christoph Linhardt).

ions (OH^- , H^+ , O^{2-}) lead to the formation of hydrogen and oxygen after water splitting:

■ Alkaline electrolysis (AEL) is a mature technology that has been used on a technical scale for decades (Fig. 4). Inexpensive catalyst materials and comparatively low investment costs are advantageous here. However, high long-term stability is offset by a limited partial load range, longer cold start processes, and high material costs – and thus an unfavourable plant "footprint".

■ Membrane electrolysis processes such as PEM electrolysis are characterized by higher power densities, higher efficiency, good partial load capabilities, and extremely fast start-up performance compared to AEL. Added to this is the ability to absorb large overloads in a simple system. Furthermore, a compact stack design favours operation at higher pressures. Due to the lower long-term stability, especially at high operating pressures, and the expensive precious metal catalysts (platinum), this technology has only become established on an industrial scale in recent years.

■ The first high-temperature electrolysis plants based on SOECs are already being marketed on a smaller scale. Synergy effects result from coupling them with available heat sources, and promise to significantly increase efficiency in the power-to-gas process chain. Currently, the temperature-dependent stability of the materials used still represents an obstacle which is to be eliminated by further development work.³

As described above, methane (CH_4) can be produced from H_2 and CO_2 , typically at temperatures around 200 degrees Celsius and with the use of catalysts, for example nickel. The reaction is exothermic and thus

leads to a release of heat. If this heat is not utilized, it represents a disadvantage in terms of the efficiency of the process. In theory, however, an efficiency of 83 percent can be achieved (ratio of the lower calorific value of the CH₄ produced to that of the H₂ used). As CO₂ sources, processed flue gases from power plants, the cement and steel industry, biogas and, in the future, perhaps atmospheric CO₂ could be used.

A closed methane cycle based on "green" hydrogen

A particularly interesting option is the use of a cycle (Fig. 5), in which the methane produced is used to generate electricity in an oxyfuel power plant:

- $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$ (oxyfuel power plant, efficiency up to 60 percent).

The water vapor can be separated very easily by cooling the flue gas (condensation). Practically pure CO₂ is then available for methane production by reaction with regeneratively produced hydrogen:

- $4 \text{H}_2\text{O} \rightarrow 4 \text{H}_2 + 2 \text{O}_2$ (electrolysis with regenerative electricity, efficiency 75 percent),
- $4 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$ (methanization, efficiency 80 percent).

The two reactions in conjunction result in the reversal of methane combustion, meaning that the climate-neutral cycle is closed. This would make it possible to convert excess regenerative electricity into methane that can be easily stored and transported, which could then be converted back into electricity as required (in terms of time and place). The overall efficiency of wind/PV electricity into "methane" electricity would be $0,75 \times 0,8 \times 0,6 = 36$ percent, which corresponds to the current efficiency of a typical nuclear or coal-fired power plant.⁴

A cooperation project between the University of Bayreuth and TenneT TSO GmbH

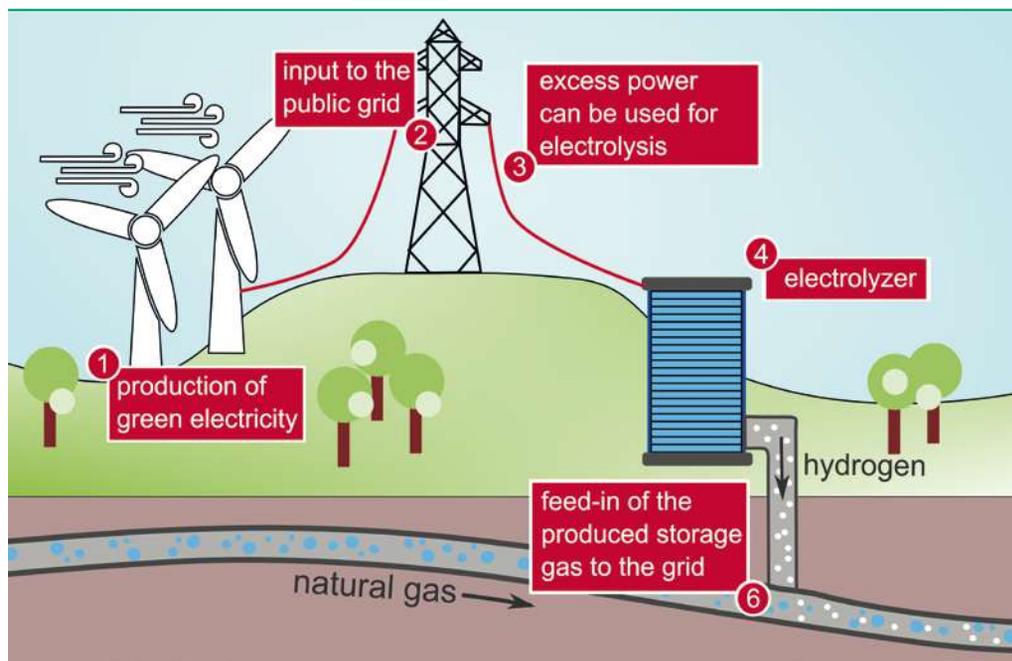
The current efforts to achieve a sustainable and renewable energy supply in Germany present major challenges to the existing infrastructure. The "green" energy sources available on a large scale (wind, solar radiation) are proving to be volatile and spatially dependent on geographical conditions and established development plans. Another problem is the oft-encountered local separation of energy production and consumption. For this reason, the transmission system operator TenneT TSO GmbH at its Bayreuth site and the Center for Energy Technology (ZET) at the University of Bayreuth have agreed to cooperate. In a research project supported by

Key data on the electricity grid and natural gas network in Germany

The German power grid, with a total length of 36,800 kilometres at the level of the transmission system operators, is the backbone of the German electricity supply. In order to maintain network and system security, it is sometimes necessary to temporarily shut down plants that are eligible for EEG or KWKG compensation. In addition to the shutdown of wind energy plants on land (onshore), plants at sea (offshore) must now also be shut down to a greater extent when the energy generated cannot be absorbed by the transmission grid. With the target of an 80 percent share of renewable energies in the grid by 2050 and the associated further expansion of renewable energy supply, the situation can be expected to become even worse. The optimisation, reinforcement, and expansion of the grid is therefore crucial.

The German natural gas network at the level of transmission system operators comprises 3,270 exit points to end consumers, distributors, or downstream networks, and extends over 38,500 kilometres. In 2018, 928 TWh of energy was tapped and a total of 1,777 TWh of natural gas was transported. The difference results from the fact that Germany is a transit country for neighbouring countries. Underground storage facilities (cavern and pore storage facilities) have a working gas volume of approx. 240 TWh, which can be used both as a strategic reserve and as a seasonal buffer.

Source: 2019 monitoring report by Bundesnetzagentur (Federal Network Agency) and Bundeskartellamt (Federal Cartel Office).



■ Fig. 6: Simplified representation of the power-to-gas process path (Illustration: Christoph Linhardt).

the Chair of Engineering Thermodynamics and Transport Processes and the Chair of Chemical Engineering, the potential of power-to-gas storage technology for the German grid area is to be evaluated. The aim is to optimize the ongoing network planning process. On the basis of a detailed and scientifically sound consideration of the entire process chain, combined with forecasts of the economic and legal frameworks, the advantages and disadvantages of large-scale chemical storage of electrical energy are to be determined. Such storage would include the downstream use of renewable energy in the form of a storage gas (H₂, CH₄). The staff members of TenneT support the research work with their expertise in the planning and evaluation of measures.

In addition to better utilization of installed capacity, the use of power-to-gas plants is intended to reduce CO₂ emissions of the German energy industry and decarbonize it by coupling the electricity and gas sectors. The use of hydrogen in transport and in the chemical industry could also contribute to economic efficiency. In addition to the necessary network expansion and the not inconsiderable costs associated with the use of PtG technology, the challenges that the two project partners wish to tackle together

include, above all, uncertainties in forecasts and the political environment.

The first results of the three-year project, which was started in March 2019, indicate that there is great potential in the TenneT grid area, depending on the location. The aim of the next two years is to develop recommendations for TenneT's strategic decision-making. Both short-term measures and long-term developments up to the year 2050 will be investigated.

- 1 Federal Ministry of Economics and Energy (2020): Das Erneuerbare-Energien-Gesetz: www.erneuerbare-energien.de/EE/Redaktion/DE/Dossier/eeg.html
- 2 Cf. Fraunhofer ISE (2020): Monthly electricity generation in Germany. www.energy-charts.de/energy.htm
- 3 M. Sterner, I. Stadler (eds.): Energiespeicher – Bedarf, Technologien. Berlin, Heidelberg 2017. DOI: 978-3-662-48893-5.
- 4 N. Armaroli, V. Balzani: Towards an electricity-powered world. *Energy and Environmental Science* (2011), 4(9), 3193-3222. DOI: 10.1039/c1ee01249e.

AUTHORS



■ Prof. Dr.-Ing. Dieter Brüggemann is the Chair of Engineering Thermodynamics and Transport Processes (LTTT) and Director of the Center for Energy Technology at the University of Bayreuth.



■ Prof. Dr.-Ing. Andreas Jess is the Chair of Chemical Engineering (CVT) and Deputy Director of the Center for Energy Technology at the University of Bayreuth.



■ Christoph Linhardt M.Sc. is a research associate at the Center for Energy Technology at the University of Bayreuth.



■ Christoph Linhardt
Christian Wißler

INTERVIEW WITH DR. PETER HOFFMANN AND NORBERT LECHNER, TENNET TSO GMBH

Powering into the future with hydrogen

■ Power line near Schwandorf in Upper Palatinate (Photo: Christoph Linhardt).

Hydrogen, the most common chemical element in the universe, is a beacon of hope on our way to a sustainable energy economy. With innovative technologies such as power-to-gas, surplus green electricity can be both stored and transported. Dr. Peter Hoffmann and Norbert Lechner, experts for energy system planning at the German-Dutch transmission grid operator TenneT, were recently interviewed on the current challenges in grid expansion, and explain the role hydrogen will play in addressing them. The contribution of the Federal Government's national hydrogen strategy to the *Energiewende* ("energy turnaround") is becoming increasingly evident.

Where do we currently stand with the *Energiewende*?

As early as 2019, around 43 percent of electricity consumption in Germany came from renewable energies. The *Energiewende* is continuing apace, and electricity generation from wind and photovoltaic plants is increasing. However, this is very much subject to weather-related fluctuations. If the installation of these systems continues to grow, the number of hours with negative electricity prices will also increase. At the same time, Germany is phasing out nuclear power, in particular, and coal in the foreseeable future – in other words, energy sources that have so far kept the electricity grid stable by balancing out fluctuations in generation and consumption. That's why our future energy system needs a new reliable constant in addition to renewables, grids, and storage facilities. Gas-fired power plants are a good option here, although it must be remembered that natural gas reserves are finite. Innovative technologies like power-to-gas offer an alternative here.

What are the current and future challenges of the *Energiewende*?

It made a lot of sense to start in the electricity sector, but now other areas need to be brought into focus. Renewable energy only accounts for a small share in the transport sector or demand for heating. To reduce the CO₂ balance there, however, is not as easy as switching to electricity. Green hydrogen and its derivatives could be a solution. The national hydrogen strategy recently published by the German government highlights the possibilities for Germany to establish a hydrogen economy.

INTERVIEW PARTNERS

Dr. Peter Hoffmann

is Head of Energy System Planning at TenneT TSO GmbH in Bayreuth.



Norbert Lechner

is Head of the team System Outlook Germany in the department Energy System Planning at TenneT TSO GmbH in Bayreuth.



What does the *Energiewende* currently mean for electricity grids in Germany?

We have very good wind areas on the North Sea and Baltic Sea, as well as sunny regions in the south of Germany. Furthermore, a large part of our industry is concentrated in conurbations such as the Ruhr area and southern Germany. This is why TenneT, together with the other German transmission system operators, is pushing ahead with the necessary network expansion to connect regions boasting high energy production with regions of high consumption. The existing extra-high voltage grid was designed when the power load was covered regionally by large power plants, and hence it was not designed for the aforementioned new transport tasks.

What contribution can hydrogen make to the German energy system?

As mentioned, the generation of energy from wind and photovoltaic systems is highly weather-depen-

dent and therefore subject to strong fluctuations. In order to keep the grid stable, hydrogen technology may provide alternatives. Germany has a very well-developed gas transport system with large storage capacities, for example in the form of underground storage facilities. Among other things, this can currently cover the country's considerable heat demand in the winter months. These storage capacities are mainly located in close proximity to the offshore wind farms in the North Sea and the import points for conventional natural gas. These are all good preconditions for using hydrogen from renewable energies for other sectors without major infrastructure conversion becoming necessary.

Against this background, how do you assess the Federal Government's national hydrogen strategy?

With its national hydrogen strategy, the Federal Government is taking the first right step. It is necessary that the strategy should now be implemented, electricity and gas will have to complement each other in future, and the infrastructure required for this must be planned in an integrated manner. Only in this way can the energy system remain reliable and affordable. To achieve this, power-to-gas technology must continue to advance, for example by

the timely building of industrial-scale electrolysers. In addition, pilot projects such as ELEMENT ONE, which TenneT is planning together with partners in Lower Saxony, are providing new findings that show how large-scale power-to-gas plants and the electricity grid can best interact.

What challenges in the transmission grid could be solved with power-to-gas or sector coupling?

In total, the quantities of renewable electricity that remain unused in Germany are now in the region of terawatt hours. If the expansion of the electricity grid continues to lag behind, or if sufficient storage capacities do not become available, these quantities will continue to rise and have an impact on electricity charges. Solutions such as power-to-gas or power-to-heat can be helpful in using these quantities of previously surplus electricity, and integrating them into the system in a sensible manner.

To what extent can the objectives of the recently adopted hydrogen strategy be incorporated into the electricity grid development plan?

With the timely adoption of the national hydrogen strategy, the targets described in it, such as the

RECOMMENDED LINK

The project „ELEMENT EINS. Energiewende mit Sektorkopplung“ (Element One. Energy transition with sector-coupling) involves, over a series of stages, developing a power-to-gas facility in Germany, envisaged to reach a capacity of 100 megawatts (MW) by 2030.

www.element-eins.eu



■ Fig. 1: The main building of TenneT TSO GmbH in Bayreuth (Photo: TenneT TSO GmbH).

target for installed electrolyser capacity by 2040, could be included in the 2021-2035 network development plan. Electrolysers as an interface to the gas grid are a rather new possibility. On the other hand, the other direction – coupling the gas sector with the electricity sector via gas-fired power plants – has always been taken into account; and fuel cells representing only one new technology here. Electrically generated steam and heat for industrial processes and district heating systems could also play an increasingly important role in planning considerations. Cooperation projects, such as those with the University of Bayreuth will help prepare our models for the future.

Practically speaking, this means that TenneT would like the electrolysers to be located in northern Germany?

For the success of the *Energiewende* in Germany, it is important for the majority of plants to be optimally positioned on the grid side. In the national hydrogen strategy adopted in June 2020, the focus of power-to-gas is primarily on the steel, chemical, and petrochemical industries. As these are mainly located near centres of consumption such as the Ruhr area or southern Germany, this could further

aggravate the bottlenecks in the power transmission grid. The study "Phase II – Pathways to 2050", published at the beginning of the year, shows that it would make sense, not only from a technical but also from an economic point of view, to mainly locate the electrolysers in northern Germany.

How could network expansion facilitate the creation of hydrogen infrastructure?

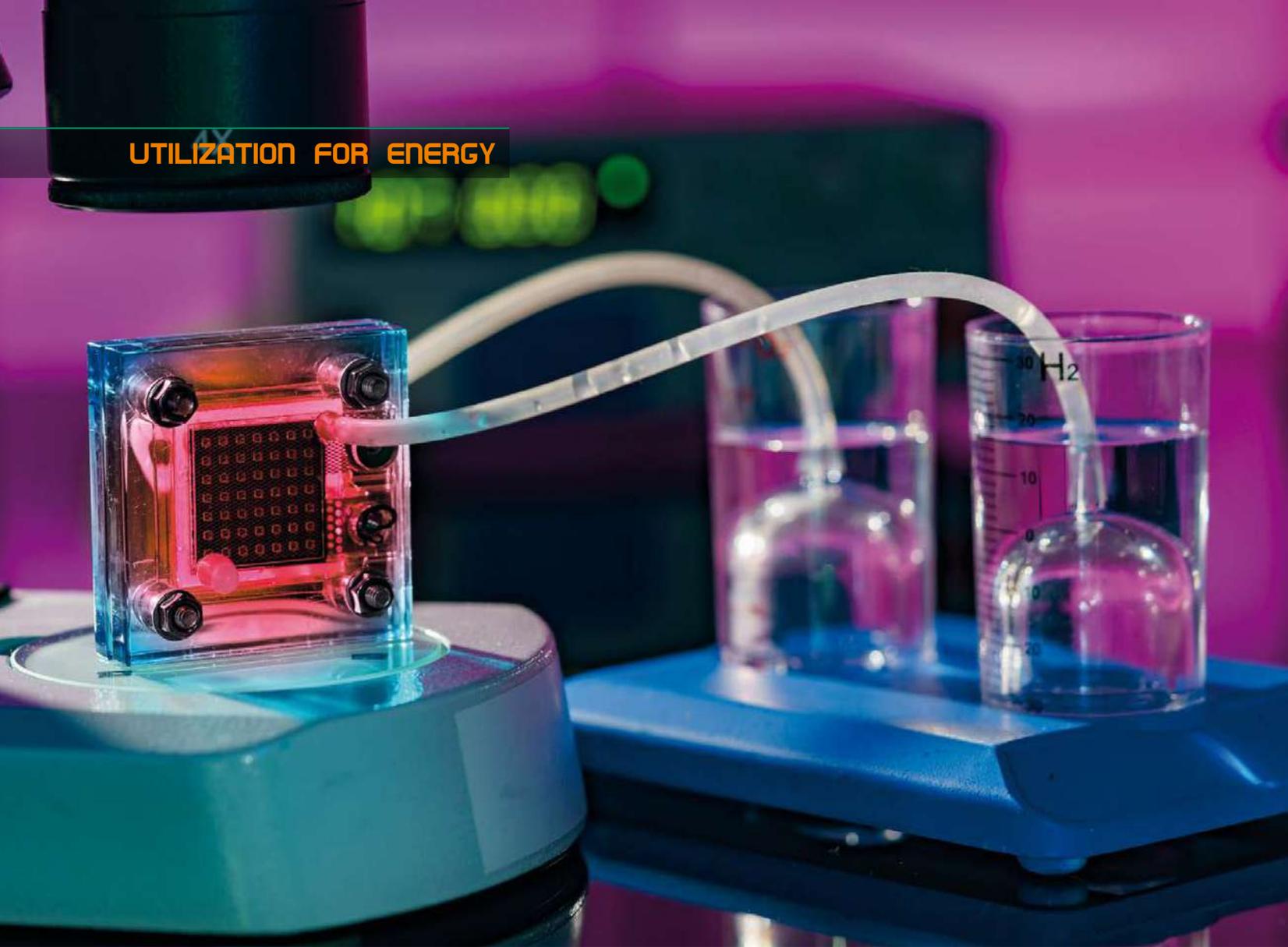
To transport the hydrogen from the electrolysers to the consumers, existing natural gas pipelines as well as new hydrogen pipelines could be used. The infrastructure for natural gas is already very well developed in Germany. In contrast, the hydrogen infrastructure must be built up in a targeted and timely manner, and it goes hand in hand with the planning of other infrastructure. If certain large-scale consumers such as industrial users cannot be supplied with hydrogen on a secure supply basis, power-to-gas plants may have to be built right on the user premises. This would require an additional expansion of the electricity grid. However, this requirement could be reduced to a minimum by forward-looking and integrated energy system planning, including hydrogen networks.

Are there other research activities besides the cooperation project with the University of Bayreuth in the area of sector coupling?

In addition to involvement in its ELEMENT ONE power-to-gas pilot project, TenneT has presented two studies in recent months together with the transmission system operator Gasunie. These deal with the effects of coupling electricity and gas network infrastructures on the *Energiewende*, and focus on the transition to an integrated energy system. According to these studies, sector coupling of energy infrastructures for electricity, gas (hydrogen and methane), and heat is a key factor for the integration of renewable energies and for ensuring security of supply. Power-to-gas will also play an important role in the seasonal storage of renewable electricity.

Our aim at TenneT is integrated planning that takes into account the political guidelines, the technological developments, and the forecast energy requirements of the future as carefully as possible. This is where our cooperation with the University of Bayreuth comes in – together with our partners in research, we can better assess future trends.





■ Andreas Rosin
Jörg Exner
Patrick Heimerdinger
Ralf Moos

On our way to post-fossil energy supply

Innovative research on fuel cells in the ForOxiE² research network

■ *Hydrogen fuel cell in a research laboratory (sst).*

Fuel cells convert the chemical energy of hydrogen into electric current. For this purpose, they use the catalytically forced "cold" combustion of hydrogen and oxygen to produce water. They can be used both in mobile and stationary applications. Current studies recommend the simultaneous expansion of both battery and fuel cell-based electric transport.¹ In the area of stationary and decentralized applications, fuel cells feature high efficiency since they combine heat and power generation.² However, in order to enable fuel cells to become a central component of the energy generation in a future that is no longer dependent on fossil raw materials, improvements in service life, robustness, functionality, and cost are necessary for this technological and economic breakthrough.

The Bavarian research network ForOxiE²

The work of the ForOxiE² fuel cell research network, funded by the Bavarian Research Foundation, came to a successful conclusion at the end of 2018.³ Four Bavarian university partners from Bayreuth, Munich, Erlangen, and Coburg, as well as eight Bavarian industrial partners, cooperated closely in this network. Under the leadership of the University of Bayreuth, new materials and components were developed and tested, both for low-temperature fuel cells with polymer electrolyte membranes (PEMFCs) and for high-temperature solid oxide fuel cells (SOFCs) with ceramic membranes. The engineering research groups for Functional Materials (Prof. Dr.-Ing. Ralf Moos), Chemical Engineering (Prof. Dr.-Ing. Andreas Jess) and Materials Processing (Prof. Dr. Monika Willert-Porada)⁴ at the University of Bayreuth were involved in the development of new materials and testing of new production methods. The intensive cooperation between university research and industry resulted in pioneering findings for the innovative ongoing development of fuel cell technology.⁵

New materials optimize the polymer electrolyte fuel cell

In the PEM fuel cell, a polymer membrane provides for the spatial and electrical separation of the two electrodes. On the anode side, hydrogen as the fuel gas is split into electrons and protons. The protons migrate through the membrane; and to balance charge, electrons flow through the external circuit and thus perform electrical work. Oxygen from the air serves as the oxidant and reaction partner at the

cathode. Water is formed at the cathode as the reaction product (Fig. 1).

The low-temperature PEM fuel cell operates at between 50 and 80 degrees Celsius, while the high-temperature PEM is designed for a temperature range from 160 to over 200 degrees Celsius.⁶ Although

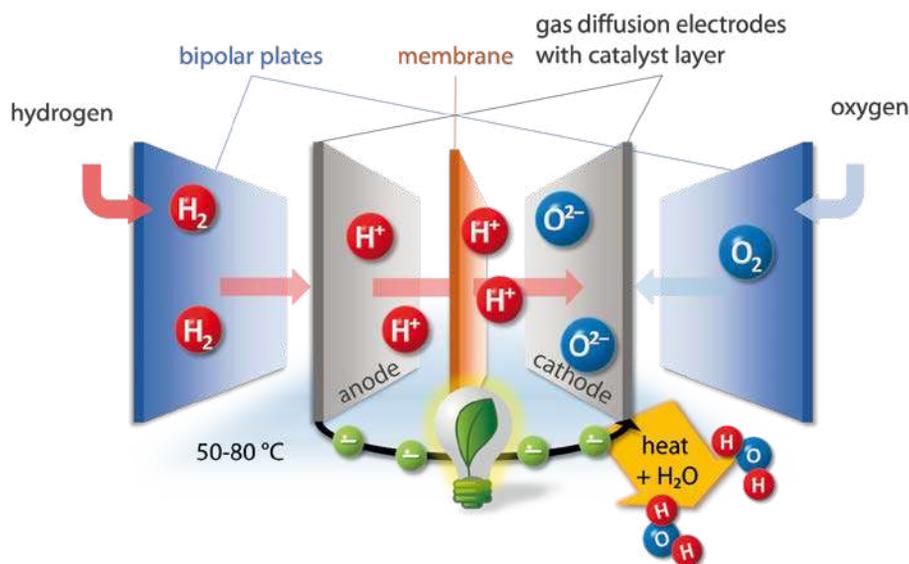


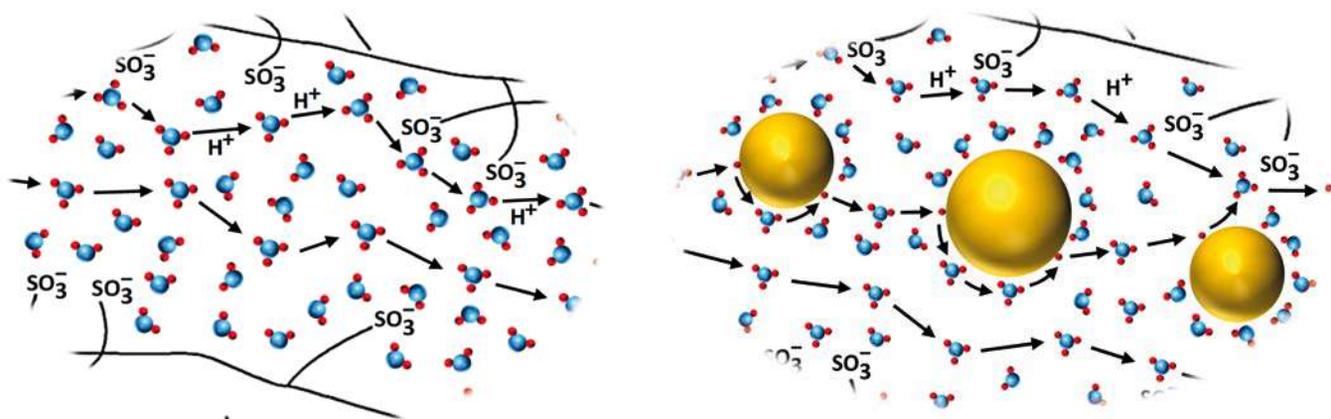
Fig. 1: Functional diagram of a polymer electrolyte fuel cell (PEMFC) (Illustration: Andreas Rosin).

temperatures around 130 degrees Celsius have not yet been used technically, they would be equally advantageous for the operation of PEM fuel cells. Here, two factors in particular would increase the overall efficiency of a fuel cell system: higher diffusion and reaction rates, as well as an easier heat management.⁷ In addition, this system would be far more tolerant of production-related impurities in the fuel gas, such as carbon monoxide.

The membranes of low-temperature PEMFCs (LT-PEMFCs) usually consist of perfluorosulfonic acid ionomers. These polymers combine several advantages under common operating conditions:

- high chemical and mechanical stability,
- electrical insulation capacity,
- and good proton conductivity in a water saturated state.

However, the technical maturity of LT-PEMFCs is (still) limited as far as its use at an operating temperature of 130 degrees Celsius is concerned. This is because good proton conductivity is based on water stored in the membrane, which evaporates at 100 degrees Celsius. Consequently the proton flow from the anode to the cathode is reduced. Another factor



■ Fig. 2: Left: Proton conduction in a water-saturated ionomer membrane. Right: Proton conduction in a water-saturated composite membrane with metal fluoride particles (shown here as yellow spheres). The particles cause a larger number of protons to be transported faster within the membrane (Illustrations: Patrick Heimerdinger).¹³

AUTHORS



■ Dr.-Ing. Andreas Rosin is a research associate at Ceramic Materials Engineering at the University of Bayreuth.



■ Dr.-Ing. Jörg Exner is a research associate at the Functional Materials research group at the University of Bayreuth.

is that the ionomers are thermoplastic polymers and therefore become soft and malleable at higher temperatures. Both the mechanical stability and ionic conductivity of the membrane, which is only a few micrometers thick, are therefore impaired at 130 degrees Celsius.

In the field of PEMFC technology, the ForOxiE² joint project hence pursued the goal of developing membranes that remain mechanically stable, electrically insulating, and at the same time, have good proton conductivity at temperatures around 130 degrees Celsius. To extend the operating window of LT-PEMFCs up to 130 degrees Celsius, the water content of the membrane was stabilized and the proton conductivity increased. Researchers at the University of Bayreuth succeeded in doing this by developing organic-inorganic composite membranes.

Therefore, an ionomer of high proton conductivity⁸ developed by the 3M company was significantly modified by the use of additives. Metal salts from the fluorides group (also called metal fluorides) have strong propensity to binding liquid from the environment to themselves (hygroscopy). They can therefore bind additional water in the membrane at temperatures below 100 degrees Celsius. The bond between the water molecules and the metal fluorides is so strong that it is possible to retain water in the membrane even at temperatures above 100 degrees Celsius. The interaction of the metal fluoride particles with the ionomer ensures that the water is bound at the right place in the membrane, and that the protons are quickly guided through the composite membrane (Fig. 2).

Compared with conventional ionomer membranes, these composite membranes have proven to be sig-

nificantly more efficient in fuel cell tests on the test rig, especially at the targeted operating temperatures of 130 degrees Celsius (Fig. 3 and 4). Due to the higher water content of the composite membranes, increases in performance yield of up to 45 percent higher are possible.

The results of the project are currently being used in the follow-up HyRunCell project, funded by the Bavarian State Ministry of Economic Affairs, Regional Development and Energy as part of its energy research program. Together with the University of Bayreuth, the companies 3M and Freudenberg Sealing Technologies are involved in the project. Cooperation with the Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (HI-ERN) is also planned. The project partners intend to develop a new generation of medium-temperature fuel cell stacks based on the composite membranes described above. This technology, in which several fuel cells are connected in series, could be used in the future, especially in the field of mobile applications.

Bayreuth successes in optimizing the solid electrolyte fuel cell

In contrast to PEMFCs, a reversal of charge transport takes place in the solid oxide fuel cell (SOFC): The solid-state electrolyte of the SOFC does not conduct protons to the cathode, but oxygen ions to the anode. For this transport, an ion-conductive ceramic based on doped zirconium oxide is used, which achieves sufficient ion conductivity at 600 degrees Celsius and above. The overall reaction of the hydrogen conversion, $2 \text{H}_2 + \text{O}_2 \rightarrow 2 \text{H}_2\text{O}$, still applies, even if the ion transport is reversed. However, the reaction product water is not formed at the cathode but at

the anode (Fig. 5). In contrast to the gas-tight electrolyte, the oxygen electrode (cathode) and the hydrogen electrode (anode) must be gas-permeable so that the gases flowing through (oxygen or hydrogen) each have a sufficiently large surface area for the reaction to proceed. In order to minimize the transport distances between electrode and electrolyte, the electrodes arranged in layers and the electrolyte are only a few hundredths of a millimeter thick.

SOFC electrolyte and SOFC anode

At the Functional Materials research group at the University of Bayreuth, SOFC research is advancing with a view to its technical optimization. This involves, on the one hand, material science studies on new functional ceramics that exhibit improved ionic conductivity at lower operating temperatures, and on the other hand, research into new processes with which the thin, gas-tight membranes can be produced.

As part of ForOxiE², barium-based oxide materials were investigated, in particular barium cerate (BaCeO₃), barium zirconate (BaZrO₃) and barium stannate (BaSnO₃). The special feature of these materials is that they do not transport oxygen ions, as is the case of conventional zirconium oxide-based fuel cells, but predominantly make use of protonic charge carriers. In addition to material synthesis, various dopants were examined in detail to see how functional electrical properties could be enhanced by their incorporation. It was shown that the ionic conductivity of all three tested materials could be significantly improved by doping with 20 percent yttrium.⁹ In the case of barium cerate, this would make it possible to lower the temperature of application by several

hundred degrees Celsius, while barium zirconate, with its good electrical properties, also exhibited a significantly higher degree of chemical stability.

During the processing of these materials, however, it became apparent that it was not possible to produce gas-tight membranes by conventional methods – like foil drawing or pressing and subsequent sintering - despite high temperatures of up to 1,650 degrees Celsius. However, this problem was solved with a new spray coating process for ceramics, called powder aerosol deposition (*Powder Aerosol Deposition, PAD*).¹⁰ The University of Bayreuth is a European leader in the development and optimization of this process. With PAD, dense ceramic films can be applied to very different types of materials. For this purpose, a dry ceramic powder is converted into an aerosol using a carrier gas, i.e. into a mixture of gas and solid particles. The aerosol is then accelerated through a nozzle in a vacuum chamber up to several hundreds of meters per second, and directed onto the substrate to be coated. On impact, the tiny ceramic particles fracture. The resulting fragments, which are only a few nanometers in size, form firmly adhering, dense coatings with a thickness of between one and 100 micrometers.

This process made it possible for the first time to produce micrometer-thin yet gas-tight membranes without any heat treatment. This not only enabled to produce dense films for membrane applications made of the three materials mentioned above, but also of conventional zirconium oxide and cerium oxide based solid electrolytes.¹¹ It was even possible to spray the gas-tight membranes onto open-porous electrodes, which is an important prerequisite for the use of this coating technology in fuel cells (Fig. 6).

AUTHORS



■ Dr.-Ing. Patrick Heimerdinger was research associate at the Electrochemical Process Engineering research group, and in the Keylab Glass Technology at the University of Bayreuth until June 2020. He is currently working as a project engineer at InVerTec – Institut für Innovative Verfahrenstechnik e.V.

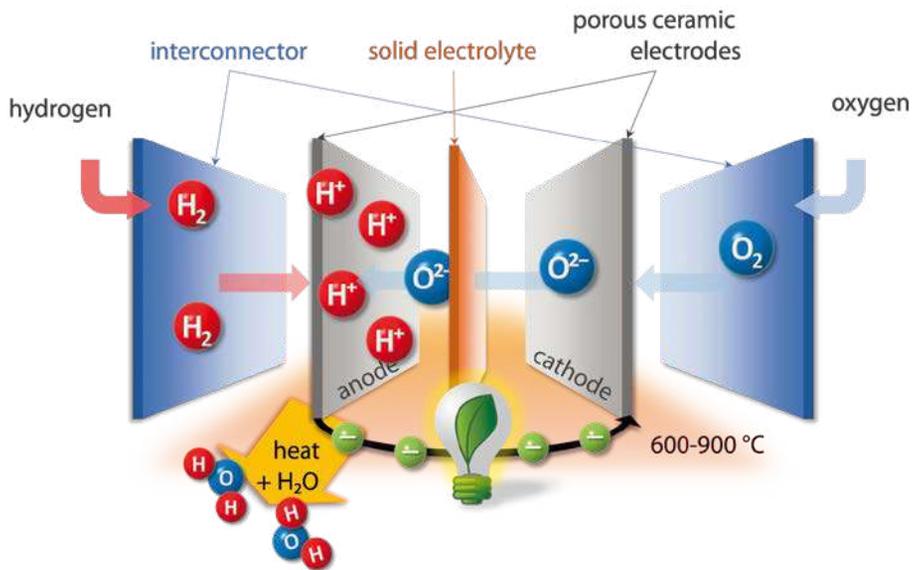


■ Prof. Dr.-Ing. Ralf Moos is the Chair of Functional Materials at the University of Bayreuth.



■ Fig. 3 (left): Preparation of a PEMFC test. A membrane electrode assembly with composite membrane is inserted into the measuring cell (Photo: Andreas Rosin).

■ Fig. 4 (right): Dr. Patrick Heimerdinger preparing a PEMFC at the fuel cell test stand (Photo: Maximilian Kutter).



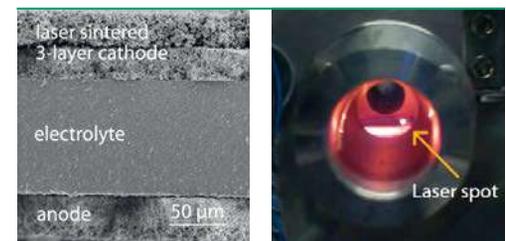
■ Fig. 5: Functional diagram of a solid oxide fuel cell (SOFC) (Illustration: Andreas Rosin).

SOFC cathode

Within the framework of ForOxiE², the University of Bayreuth researchers were successful in one more respect. For the first time, they managed to produce a SOFC cathode in the form of a porous layer system by laser sintering with a CO₂ laser. Selective laser sintering is one of the so-called additive manufacturing processes.¹² A laser beam is guided over a coated powder surface. At the point where the laser strikes the powder surface, the laser energy is absorbed by the ceramic powder and converted into heat. The heat penetrates into the powder layer and causes the previously loose individual particles to combine and any cavities to be partially or completely closed. This process is called sintering.

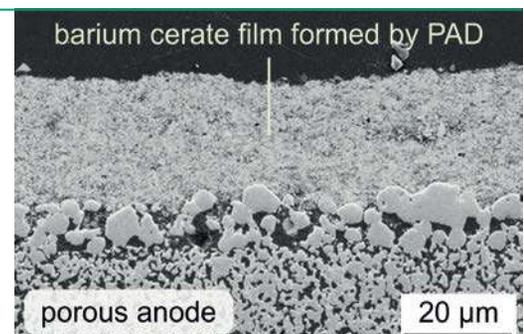
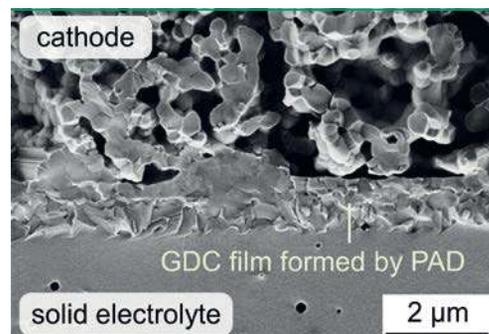
In the main, printing processes have been used in the production of the electrodes and electrolyte of solid electrolyte fuel cells up to now, in particular screen printing or spraying, and less frequently inkjet printing or stereolithography. Compared to these processes, selective sintering by CO₂ laser as applied

in Bayreuth has one important advantage. It enables the direct production of a porous electrode layer without subsequent sintering of the component. When designing the process, it is crucial that the powder layer to be heated bonds with the underlying material layer without reducing the porosity (Fig. 7). If the energy of the laser is too low, the powder layer does not adhere; if the energy is too high, the powder melts and blocks the gas channels. In order to achieve surfaces that are as flat as possible for the subsequent layers, an even distribution of the laser energy transmitted at a given point is critical.



■ Fig. 7: Left: Electron microscope image of a SOFC full cell, with ZrO₂ electrolyte as supporting structure, laser-sintered 3-layer cathode made of strontium-doped lanthanum manganate, and screen-printed Ni/ZrO₂ anode. Right: View into the process chamber during laser sintering - the illuminated dot shows the current laser position (Photos: Andreas Rosin).

The key to optimizing this process lies in energy management. The Bayreuth researchers have optimized the preheating stage, and have adapted both laser energy and beam control to the material composition and the construction progress of the electrode. This enabled them to achieve a crack-free and delamination-free layer structure. It turned out, however, that with increasing overall height the dissipation of laser energy into the porous material composite becomes increasingly difficult to promote (Fig. 8). Future research work is to be devoted to finding a technical solution to this problem.



■ Fig. 6: Scanning electron microscope image of a thin, PAD-generated diffusion barrier layer of gadolinium-doped cerium oxide on a zirconium oxide substrate (left) and a barium cerate layer on a porous anode (right) (Images: Jörg Exner).

RECOMMENDED READING

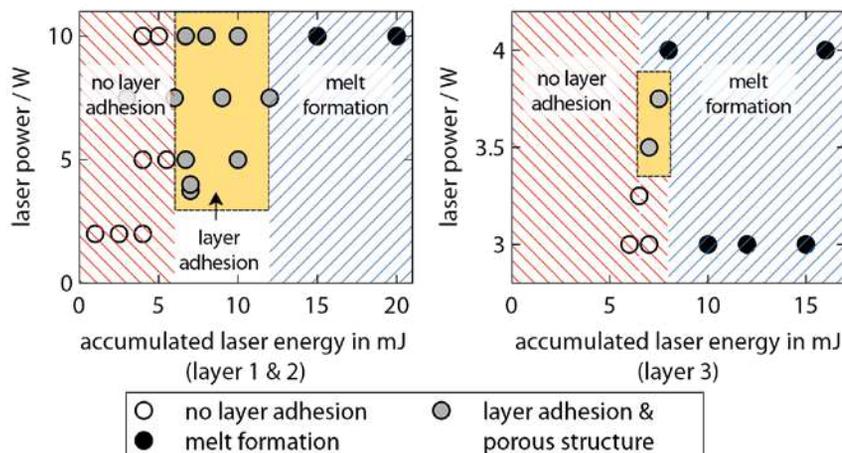
J. Exner, T. Nazarenius, J. Kita, R. Moos: Dense Y-doped ion conducting perovskite films of BaZrO₃, BaSnO₃, and BaCeO₃ for SOFC applications produced by powder aerosol deposition at room temperature. *International Journal of Hydrogen Energy* (2020), 45, 10000-10016. DOI: 10.1016/j.ijhydene.2020.01.164.

J. Exner, J. Kita, R. Moos: In- and through-plane conductivity of 8YSZ films produced at room temperature by aerosol deposition. *Journal of Materials Science* (2019), 54, 13619-13634. DOI: 10.1007/s10853-019-03844-7.

J. Exner, H. Pöpke, F.-M. Fuchs, J. Kita, R. Moos: Annealing of Gadolinium-Doped Ceria (GDC) Films Produced by the Aerosol Deposition Method. *Materials* (2018), 11, 2072. DOI: 10.3390/ma11112072.

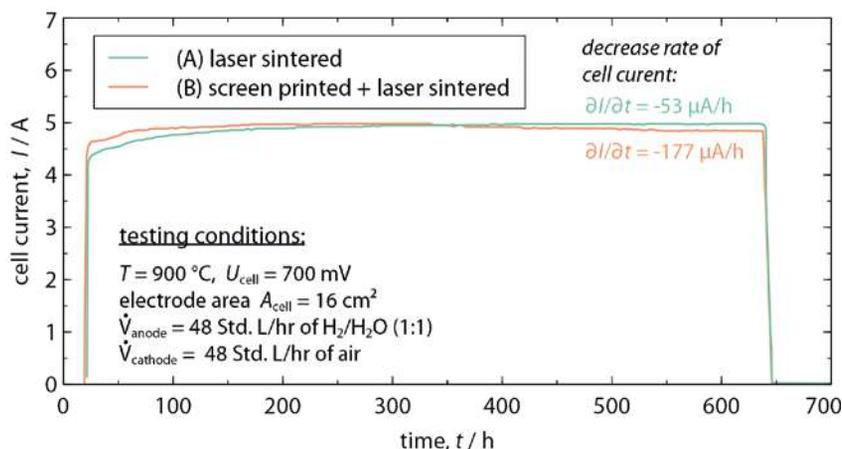
■ Fig. 8 (above): The ratio of laser power and accumulated laser energy at the focal point is critical for layer adhesion and the preservation of porosity. In the first layers, the process window (left) is still comparatively large, yet from the third layer on, the process window becomes significantly smaller (right) (Graphics: Andreas Rosin).

■ Fig. 9 (below): Test of SOFC full cells at 900° Celsius, each with a three-layer cathode: (A) completely laser-sintered, (B) combined screen-printed and laser-sintered. Display of the generated cell current over time. (Measurement: Kerajol GmbH, Dr. H. Pöpke) (Graphics: Andreas Rosin).



The laser-sintered SOFC cathode half cells were supplemented with screen-printed anodes to form complete cells on the premises of the industrial partner in the project, Kerajol GmbH in Eschenbach. These were then tested on the fuel cell measuring bench (Fig. 9). A comparison between two fuel cells proved to be quite enlightening. In one cell, the cathode was fully laser sintered out of layers of powder, while in the other cell, screen-printed cathode layers were sintered by laser. Both cells achieved 210 to 215 milliwatts per square centimeter at 700 millivolts cell voltage at a cell temperature of 900 degrees Celsius. And both cells showed a slight drop in performance during the test period of 600 hours. An increase in performance of these laser-sintered cells is likely to be linked to further optimization of porosity and laser irradiation. By comparison, commercial cells deliver 300 to 800 milliwatts per square centimeter under similar test conditions, depending on their design.

Laser sintering is ideal for the heat treatment of thin powder coatings. It could accelerate the production of solid electrolyte fuel cells and make the technology more commercially viable. It would be quite realistic to expect laser sintering to deliver cost and energy savings of up to 40 percent compared to the conventional sintering process in electric or gas furnaces, even at medium production volumes – i.e. in the order of several 10,000 SOFC cells per year.



- 1 M. Robinius et al.: Comparative Analysis of Infrastructures: Hydrogen Fueling and Electric Charging of Vehicles. Schriften des Forschungszentrums Jülich, Reihe Energie & Umwelt, 408. Jülich 2018; Z.P. Cano et al.: Batteries and fuel cells for emerging electric vehicle markets. Nature Energy (2018), 3, 279-289. DOI: 10.1038/s41560-018-0108-1.
- 2 H.R. Ellamla: Current status of fuel cell based combined heat and power systems for residential sector. Journal of Power Sources (2015), 293, 312-328. DOI: 10.1016/j.jpowsour.2015.05.050.
- 3 <https://forschungsstiftung.de/Projekte/Details/ForOxiE-Oxidationsstabile-und-katalytisch-aktive-Werkstoffe-fuer-atmende-thermo-elektrochemische-Energiesysteme.html>
- 4 Since 2019, the research group, renamed “Chair of Electrochemical Process Engineering”, has been chaired by Prof. Dr.-Ing. Christina Roth.
- 5 This success is underlined by the extraordinarily positive report on the evaluation of the research network.
- 6 Cf. the article by Prof. Dr.-Ing. Christina Roth in this SPEKTRUM issue, 32-37.
- 7 A. Albarbar, M. Alrweq: Proton Exchange Membrane Fuel Cells. Design, Modelling and Performance Assessment Techniques. Cham 2018; R.E. Rosli et al.: A review of high-temperature proton exchange membrane fuel cell (HT-PEMFC) system. International Journal of Hydrogen Energy (2017), 42, 9293-9314. DOI: 10.1016/j.ijhydene.2016.06.211.
- 8 M. Emery et al.: The Development of New Membranes for Proton Exchange Membrane Fuel Cells. ECS Transactions. 212th ECS Meeting, Washington DC, 7.-12. Oct. 2007, 3-14.
- 9 J. Exner et al. (2020), see Recommended Reading.
- 10 J. Exner et al.: What Happens during Thermal Post-Treatment of Powder Aerosol Deposited Functional Ceramic Films? Explanations Based on an Experiment-Enhanced Literature Survey. Advanced Materials (2020), 32, 1908104. DOI: 10.1002/adma.201908104.
- 11 J. Exner et al. (2019) and (2018), see Recommended Reading.
- 12 In principle, the additive production of ceramic parts and components has so far proven to be very promising and offers advantages over classical ceramic manufacturing processes. See also Z. Chen et al.: 3D printing of ceramics: A review, Journal of the European Ceramic Society (2019), 39 (4), 661-687. DOI: 10.1016/j.jeurceramsoc.2018.11.013.
- 13 Cf. P. Heimerdinger: PFSA-Ionomer-Komposit-Membranen für Mitteltemperatur-Polymer-elektrolyt-Brennstoffzellen. Dissertation, University of Bayreuth 2020.

UTILIZATION FOR ENERGY

■ Christina Roth
Maximilian Kutter
Patrick Heimerdinger



The secret of the HT-PEM fuel cell

Phosphoric acid replaces water

■ Dr. Bruna Lobo, research associate at the Electrochemical Process Engineering research group, at a measurement set-up to evaluate the catalyst performance. The measurements can provide information about the poisoning effect of the platinum catalyst (Photos: Christian Wißler).

Fuel cells are not really that new. As early as 1838, the Swiss-German physicist Christian Friedrich Schönbein described the basic principle of "cold" combustion, which converts hydrogen and oxygen into water, thus reversing the principle of electrolysis – the splitting of water into hydrogen and oxygen. Following on from this, the Welsh lawyer and physicist Sir William Robert Grove developed a "gas battery" one year later, in which electric current was generated in this way.¹ So why is the fuel cell on everyone's lips again now, almost 200 years later? And what are the special advantages of the high-temperature polymer electrolyte membrane fuel cell (HT-PEMFC), as is currently being researched at the University of Bayreuth by the Electrochemical Process Engineering research group?

One clue is provided by the hydrogen strategy of the Federal Government, which was presented at the beginning of 2020.² The colourless and odourless gas has been earmarked to significantly help reduce climate-damaging CO₂ emissions in the industry and transport sectors. Hydrogen is thus a key element in the energy turnaround – provided it is produced by water electrolysis powered by renewable energy sources such as wind and sun. By means of efficient and decentralized storage, it can then be used as a "green" energy source and converted into electricity in fuel cells as needed.

Hydrogen-powered fuel cells are therefore a key technology for Germany's emission-free future.

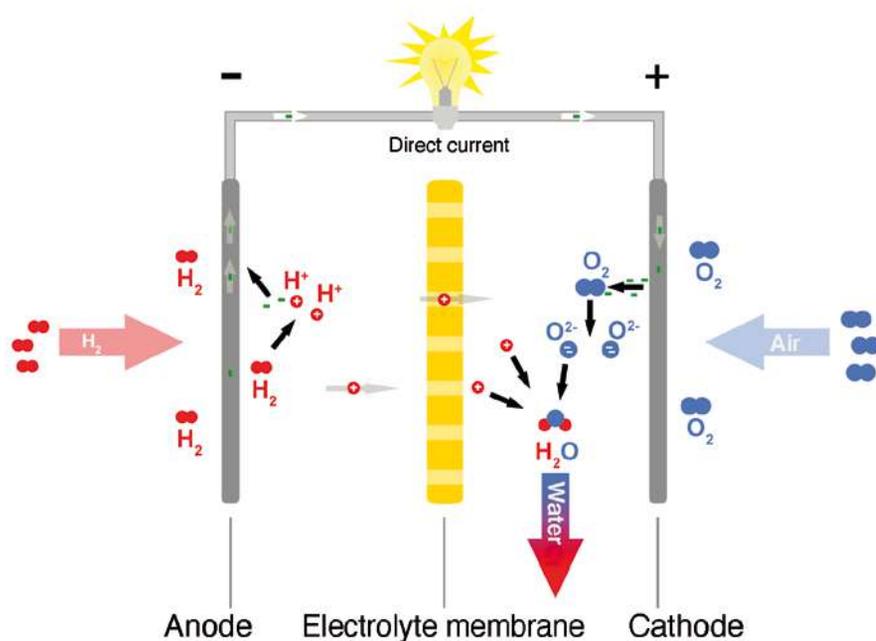
The working principle of the fuel cell

When hydrogen and oxygen combine to form water, chemical energy is released as an explosion, or as an "oxyhydrogen gas reaction" in this context. The chemical energy is lost unused – unless the two reactions are separated by a membrane, as happens in fuel cells. This converts the chemical energy into electrical energy that can be fed into the power grid. Another advantage of this process is that the reaction sequence can be controlled much more effectively.

The fuel cell contains two electrodes, and at the anode, hydrogen is oxidized into protons. The expensive precious metal platinum serves as an "accelerator" (catalyst) for this reaction. It is present in the form of nanoparticles which are supported on a carbon material. The extremely small size of these particles enables their particularly efficient use, and thus helps to reduce costs. The protons produced now migrate through the proton-conducting membrane to the cathode, where they combine with oxygen and electrons from the electrical circuit to form water. At this point, the membrane plays an important role in guiding the protons from the anode to the cathode as smoothly as possible.



■ Fig. 1: Sir William Robert Grove. At the Royal Institution of South Wales he conducted his first fuel cell experiments in 1839 (Portrait of Lock & Whitfield from the National Portrait Gallery in London, Photo: wikimedia commons / CC-PD-Mark).



■ Fig. 2: Operating principle of a fuel cell. Hydrogen is oxidized at the anode, while oxygen is reduced at the cathode. This produces water and electricity (Illustration: Christoph Lingg / wikimedia commons / public domain).

AUTHORS



■ Prof. Dr.-Ing. Christina Roth is the Chair of Electrochemical Process Engineering at the University of Bayreuth.



■ Maximilian Kutter M.Sc. is research associate at the Electrochemical Process Engineering research group.



■ Dr.-Ing. Patrick Heimerdinger was a research associate at the Electrochemical Process Engineering research group and the Keylab Glass Technology at the University of Bayreuth until June 2020. He is currently a project engineer at InVerTec – Institute for Innovative Process Engineering.

Phosphoric acid instead of water: A new generation of fuel cells

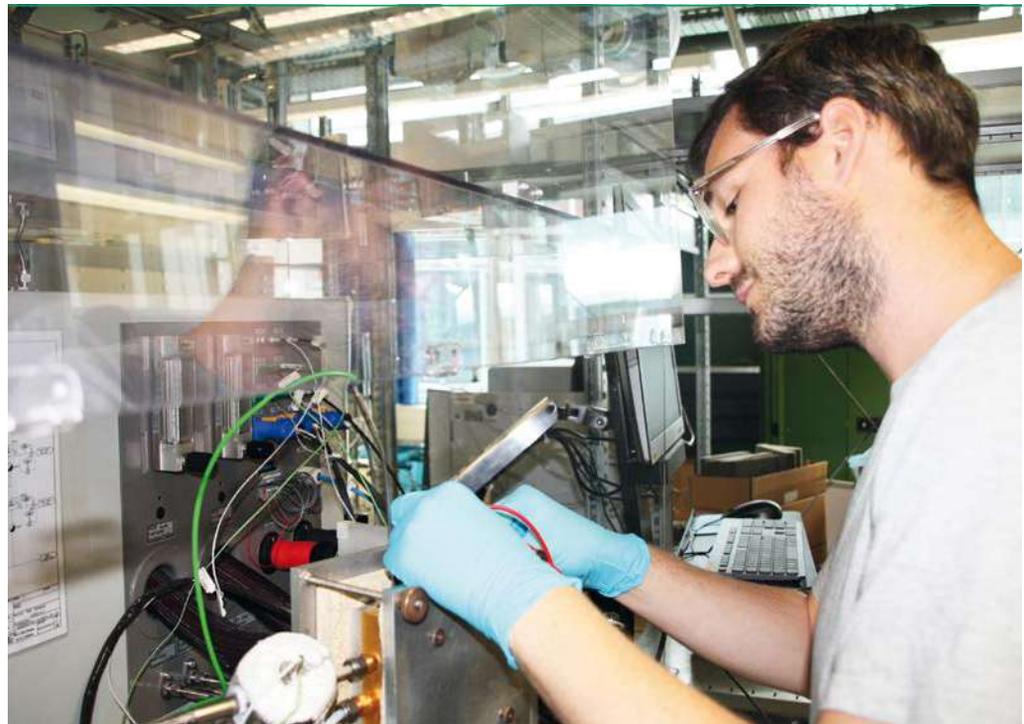
Conventional membranes only provide good conductivity if, as a result of water swelling of the material used, they contain water-filled channels in which the protons can easily move.³ The protons pass here from the anode to the cathode by being passed from one water molecule to the next. This mechanism, named after its discoverer Theodor von Grotthuß, can be imagined like people in a chain, passing filled buckets of water to their respective neighbours, always in the same direction. Yet since water boils at around 100 degrees Celsius, the operating temperature of the fuel cell must not exceed this temperature. For if the water were to evaporate, proton conduction in the channels would cease. This is precisely where the great advantage of the HT-PEM fuel cell comes into play. This new type of fuel cell uses a different membrane imbued with phosphoric acid, which is also a very good proton conductor, instead of water. Critically, phosphoric acid remains liquid even at 200 degrees Celsius, and is therefore far more versatile than water as a proton conductor.

But why is it so advantageous to operate a fuel cell at higher temperatures? There are various reasons

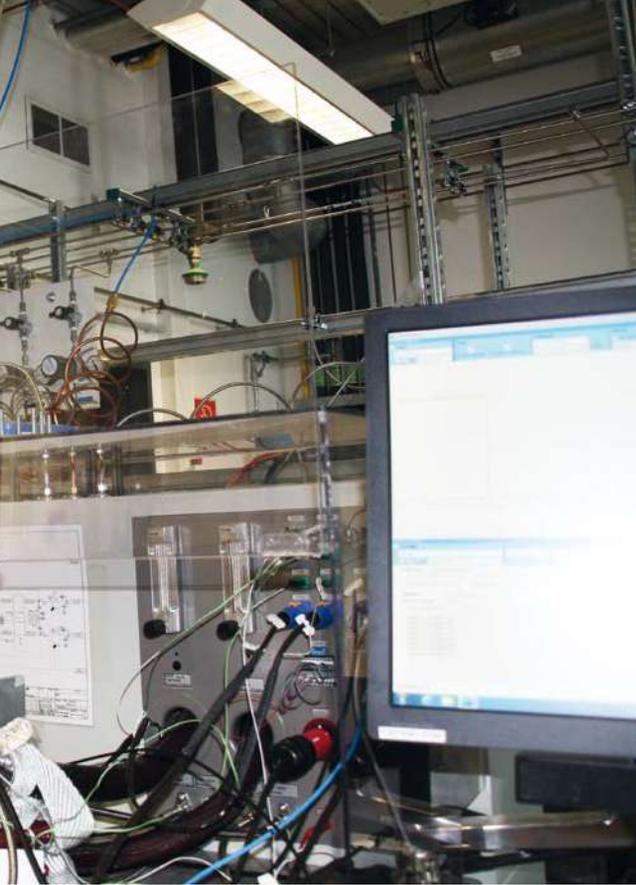


for this:

- At high temperatures, the fuel cell reacts much less sensitively to impurities in the fuel, which can arise in its production. For example, an HT-PEM fuel cell can tolerate several percent



■ Fig. 3 and 4 (Center above): Maximilian Kutter M.Sc. installing a single fuel cell in a fuel cell test bench. With this set-up, specific components such as modified electrodes can be tested on their influence in the fuel cell system (Photos: Christian Wißler).



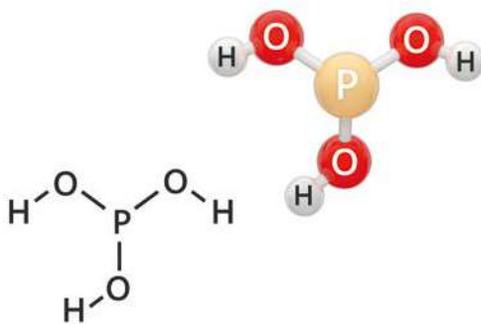
within the cell. At temperatures above 100 degrees Celsius, the water produced is gaseous and can be transported out of the fuel cell as steam much more easily than liquid water.⁴

New scientific challenges: Current research projects in Bayreuth

These are all convincing reasons for replacing the fuel cells commonly used to date with HT-PEM fuel cells. But why is research on such systems currently still being conducted at all instead of simply adapting them for commercial application? The reason is that it is phosphoric acid in particular that is used as a proton conductor instead of water. What makes HT-PEM fuel cells far superior to low-temperature cells poses its own, new, technical challenges. In fact, phosphoric acid is extremely acidic and therefore necessitates additional protective measures against corrosion. It is also distributed unevenly in the membrane and electrodes, so that proton conduction cannot take place over the entire surface. And because phosphoric acid is easily washed out of the cell by the water produced in the cell, less and less of this indispensable proton conductor remains available as the cell's operating time increases. Moreover, the longer the cell is in operation, the more the phosphoric acid decomposes. The resulting decomposition products bind to the platinum particles in the catalyst and thus make it inactive. Researchers call this "poisoning", because hydrogen and oxygen molecules no longer find free sites on the platinum particles of the anode or cathode, and cannot be converted to water and electricity.

carbon monoxide in the hydrogen. In contrast, the low-temperature variant with a water-filled membrane fails at as little as 0.0001 percent carbon monoxide in the hydrogen – in other words, when there is only one CO particle for every million hydrogen particles.

- Furthermore, the conversion of hydrogen and oxygen to water is faster at higher temperatures and therefore requires less catalyst material. Hence, the new HT-PEM fuel cells would be significantly cheaper to manufacture, since in use, catalysis requires much smaller quantities of expensive precious metal such as platinum.
- Moreover, a higher operating temperature also has a positive influence on water balance

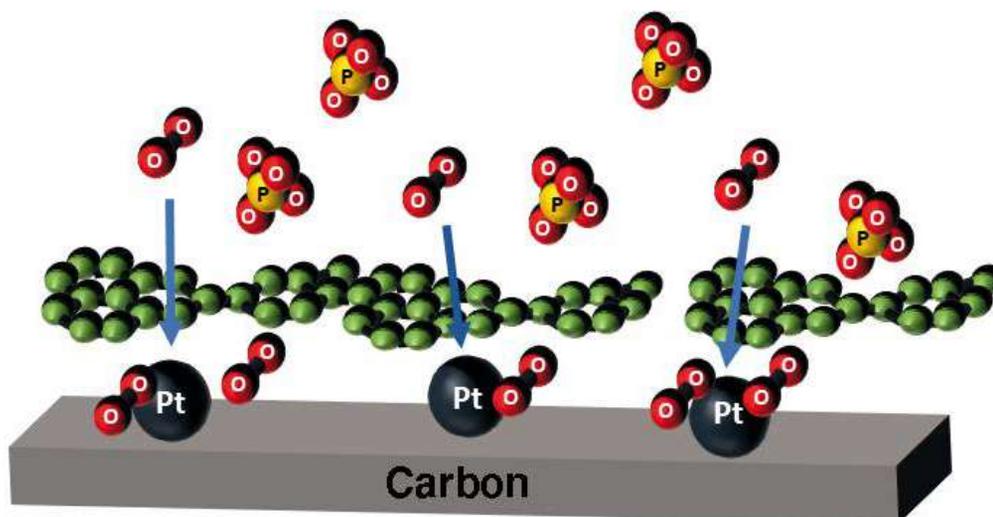


■ Fig. 5: Structure formula of phosphoric acid (sst).

"Hydrogen-powered fuel cells are therefore a key technology for Germany's emission-free future."

The Electrochemical Process Engineering research team led by Prof. Dr.-Ing. Christina Roth at the University of Bayreuth, together with external partners,⁵ is working on several projects to find a solution to these problems:

- In cooperation with a working group at Freie Universität Berlin, organic additives were developed to prevent or at least reduce the poisoning



■ Fig. 6: Large organic molecules (green) bind to the platinum particles (black) with their functional groups and block the decomposition products of the phosphoric acid (yellow-red). In contrast, oxygen molecules (red) continue to find their way to the platinum particles and can react unhindered (Illustration: Timon Günther).

of platinum particles by decomposition products of phosphoric acid.⁶ For this purpose, large organic molecules were provided with special functional groups that specifically bind to the surface of the platinum particles. Catalysts modified in this way show higher activity in the fuel cell. However, it is not yet clear exactly how this improvement will be achieved. It is an obvious, but not yet confirmed, assumption that the large organic molecules behave "blocked" and that the phosphoric acid blocks the way to the platinum particles, while, for example, the smaller oxygen molecules can get to free sites (Fig. 6).

■ Together with research partners at the University of Chemistry and Technology in Prague and at Helmholtz-Zentrum Berlin, the researchers are in-

vestigating in detail how phosphoric acid poisons the platinum surface. This requires synchrotron radiation, which is only available at a few large-scale research facilities, such as Deutsches Elektronen Synchrotron DESY in Hamburg. Due to its special properties, especially its high intensity, this radiation makes it possible to take a look inside the fuel cell in operation⁷ (Fig. 7). The measurement data obtained in this way contains information about which and how many molecules bind to the platinum particles and how the platinum particles change depending on the operation of the fuel cell. These findings will help to tailor large organic molecules which, on the one hand, specifically block phosphoric acid while, on the other hand, support the binding of oxygen molecules to the platinum particles.

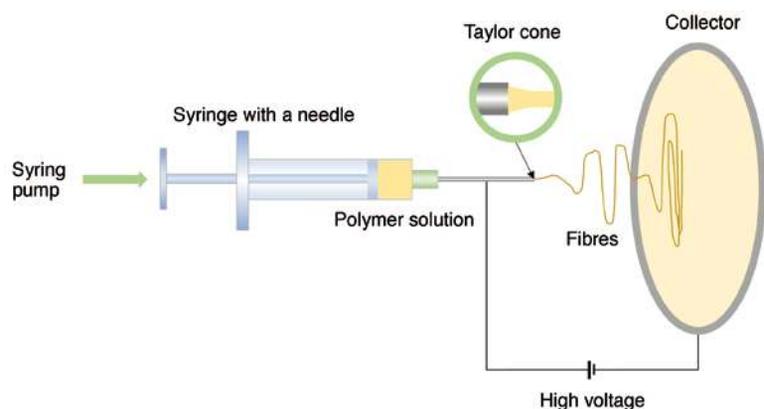
RECOMMENDED READING

Ö. Delikaya, M. Zeyat, D. Lentz, C. Roth: Organic Additives to Improve Catalyst Performance for High-Temperature Polymer Electrolyte Membrane Fuel Cells. *ChemElectroChem* (2019), Vol. 6, Issue 15, 3892-3900. DOI: 10.1002/celec.201900251.

Ö. Delikaya, N. Bevilacqua, L. Eifert, U. Kunz, R. Zeis, C. Roth: Porous electrospun carbon nanofibers network as an integrated electrode@gas diffusion layer for high temperature polymer electrolyte membrane fuel cells. *Electrochimica Acta* (2020), Vol. 345, 136192. DOI:10.1016/j.electacta.2020.136192.

■ Fig. 7: Dr. Ditty Dixon at Deutsches Elektronen-Synchrotron DESY in Hamburg preparing a measurement. High-intensity X-rays provide insights into the fuel cell during operation. (Photo: Heiner Müller-Elsner).

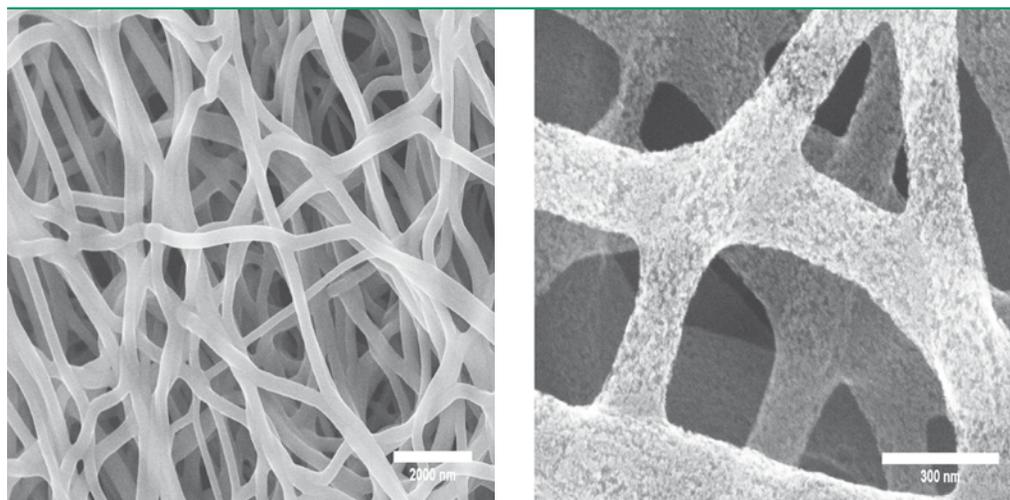




■ Meanwhile, a cooperation project with Helmholtz Institute Ulm is pursuing a completely different strategy. It aims to optimize the entire porous electrode and not just the catalyst. For this purpose, an electrospinning process is being developed in the Bayreuth laboratories in which a polymer thread is drawn from a needle tip by means of high voltage, and is swirled about to form a fibrous felt on a collector plate. Using a double needle and several polymers, fibres can be

produced which are hollow inside and have a porous shell. The intention is to fix molecules of phosphoric acid to the inside of these fibres by capillary forces, so that they remain inside the electrode (Fig. 8 and 9). This procedure would lead to a more uniform distribution of the proton-conducting phosphoric acid in the electrode. It is also likely that less phosphoric acid is transported out of the system by the water produced in the fuel cell.

■ Fig. 8: Principle sketch of the electrospinning process (left). Dr. Öznur Delikaya prepares a syringe of the polymer solution and places it in the holder (right) (Picture credits: Öznur Delikaya, published in her dissertation, FU Berlin).



■ Fig. 9: Electron microscopic images of the hollow-porous fibre felt produced by electrospinning, which is very promising material for the electrodes of phosphoric acid-based fuel cells. The picture on the right clearly shows the pores on the fibre surface (Picture left: Öznur Delikaya, Freie Universität Berlin; picture right: Roswitha Zeis, Helmholtz Institute Ulm).

- 1 Cf. G. Sandstede, E. J. Cairns, V. S. Bagotsky, K. Wiesener: History of low temperature fuel cells, in: W. Vielstich, A. Lamm, H.A. Gasteiger (eds.): Handbook of Fuel Cells. Weinheim 2010); see also www.fuelcelltoday.com/history
- 2 Published on the homepage of the Federal Ministry for Economic Affairs and Energy: www.bmwi.de/Redaktion/DE/Dossier/wasserstoff.html
- 3 H.-G. Haubold et al.: Nanostructure of Nafion: a SAXS study. *Electrochim. Acta* 46 (2001), 1559-1563. DOI: 10.1016/S0013-4686(00)00753-2.
- 4 A. Chandan, M. Hattenberger, A. El-kharouf, S. Du, A. Dhir, V. Self, B. G. Pollet, A. Ingram, W. Bujalski, High temperature (HT) polymer electrolyte membrane fuel cells – A review. *J. Power Sources* (2013), 231, 264-278. DOI: 10.1016/j.jpowsour.2012.11.126.
- 5 The working groups at the partner institutions are headed by Prof. Dr. Dieter Lentz (FU Berlin), Prof. Dr. Karel Bouzek (University of Chemistry and Technology, Prag), Prof. Dr. Marcus Bär (Helmholtz-Zentrum Berlin) und Dr. Roswitha Zeis (Helmholtz-Institut Ulm).
- 6 See recommended reading.
- 7 S. Kaserer, K. M. Caldwell, D. E. Ramaker, C. Roth: Analyzing the Influence of H_3PO_4 as Catalyst Poison in High Temperature PEM Fuel Cells Using in-operando X ray Absorption Spectroscopy. *J. Phys. Chem. C* 117 (2013), 6210–6217. DOI: 10.1021/jp311924q.
- 8 See recommended reading.

■ Marius Gernhard

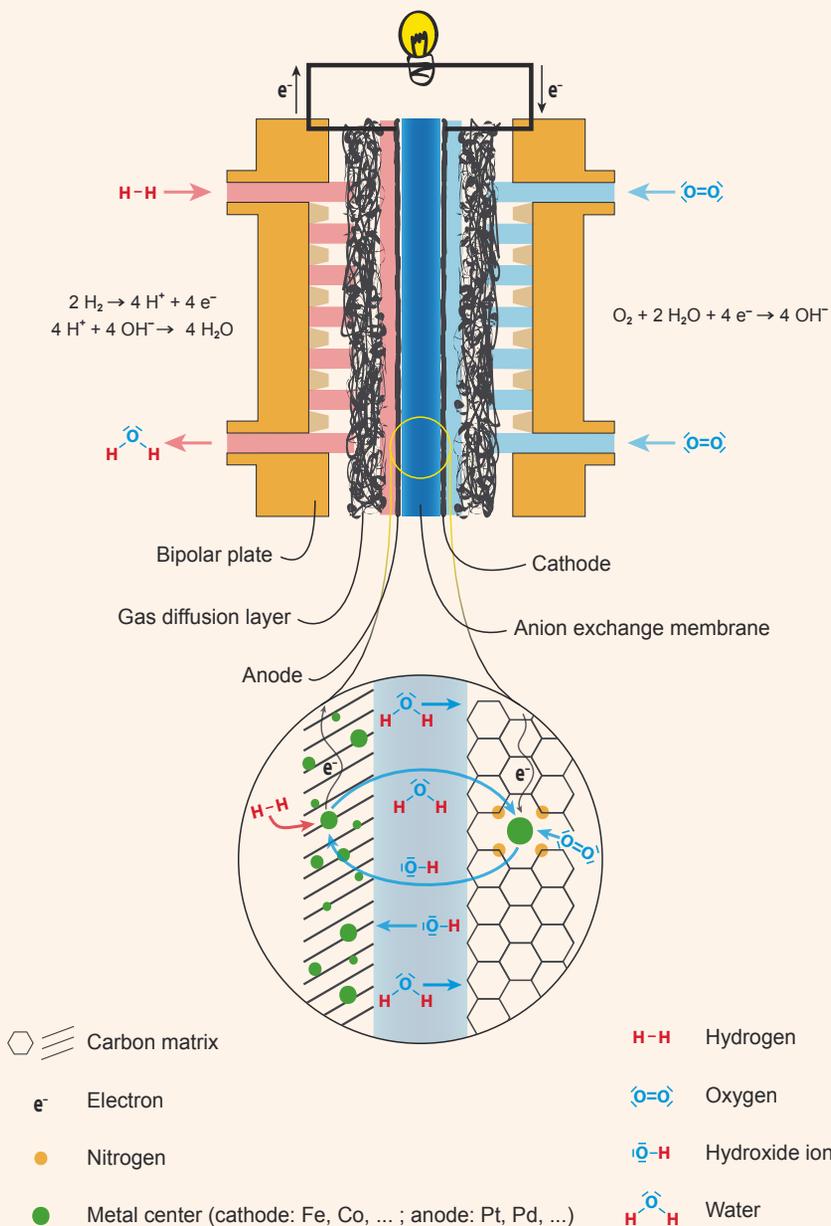
Far from old hat:

The history of the alkaline fuel cell (AFC) dates back to the beginning of the 20th century. This makes it one of the oldest types of fuel cell, which, as a result of continuous development, has remained technologically relevant to this day. Indeed, AFCs played a significant role in the development of manned space travel, for example in the U.S. Apollo programme.

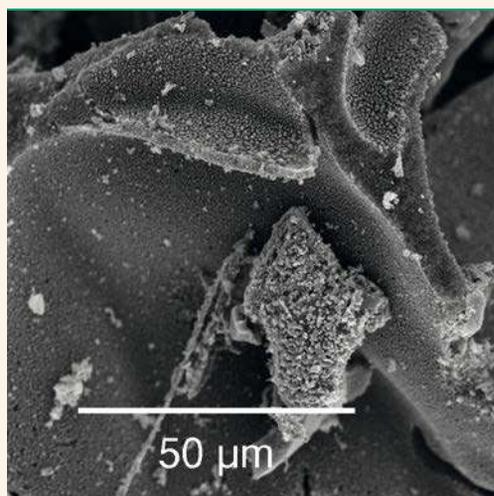
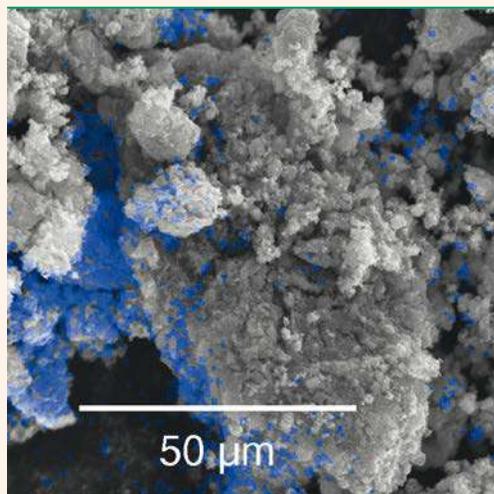
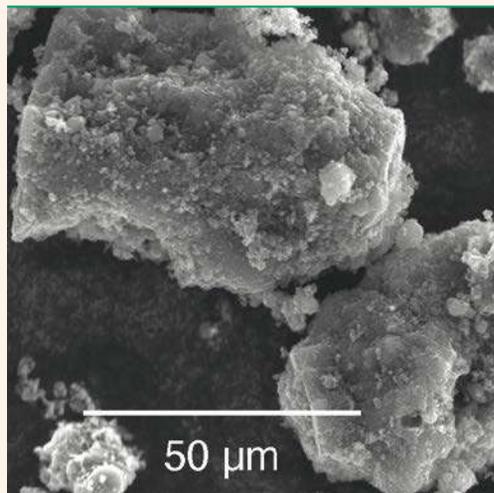
The name is derived from the aqueous, strongly alkaline potassium hydroxide solution used as the electrolyte in these cells. At the anode of an AFC, hydrogen is oxidized to H^+ ions, while oxygen is reduced at the cathode. The OH^- ions released in the process are transported to the anode. This is where the chemical reaction of the ions takes place. Water is formed, which is removed from the fuel cell. Compared with proton exchange membrane fuel cells (PEMFCs) and their spin-offs, AFCs have the disadvantage of limited service life due to their alkaline electrolyte being highly corrosive towards the structure of the fuel cell itself. In addition, an AFC may not simply be operated with carbon dioxide containing gases, as it would severely impair the functionality of the electrolyte. However, providing the cell with purified gases makes it considerably more expensive to operate. For this reason, there has been increased research interest in so-called anion exchange membrane fuel cells (AEMFCs) since the beginning of the 2000s. AEMFCs work on the same principle as AFCs, but use a durable OH^- -conducting polymer membrane which does not corrode the fuel cell structure.

An important advantage of anion exchange fuel cells (both AFCs and AEMFCs) is that non-precious metal catalysts can be used for the reduction of oxygen on the cathode side. Precious metals such as platinum, palladium, ruthenium, and iridium are highly active catalysts, but they are rare and expensive. Moreover, their extraction in countries of the Global South often takes place under unacceptable social and ecological conditions. Metals such as manganese, iron, and nickel, on the other hand, are much more abundant in the earth's crust. Consequently, scientists began investigating how they might be used in catalyst technology as far back as the 1960s. Since 2009, a promising group of catalysts of a specific molecular structure have gained scientific attention. In particular, a centre of metal (M), for example iron, is surrounded by four nitrogen atoms (N), which in turn are embedded in a carbon matrix (C). These structures are also called MNC catalysts. In proton exchange fuel cells, the acidic conditions dictate the low stability of any conventional catalysts. The metal is dissolved out and the nitrogen is attacked by the acid or by hydrogen peroxide. In fuel cells with an anion-conducting

■ Fig. 1: Schematic representation of the functioning of alkaline fuel cells (Illustration: Marius Gernhard).



Alkaline fuel cells



electrolyte, i.e. AFCs or AEMFCs, these problems do not occur. A research project of the Electrochemical Process Engineering research group at the University of Bayreuth is therefore aimed at investigating MNC catalysts more closely, and optimizing them specifically for use in AEMFCs. This research is funded by the German Research Foundation (DFG) within the framework of the "Fluorine-specific interactions" Collaborative Research Centre. In parallel, ways are being sought to mitigate the aforementioned problems occurring in fuel cells in an acidic environment, meaning that the MNC catalysts could in principle even function in these cells.

Of particular interest in this context are metal organic frameworks (MOFs). These are complex structures in which organic molecules (linkers) and metals are cross-linked. They are particularly well suited as precursors for catalyst synthesis thanks to the many small channels in their interior, which lend them especially high porosity. After all, in principle, the larger the surface of a catalyst, the higher its activity. Indeed, due to their porosity, MOFs have a surface area of up to 3,000 square meters per gram. Controlled heating of the MOFs to temperatures around 900 degrees Celsius creates the carbon matrix in which the catalytic centres are embedded. The resulting material can then be used as part of the electrode in fuel cells – in the case of oxygen reduction, in the cathode. One particular type of MOF has now been shown to hold great promise: zeolitic imidazolate framework compounds (ZIFs). These are not only highly porous, but also reliably bind a large number of different metals which are potentially suitable as catalytic centres. Using a model system, the Bayreuth scientists have succeeded in placing cobalt atoms in zinc-containing ZIFs – a process known in research as doping. These cobalt-doped MOFs formed the basis for a functioning catalyst (Fig. 1 to 3). The next step will be to incorporate other metals, for example iron.

A further important goal of the research work is to increase the stability of the catalytic centres by using fluorine-containing linkers, thus increasing the service life of non-precious metal fuel cells. In view of a burgeoning hydrogen economy, this would be a necessary step in attaining the *Energie-wende*.

AUTHOR



■ Marius Gernhard M.Sc. is a research associate and doctoral candidate at the Electrochemical Process Engineering research group of the University of Bayreuth.

■ Fig. 2-4: Scanning electron microscope images of temperature-treated MOFs. Left: only Zink (ZIF-8), right: only Cobalt (ZIF-67); centre: Cobalt-doped ZIF-8 (marked blue: Cobalt). (Images: Marius Gernhard).

UTILIZATION FOR ENERGY



■ Carolin Sitzmann
Walter Krenkel

Material development, design, viability

The KOSOS project optimizes stack technology

■ Dipl.-Ing. Tom Liensdorf, research associate at Ceramic Materials Engineering at the University of Bayreuth, conducting a ring on ring test (Equipment: Inspekt table blue, Hegewald & Peschke Meß- und Prüftechnik GmbH) (Photo: Christian Wißler).

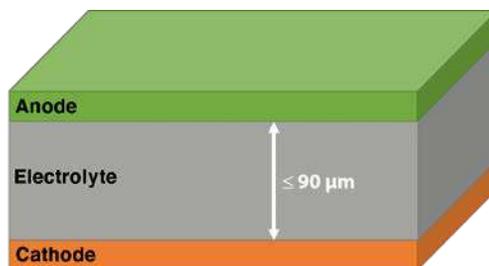
In order for hydrogen technology to establish itself permanently on the energy market, innovations in the field of fuel cells must combine technical advancements with tangible economic advantages. This is particularly true for stack technology in the field of solid oxide fuel cells (*Solid Oxide Fuel Cell*, SOFC), which are being researched extensively at the University of Bayreuth, especially from a materials science perspective. SOFC stacks are fuel cells connected in series, which in this project have been purposed for energy generation without being connected to the power grid (*offgrid*).

"Membrane electrode assemblies out of solid oxide fuel cell stacks that were in operation for tens of thousands of hours and suddenly failed are subjected to a meticulous post-mortem."

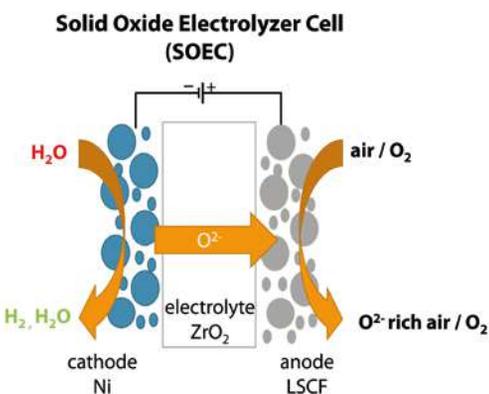
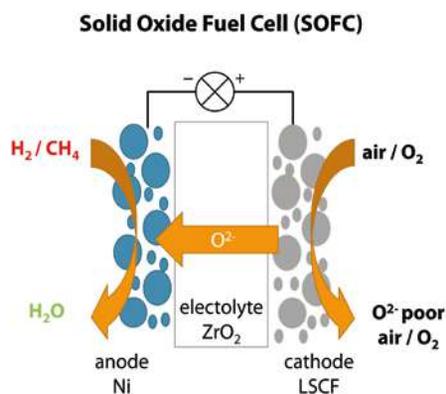
This is where the joint project "Cost-optimized stack and improved off-grid system (KOSOS)" comes in, funded by the Federal Ministry of Economics and Energy (BMWi) as part of the Federal Government's Sixth Energy Research Programme. It began its three year run time in 2018, and is being coordinated by Ceramic Materials Engineering at the University of Bayreuth. Project partners are the German Aerospace Center (DLR) in Stuttgart and Karlsruhe Institute of Technology (KIT), as well as the companies Kerafol GmbH (Eschenbach) and Sunfire GmbH in Dresden. The members of the joint project are working together to significantly increase

the market opportunities for solid oxide fuel cells and especially for stack technology. To this end, the thermomechanical and microstructural properties of SOFCs are being investigated in Bayreuth.

The research work within this project focuses on electrolyte supported solid oxide fuel cells (Fig. 1). These differ from anode supported SOFCs in that the electrolyte is the layer that supports the whole cell and lends it rigidity. An electrolyte thickness of 90 micrometres is the current state of the art. Yttria-stabilized zirconia (YSZ) is used as the electrolyte material. This material is characterized by good conductivity for oxygen ions and is also gas-tight. In a SOFC, the anode is the electrode to which hydrogen or another fuel gas is applied during fuel cell operation. It is composed of porous nickel oxide. The oxygen electrode in contact with the air acts as the cathode. It is also porous, but is made of lanthanum-strontium-cobalt-ferrite.



Importantly, solid oxide fuel cells can also be used in electrolysis mode, i.e. for hydrogen generation (Fig. 2). In this case, the overall reaction¹ is reversed: Water, air, and energy, preferably from renewable energy sources, are used to generate hydrogen or – with the



AUTHORS



■ Dr.-Ing. Carolin Sitzmann is Academic Councillor at Ceramic Materials Engineering at the University of Bayreuth.



■ Prof. Dr.-Ing. Walter Krenkel is the Chair of Ceramic Materials Engineering at the University of Bayreuth.

■ Fig. 1: Layout of an electrolyte supported solid oxide fuel cell (not to scale) (Illustration: Tom Liensdorf).

■ Fig. 2: Function of fuel cell or electrolysis operation (Illustrations: Carolin Sitzmann).

¹ Cf. the article by Dr. Andreas Rosin et al. on current research on solid electrolyte fuel cells (SOFCs) in this issue of SPEKTRUM, 26-31.



■ Fig. 3: Dipl.-Ing. Tom Liensdorf at work with a scanning electron microscope (Photo: Christian Wiffler).

and extending to the overall design, including the necessary peripherals. An absolute imperative here is the reduction of electrolyte thickness. The aim is to conserve resources while simultaneously reducing the electrochemical resistance of the electrolyte. However, a reduction in electrolyte thickness is inevitably accompanied by increased mechanical stress on the MEA. For this reason, it is particularly important to know the mechanical properties of the individual components. For the demanding material tests of this kind, Ceramic Materials Engineering at the University of Bayreuth has some extremely modern equipment at its disposal.

The great challenge in mechanical testing is determining test methods that can be applied to these particular electrolytes, which are only 90 micrometres thick (target values < 60 micrometres). The three-point and four-point bending tests often used in the ceramics sector are not an option in this case, because the ceramic foils display too much deflection and the test geometries necessary cannot be carried over (Fig. 4). For this reason, the ring on ring test (RoR) was selected, which has proven to be effective for thicker foils and types of glass (Fig. 5). In this test method, the circular sample is positioned on a support ring. From above, the smaller diameter load ring is moved coaxially in the direction of the

addition of carbon dioxide – a synthesis gas. Thus, electrolysis can be used to store excess regenerative energy at times of peak supply.

Supported by:



Federal Ministry for Economic Affairs and Energy

on the basis of a decision by the German Bundestag

Material development

The KOSOS project deals with three major areas. The first focus is the material development for solid oxide fuel cells. This involves, for example, developing and testing potential new materials for electrolytes based on new powders. With this goal in mind, Ceramic Materials Engineering in Bayreuth first determines the distribution of particle sizes in a given powder. The size of the individual powder particles, their morphology, and the phase composition of the powder are all thoroughly investigated. On the basis of the knowledge gained, project partner Kerafol produces a ceramic foil out of the respective powder for later use as an electrolyte. The working group in Bayreuth then tests its mechanical and microstructural properties. After the foil has been printed with electrodes, the resulting membrane electrode assemblies (MEAs) are again subjected to mechanical testing.



RECOMMENDED LINK

The KOSOS project:
www.cme-keramik.uni-bayreuth.de/de/forschung/projekte/KOSOS/



■ Fig. 4 (right column above): Four-point flexural test on a ceramic matrix composite (Photo: Tom Liensdorf).

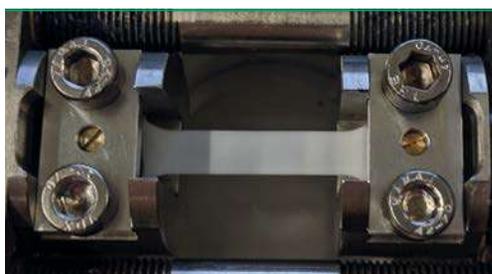
■ Fig. 5 (right column below): Ring on ring test of an MEA sample (Photo: Tom Liensdorf).

Design and materials testing

Meanwhile, the second focus is all about the design of the fuel cell stack itself – starting with the MEAs,

support ring. This deforms the specimen and induces a multi-axially stressed state it cannot withstand for long. The breaking of the sample provides important information regarding the load capacity of the material (Fig. 6).

Tensile tests are another important stage in the series of material tests (Fig. 7). They are not usually used for monolithic ceramics because these are very brittle. In the case of ceramic foils used as an electrolyte, however, this does become possible because they are so thin. However, the edges of the tensile specimens must be ground beforehand to prevent



premature failure due to edge effects. Using these two methods – both the ring on ring test and the tensile test – a strength of more than 1,000 megapascals was determined for the yttria-stabilized zirconia. This value corresponds to the strength of monolithic zirconia. With the help of a high-speed camera (127,500 fps) provided by the Department of Sport Science of the University of Bayreuth, the breaking of the electrolyte sample could even be filmed.

Real-world deployment of fuel cells

The third focus of the KOSOS project involves the Bayreuth researchers characterizing SOFC cells already in operation. Membrane electrode assemblies made of fuel cell stacks that were in operation for tens of thousands of hours and suddenly failed are subjected to a meticulous post-mortem. Based on this "operating history" of fuel cells already in use, it is possible to verify material fatigue specifications derived in the laboratory in studies using new fuel cells. Furthermore, the laboratory characterizes the material changes that occur during continuous operation of the cells at 850 degrees Celsius.

Cost reduction and improvement in durability

Thanks to the material tests carried out in Bayreuth, and the measures developed as a result, the research team was able to radically improve their system of solid fuel cells even before the end of the KOSOS project. In fact, it was possible to reduce stack costs to less than 1,500 €/kW (in 2017 3,500 €/kW). The stack's resistance to wear and fatigue has also been significantly improved. In the remaining project period until 2021 further long-run test units are to be analysed. Of particular interest are the mechanical properties of the stacks at an operating temperature of about 850 degrees Celsius, and also the correlations between microstructure, mechanical strength, and electrochemical properties.

With its research work in this field, the University of Bayreuth is helping to make solid oxide fuel cells an increasingly attractive energy technology from both a technical and economic point of view, expecting it to play an important role in the sustainable energy economy of the future.



■ Fig. 6: Failed electrolyte sample made of ZrO_2 (\varnothing 24 mm) (Photo: Tom Liensdorf).

■ Fig. 7 (left column): Zirconia sample held in place for tensile testing (Photo: Tom Liensdorf).

RECOMMENDED READING

Carolin Sitzmann et al.: Mechanische Charakterisierung von Festoxid-Brennstoffzellen. *Keramische Zeitschrift* (2020), 72(2), 48-53. DOI: 10.1007/s42410-020-0122-3.

■ Fig. 8: Ilaria Bombarda M.Sc., research associate at Ceramic Materials Engineering at the University of Bayreuth, studies the destroyed electrolyte sample (Photo: Christian Wißler).

STORAGE MATERIALS

■ Volker Altstädt
Florian Schönl
Fabian Hübner

From space travel to everyday transport

Hydrogen as a fuel for new
energy systems



■ Model of the European Ariane 6 launch vehicle on the grounds of the 2016 ILA International Aerospace Exhibition in Berlin. One special feature of the two-stage rocket are its two engines which both burn cryogenic water and oxygen (Photo: Sergey Kohl / shutterstock.com).

Small Picture: 12-cylinder hydrogen combustion engine of the BMW Hydrogen 7 (Photo: Claus Ableiter / wikimedia commons / GFDL).

Over and again, developing, innovative drive concepts in the transport sector spark debate in politics and the media as soon as they arise. Recently, the electric automobile has moved into the limelight. Initially, Germany opted for battery-powered individual transport in order to meet the political and social requirements for climate-neutral mobility. But in the meantime, it has become clear that this orientation towards e-mobility entails certain problems. Currently, these problems above all involve the storage of the large amounts of energy required to ensure sufficient range without long charging times. An additional obstacle is the permanent transport of very heavy battery cell systems, which drastically increase the unladen weight of cars.

Fuel cells: Towards sustainable transport

Well-known technologies from other industrial sectors have often served as a model for the development of energy-efficient automotive drives. A look at the manned and unmanned space industry, which is currently making the headlines again, reminds us that rocket engines driven by liquid hydrogen and liquid oxygen have long been used to generate thrust, and meanwhile other low-molecular fuels with outstanding energy densities are also in use. These examples are all based on the thermodynamic principle that energy is released when molecules are split under defined conditions. A controlled explosion takes place, just like in a conventional petrol or diesel engine. With regard to the innovative, onward development of the automotive industry, one requirement has come to the fore. Like in aerospace, lightweight construction concepts must be developed which make it possible to store more fuel and thus increase the range of vehicles. This is precisely where a new and promising approach is demonstrating great potential: In the widespread application of hydrogen gas as a hybrid drive technology for automobiles. Fuel cells, in fact, look set to become the door opener for the eco-efficient electrification of the transport system.

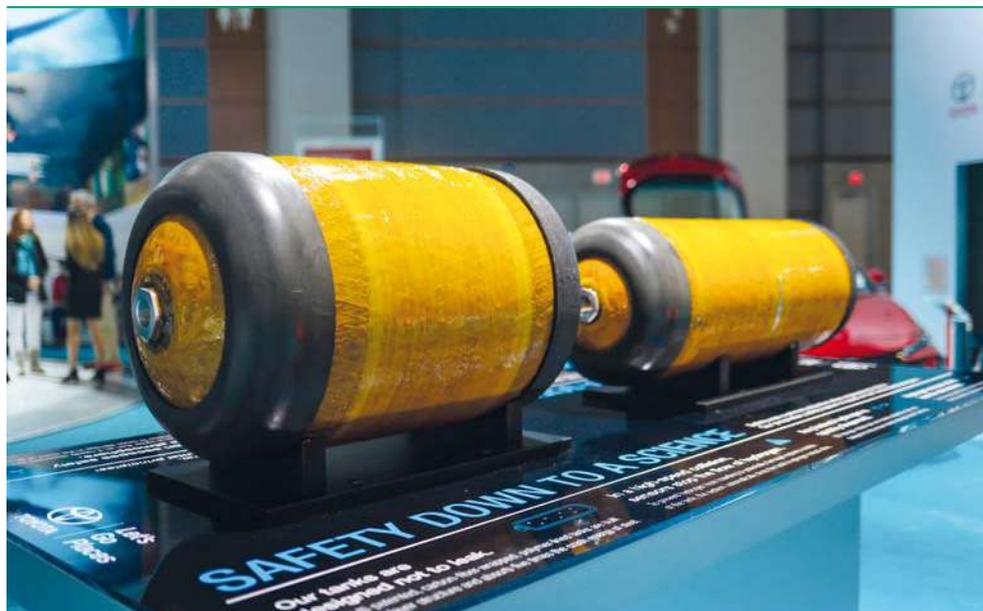
In a conventional combustion engine, carbon dioxide (CO₂), nitrogen oxides (NO_x), and soot particles are released as ecologically detrimental waste products. The situation is completely different with the fuel cell, which generates electrical energy through the chemical reaction of hydrogen and oxygen, and converts it into kinetic energy in the car. This produces water vapor, which in turn can be used for

sustainable energy generation. In comparison with electric cars that are exclusively battery-operated, fuel cells have one major advantage: It is not necessary to charge-up and store electrical energy before setting off. Instead, the electrical energy required for propulsion is continuously generated by the operation of the cells. A particular advantage of this technology is the fact that – in relation to mileage – only half as much carbon is emitted as with a battery drive. In fact, for batteries to achieve a similarly long range as a combustion engine, a great deal of energy and resources are consumed with the state of battery technology as it currently stands. Fuel cells, on the other hand, require only small battery cells that are fed and recharged during operation.

"A decisive factor in the reduction of weight and costs that was achieved along the way was the switch from metallic materials to ultra-modern plastics."

However, the production of hydrogen also needs to be carefully illuminated before its eco-efficiency can be assessed. As far as the origin of the gas is concerned, it is not only referred to as "green" hydrogen, but it is also referred to as "grey", "blue" or "turquoise" in other cases. "Green", purely CO₂-neutral production can only take place during electrolysis, i. e. the splitting of water using renewable energies. "Gray" hydrogen, on the other hand, is produced during the extraction from a natural gas mixture via the steam

■ Fig. 1: Presentation of hydrogen tanks at the Washington Auto Show in January 2018 (Photo: Nicole Glass Photography / shutterstock.com).



forming route. Significant amounts of CO₂ are released, which would have a negative impact on the climate due to the large quantities of hydrogen required in the future. If the climate-damaging greenhouse gas CO₂ is previously separated and stored, it is called "blue" hydrogen. Finally, the "turquoise" hydrogen is produced during the thermal fission of methane (CH₄). This requires large amounts of thermal energy. However, the process can be carried out with the help of carbon in solid form as an energy carrier, which is released during fission. Therefore, this process cannot be described as climate-neutral, but as CO₂-neutral.

"Type I pressure vessels" as they were called in the early days of fuel cell technology. Type II pressure vessels were soon developed, consisting of metal and partially wrapped, fibre-reinforced plastics. Glass fibre reinforced plastics (GRP) were used, for example, to provide particularly highly stressed areas of the tanks with greater strength. This resulted in a significant reduction in the tank/fuel weight ratio. In the course of the further development of this technology, the metal content was further reduced. The winding process, which ensures a rotationally symmetrical tank design, became the primary manufacturing process for the fibre plastic composite tanks.

Serial versions of this FCEV (*fuel cell electric vehicle*) drive are currently already being used on buses, trains, and ships with great success. However, before vehicles equipped with this technology can be produced in large numbers, extensive research work is still required. With regard to the generation, storage, and use of energy on the basis of hydrogen, many questions still need to be resolved in order to be able to use fuel technologies efficiently in the everyday operation of vehicles. Although hydrogen combustion engines in luxury concept cars – such as BMW's Hydrogen 7 Series – were already validated as technically viable many years ago, this technology has not been used on a large scale. On the one hand, the necessary long-term experience is lacking, but on the other, there is also a technical obstacle. Because hydrogen as a low-molecular fuel evaporates very quickly, it must be stored in very heavy steel tanks with thick walls. This is why the first fuel cell systems in automobiles were so heavy, and they consumed such large amounts of energy during operation.

The next step in development was the Type III pressure vessels. Here, only the metal inner shell of the tank, the so-called "liner", was wrapped with a fibre-plastic composite. Due to this reinforcing material, the liner was left to fulfil only the task of ensuring the tightness of the system. In the period that followed, the trend from metal-based to plastic-based liners continued. In the Type IV systems, which are today's state-of-the-art, polyethylene, for example, is the main component of the liner. This reduces the weight even further, and results in additional cost savings.

The most recent development is the type V pressure vessel, which does not require a liner at all. New types of leakproof coatings made of plastic or metal, such as copper, enable a further reduction in weight and shorten the process of energy generation. This technology therefore offers realistic opportunities to develop large market share for hydrogen-powered automobiles.



■ Fig. 2: For cryogenic tensile tests of high-strength fibre-plastic composites such as those used for hydrogen tanks, machine forces of more than five tonnes at temperatures of about minus 200 degrees Celsius are required (Photo: Christian Wißler).

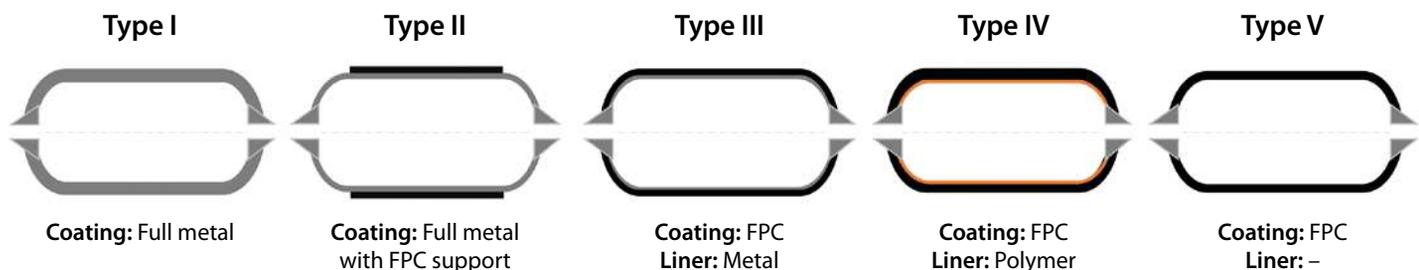
Optimization of hydrogen pressure vessels

With the aim of increasing the economic efficiency of fuel cell systems, intensive research has been carried out in recent years to find alternatives to the heavy

Space travel as role model

The journey from the first Type I pressure vessels to the new Type IV and Type V tank systems involved a great deal of research and empirical testing. A decisive factor in the reduction of weight and costs that was achieved along the way was the switch from

■ Fig. 3: Overview of Type I to Type V hydrogen pressure tanks (Diagram: Fabian Hübner).



metallic materials to ultra-modern plastics reinforced by carbon fibre, which gave the tank systems high strength for operating pressures above 700 bar. While the steel used for the first tank systems had a density of 7.87 grams per cubic centimetre, the ultra-light carbon fibre reinforced plastics used today for Type IV and Type V tank systems have a density below 1.6 grams per cubic centimetre. At the same time, the new hydrogen tanks in which these plastics are used are in no way inferior to the old steel tanks in terms of load capacity. On the contrary, current research and development work is aimed at further increasing this load-bearing capacity. The focus here is on pressure vessels that can withstand high burst pressures of up to 1,100 bar, while representing a component that can be manufactured as light, energy-efficient, and cost-effective as possible.

Just like hydrogen as an energy source, this lightweight construction system is also derived from space technology. This is because rockets and satellites have always had to be loaded with the greatest possible payload. With this goal in mind, innovations in material science have managed to reduce the dead weight of spacecraft even further in recent years.

Prospects

In Germany, at present, political efforts are in full swing to pave the way for fuel cell technology to have a good chance of establishing itself on the market. For example, the Free State of Bavaria is planning to build 100 hydrogen filling stations in order to create the necessary infrastructure for unchecked, sustainable driving. The motto of the future is obviously meant to remain what it is today: Free movement for free citizens.

The research work at the Polymer Engineering research group at the University of Bayreuth is specifically addressing these developments. Focal points are new materials and manufacturing processes, the structural design of hydrogen tanks, and comprehensive material testing. Close cooperation with industrial partners as well as with research institutes in the field of tape and fibre processing has resulted in innovations that will further advance the use of liquid hydrogen in transportation.

Fibre-plastic composites for the storage of liquid drive media

Since 2009, the Polymer Engineering research group at the University of Bayreuth has been engaged in the development, testing, functionalization, and design of fibre composite tank systems for aerospace applications. The special purpose of the pressure tanks is mainly the compact storage of propulsion media such as liquid hydrogen (LH₂) or liquid oxygen (LO_x) – especially under cryogenic conditions at close to absolute zero. Research in Bayreuth is focused on the optimization of Type IV and Type V pressure tanks.



As part of this research work, new fibre-plastic composites are developed from duromers, such as epoxy resins, and from carbon and glass fibres, which are tailored to specific applications. These materials are tested at storage temperatures relevant to practical applications to determine whether their properties and behaviour comply with applicable industry standards (DIN/ISO). In the conceptual design of these fibre composite tank systems, two aspects are of particular importance:

- the outgassing of the fuels, which is to be prevented by means of barrier coatings
- the behaviour of the materials at very low temperatures, below minus 150 degrees Celsius

Moreover, these fibre composite materials must be able to be used for the production of components without necessitating great technical and financial expenditure. This is where innovative material concepts and new economical manufacturing processes will make their mark.

■ Fig. 4: Cryogenic investigations of a fibre-plastic composite (Photo: Christian Wißler).

AUTHORS



■ Prof. Dr.-Ing. Volker Altstädt is the Chair of Polymer Engineering at the University of Bayreuth.

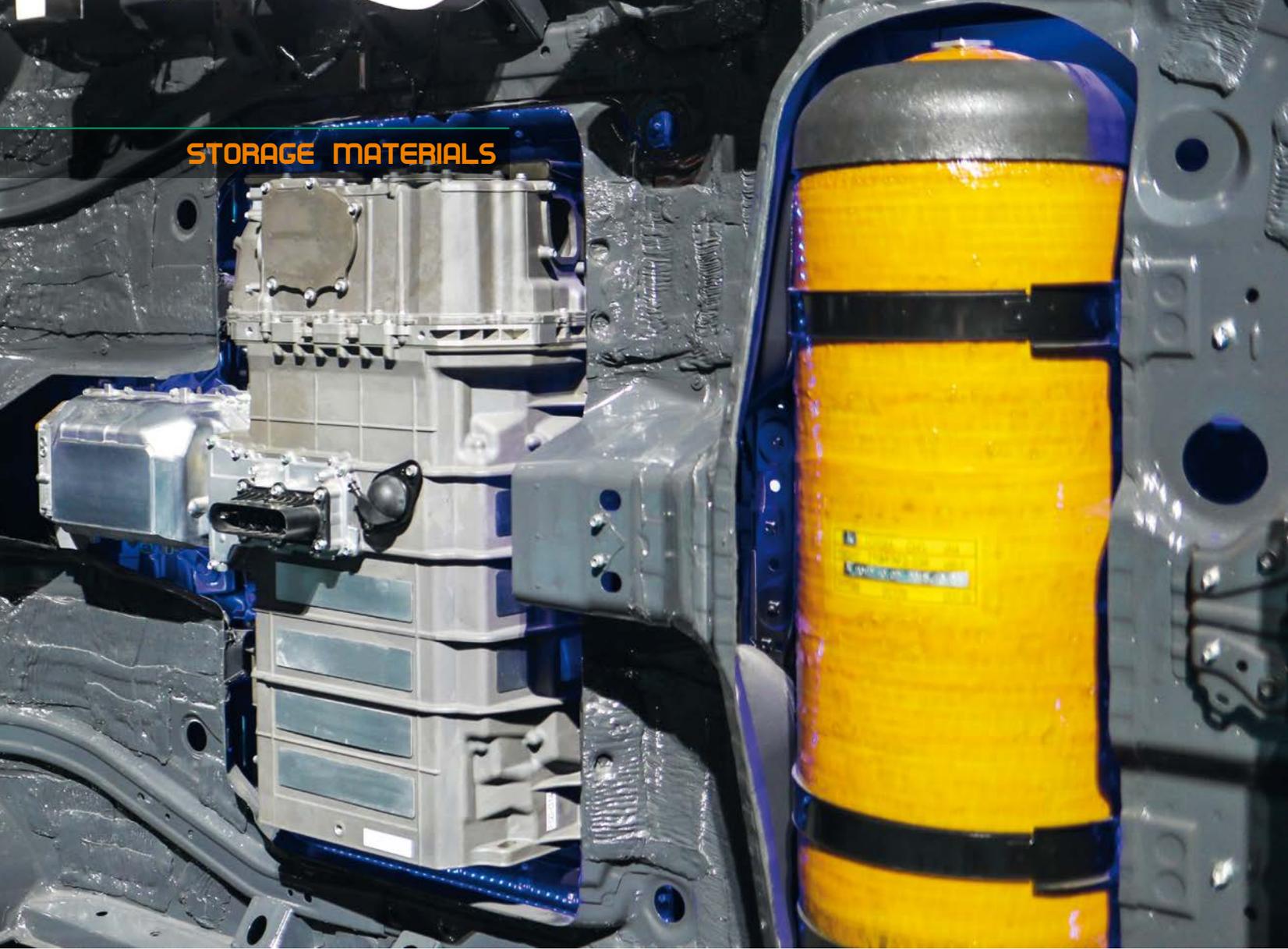


■ Florian Schön M.Sc. is a research associate at the Polymer Engineering research group at the University of Bayreuth.



■ Fabian Hübner M.Sc. is a research associate at the Polymer Engineering research group at the University of Bayreuth.

STORAGE MATERIALS



■ Fabian Hübner
Florian Schön
Volker Altstädt

Ultralight construction materials for hydrogen tanks

New plastics reinforce the efficiency of hydrogen-powered fuel cells

■ Tank for fuel cell vehicles, presented at the Washington Auto Show (Photo: Nicole Glass Photography / shutterstock.com).

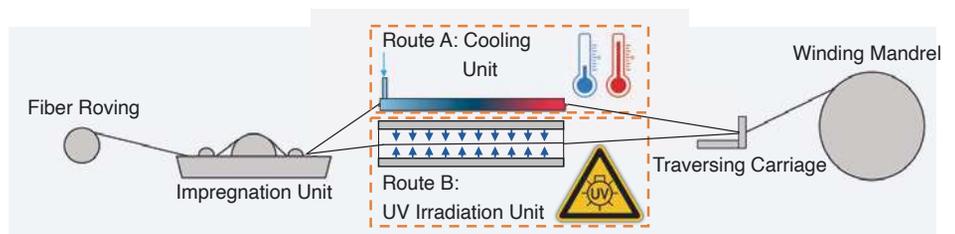
Many everyday products today contain injection-moulded plastic components made of thermoplastics. Due to their chain-like molecular structure, these components can be melted and shaped into an individual, desired form using machines. When more considerable mechanical properties are required, such as load capacity and fatigue strength, duromers are often used instead of thermoplastics. These plastics cannot be melted, and have extraordinarily high dimensional stability, because they undergo a special hardening step during their production. Similar to commercially available adhesives for private households, two components, a resin and hardener, form a reactive mixture and lead to stable molecular bonds. In industrial duromers, however, it is important that great dimensional stability is maintained even at very high or very low temperatures.

Fibre reinforced plastics: Highly stable materials with great potential

Today, the hydrogen tanks of fuel cells are increasingly made of fibre-reinforced duromers in order to achieve the highest possible rigidity. The fibre strands (rovings) consist exclusively of high-strength carbon fibres. At up to 6,000 megapascals, these have a directional specific strength that is five times higher than that of steel, while their density is much lower. The fibre strands are impregnated with a duromer in the course of various processes – this is called impregnation. The temperature-dependent nature of the duromer is particularly important here. For reasons of cost, duromers today consists almost exclusively of epoxy resin and a reactive hardener. There are basically two core technologies available for this impregnation process.

Wet winding process: Ways to increase efficiency

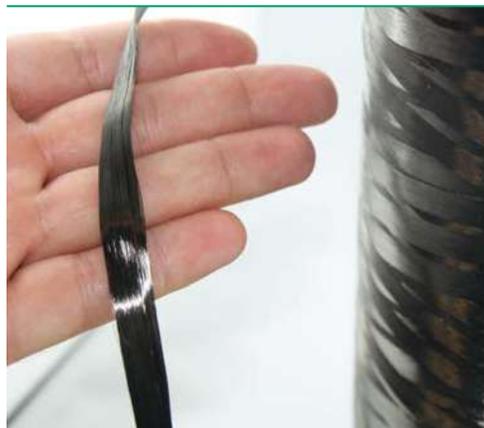
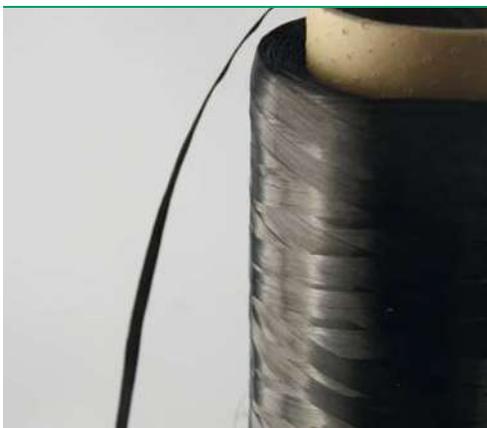
Over the last decades, "filament winding", or more precisely, the wet winding process, has become increasingly established in industry. In this process the carbon fibre rovings are drawn through a bath of liquid epoxy resin and impregnated in the process. The impregnated rovings are then fed into a winding machine, where they are transported to a depositing unit. Finally, they are deposited on the winding core in pre-defined geometric structures, in cross and parallel layers. The result is a carbon fibre reinforced plastic (CFRP).



■ Fig. 1: Schematic layout of individual stations of a wet winding line (Diagram: Florian Schönl).

During these processes, the materials involved and the process technology used must be optimally matched to each other so that the components made from the CFRPs – such as the hydrogen tanks – are of the required quality. That means, proper component quality can only be achieved if complete impregnation of the fibres and sufficient "tackiness" in the subsequent winding process are guaranteed. This way, the component contains minimal air contamination, and thanks to this low porosity, it is possible to impart to the wound layers exactly the geometrical structures planned beforehand.

■ Fig. 2-4: Wound rovings on a spool. A single roving contains more than 24,000 individual fibres arranged in parallel (Photos: Christian Wißler).





■ Fig. 5 (above): CFRP laminate structure of an ultra-light hydrogen tank concept: 12 individual layers are visible, layered in different directions to fully exploit maximal material performance. Here a reference to aircraft structural laminates becomes visible, where layers at ± 45 degrees / 0 degrees / 90 degrees / 90 degrees / 0 ± 45 degrees each result in a quasi-isotropic layered construction (Photo: Fabian Hübner).

■ Fig. 6 (below): Ready wrapped hydrogen tank (Photo: Fabian Hübner).

Unfortunately, the economic efficiency of today's wet winding technology is limited by the materials themselves and by current plant technology. This is reflected in the production speed, the upper limit of winding speed being about 50 meters per minute. This results in new challenges for materials research. The mass production of fuel cell powered automobiles will only ever become reality if the production of pressure tanks for storing liquid hydrogen can be accelerated, and thus become considerably cheaper.

The viscosity of the resin system poses a particular problem in this context. Viscosity is the flowability of

materials, and physically can be described as rheological behaviour. The lower the viscosity of a material, the more fluid it is. If one considers conditions at room temperature, viscosity rises incrementally from water, to olive oil, to honey, to cake dough. However, viscosity can also vary under the influence of external forces and different temperatures.

When producing CFRP with the help of current wet winding technology, it is important that the resin used has very low viscosity and thus delivers good impregnation. However, this requirement contributes to the limitation of the winding speed:

- On the one hand, if the resin is spun off at too high a speed, contamination of the plant and fluctuating fibre content in the resin will result.
- On the other hand, resins in the liquid state only display low stickiness, meaning the winding layers can slip at too high speeds.

In order to be able to increase winding speeds nevertheless, it is necessary to significantly increase the viscosity of the resin system at least after the impregnation process. There are two ways of attempting this:

- The viscosity of the resin can be significantly increased following the impregnation process by controlling the temperature of the resin – provided that advanced plant technologies are available, including, for example, heatable and coolable stations. Targeted temperature increases can be used to achieve good impregnation characteristics, and prevent the resin from being thrown off after impregnation. However, care must be taken to ensure that the increased temperatures do not cause the resin system to start its curing reaction too early. If there is too little time to process the material, i.e. the so-called "pot life" is too short, there is a risk that the material will cure while still being processed in the system, and cause a loss of production.
- An alternative is to fortify the resin with a component that can be cured by UV light. For this purpose, the winding system must be equipped with a UV curing station deployed directly after the impregnation process. In this way, the desired rapid increase in viscosity can be achieved within fractions of a second. However, the naturally black carbon fibres pose a chal-

"Fibre-plastic composites must also be able to withstand temperature-dependent loads that may affect the material during the refuelling process."

lenge. Because they can absorb UV light, there is a risk that the UV light will not penetrate deeply enough into the impregnated rovings, and not fully cure the component added to the resin. Quality deficits in the material would be the result.

Both possibilities are being investigated at the University of Bayreuth by the Polymer Materials research group's project "Speedpreg", funded by the German Federation of industrial Research Associations (AiF). The aim in both cases is to use material science innovations to launch new, faster, and thus more cost-efficient winding technology. Research partners are the Institute for Composite Materials (IVW) Kaiserslautern and JWS Jakob Weiß und Söhne Maschinenfabrik GmbH.



**Towpregs:
Pre-impregnated rovings on rolls**

Another possibility for the production of pressure tanks made of carbon fibre reinforced plastics are Towpregs. These are rovings which are pre-impregnated next to each other at an exactly defined width and wound onto a spool. Manufacturers of pressure tanks can purchase these rovings from external manufacturers and do not have to invest in their own wet winding system for pre-impregnation. These plastics can be used to produce components in the pre-defined geometric structures in fewer process steps than with the wet winding process. A further advantage of this technology is that the resins have high viscosity and, compared with conventional wet winding, significantly higher winding speeds can be achieved.



■ Fig. 7 and 8: Prepregs (pre-impregnated fibres) are semi-finished products pre-impregnated with polymer resins that are not fully cured, while Towpregs are a special type of these semi-finished product. The University of Bayreuth is the only university in Germany that has access to a research-scale prepreg plant. This is specially designed to allow the development of new polymer resins for use in the prepreg process. The plant also has a testing machine with which fibre-reinforced plastic composites with great load-bearing qualities can be identified. Top: After the fibres are impregnated with polymer resin, the prepregs are cooled and rolled. Below: The application unit of the prepreg plant: resin is applied as a very thin film to the backing paper (Photos: Christian Wißler).

AUTHORS



■ Fabian Hübner M.Sc. is a research associate at the Polymer Engineering research group at the University of Bayreuth.



■ Florian SchönI M.Sc. is a research associate at the Polymer Engineering research group at the University of Bayreuth.



■ Prof. Dr.-Ing. Volker Altstädt is the Chair of Polymer Engineering at the University of Bayreuth.

The goal: Highly stable and leak-proof tank systems

The design of the tanks depends very much on the mechanical properties of the fibre-reinforced plastics used and their material characteristics. For the storage of highly compressed hydrogen gas, an operating pressure of about 700 bar is often considered standard. A tank can withstand this enormously high pressure essentially because it has sufficient wall thickness. Continuous wall thicknesses of less than 10 millimetres are often sufficient. The wall thicknesses are built up in the described winding processes at very high speeds. Here, fibre strands are bundled next to each other to form a tape and placed on a winding core. In this way, a layered structure is created layer by layer from different angles. Since the greatest strength is always in

the longitudinal direction of the fibres, the aim is to allow the fibres to run in many different directions. This results in a "quasi-isotropic" layer structure, in which cross and parallel layers alternate. Such a structure has several advantages. The strength of the material becomes independent of the direction of force applied, and it is also possible to lay down additional layers in highly stressed areas, or to save weight in areas of low stress.

The current state of the art uses liners to ensure the tightness of the tank. Here, a hollow polymer cylinder made of high-density polyethylene (HDPE) is combined with the fibre composite. However, this plastic, which incidentally is used in packaging by the tonne, accounts for an enormous share of the weight of the overall system. It is necessary, however, to prevent the low wall densities from allowing the system to outgas. This is because hydrogen molecules are very small, and would otherwise escape through the tank walls into the environment. This would cause the tank to empty further and further. It would therefore be advantageous if there were a material available to line tank walls that is lighter than HDPE, but at the same time capable of preventing hydrogen molecules from diffusing into the air.

For this purpose, research is currently being conducted at the University of Bayreuth in the Bavarian joint project "Galvanospace", funded by the Bavarian Research Foundation. Project partners are MT Aerospace AG in Augsburg, Lüberg Elektronik GmbH & Co. and Rothfischer KG in Weiden, and Grip-Engineering Thümler GmbH in Nuremberg. One focus of the research work is on the metallization of the tank walls, for example by means of inner or outer shells of copper or nickel of a thickness of just a few micrometers. This seems to be a promising way to ensure greater gas tightness while reducing weight at the same time. This also increases the chances of fuel cell technology being able to establish itself on a broad front in the automotive market.

Material testing in accordance with standards ensures safety

In order to meet the high safety requirements for the automotive, aerospace, and aviation industries, characteristic values must be determined by means of strict materials testing, on the basis of DIN or ISO standards. A prepreg machine is being used at the University of Bayreuth for this very purpose. Stan-

■ Fig. 9: The prototype laminate finishes come from a low-pressure low-temperature hydrogen tank concept. They are used to test the formation of stripes in order to determine whether the material is capable of withstanding a cyclical shifting load such as the high-pressure refuelling process (Photo: Fabian Hübner).



■ Fig. 10: Stable even under very high pressures: hydrogen tank for fuel cell vehicles (sst).



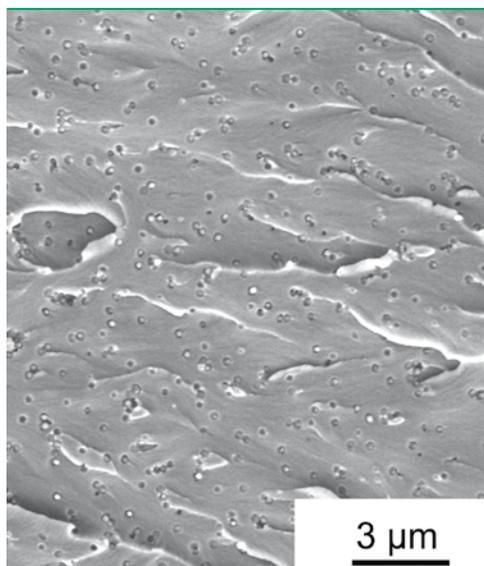


■ Fig. 11: A prototype of the BMW i Hydrogen NEXT at the International Motor Show (IAA) 2019 in Frankfurt am Main (Photo: Grzegorz Czapski / shutterstock.com).

Standard test specimens are produced on a pilot plant scale, which are then subjected to ever higher loads in the University's own test centre, until they finally fail. Special attention is paid to the load-bearing capacity of epoxy resins that have been modified by nanotechnology, and their functionality in the composite material. In accordance with the relevant standards, tensile tests or fracture toughness measurements are carried out on epoxy resins in the Bayreuth laboratories. From these tests, the exact amount of stress a respective material can withstand can be deduced, and when it will fail. For example, crack propagation at various load limits is measured in order to find out what resistance a material provides to cracking during high-performance operation. The experience gained in these measurements is used to design hydrogen tanks in such a way as to ensure their operational safety even at very high pressures.

During materials testing, fibre plastic composites are subjected to mechanical stress through tension, pressure, bending, and torsion. However at the same time, they must also be able to withstand temperature-dependent loads that may affect the material during the refuelling process. For corresponding stress tests, temperatures of minus 196 to plus 90 degrees Celsius are generated. In addition, fibre composites are tested on newly developed materials testing machines in liquid nitrogen at 77

Kelvin (minus 196 degrees Celsius). In this way it can be determined how the material of the tank reacts when it comes into contact with liquid cryogenic low-pressure hydrogen at 21 Kelvin (minus 252 degrees Celsius). Such tests are of great importance not least for space travel. The main and upper stages of the European Ariane rockets are operated with the high-energy fuel mixture of liquid hydrogen and liquid oxygen.



■ Fig. 12: Fracture surface of an epoxy resin filled with nanoparticles to increase toughness. The fracture lines are clearly visible around the particles that absorb the energy of the crack progression and thus lead to an increase in toughness (scanning electron microscopic image: Florian Schön!).

Decarbonisation by hydrogen

Questions to Peter Berek, District Administrator of the District of Wunsiedel i. Fichtelgebirge

The District of Wunsiedel in the Fichtelgebirge is one of the winning regions in the nationwide "HyLand" competition initiated by the Federal Ministry of Transport and Digital Infrastructure (BMVi) as part of the Federal Government's National Hydrogen Strategy. The District is now called upon to develop a hydrogen plan that incorporates forward-looking ideas. Can you already give us some of the key points in this plan? What are the strategic goals on which it will be oriented?



INTERVIEW PARTNER

Peter Berek

District Administrator of the District of Wunsiedel i. Fichtelgebirge

On the one hand, this plan is intended to advance the *Energiewende* and climate protection, and to help us make progress in the decarbonisation of all sectors, but above all to trigger investment in hydrogen technology in our region. To this end, the areas of construction and expansion of hydrogen production plants and storage facilities, but also the issues of filling station infrastructure and the conversion of vehicle fleets in the heavy-duty sector – both public and private – as well as rail transport will be examined in detail. The legal framework for the use of hydrogen will also be examined where necessary.

Who are the partners cooperating in the development of the plan?

The plan is being developed, under our direction, by SWW Wunsiedel GmbH with partners Endura Kommunal GmbH and Sterr-Kölln & Partner mbB. And we continue to be supported by the University of Bayreuth and its Centre for Energy Technology (ZET), OTH Regensburg, and the Fraunhofer Institute for Solar Energy Systems in Freiburg. There will also be expert workshops in the different areas, in which selected experts from politics and science, network operators and companies from the fields of public transport and logistics, as well as consumers of material flows from electrolysis will take part. Moreover, the general public

will be encouraged to get involved by means of a participation platform and a process of public workshops.

Do you also see prospects for cooperation with the University of Bayreuth?

The University of Bayreuth, in particular Prof. Brüggemann, will support us in the field of producer technology, as they already have experience in operating an electrolyser and in material technology. We are currently in discussions to jointly formulate the precise contributions to be made by the Centre for Energy Technology (ZET) in the project.

What are the priority areas in which hydrogen technology is to be promoted and expanded?

To answer that, the two projects must be considered separately. Existing hydrogen demand in the region is the top priority for the project of WUN H2 GmbH. That means, the electrolyser, storage, and transport. In the HyExpert project of the District of Wunsiedel in the Fichtelgebirge, utilizing hydrogen in transport – public as well as private – is in the primary goal. That means, the provision of further green hydrogen sources, filling station infrastructure, expansion of public transport on bus and rail, and then heavy-duty and forklift logistics. As a member of the Euregio Egrensis, cross-border rail transport to the Czech Republic is also a very important issue for us. This will hopefully demonstrate that hydrogen technology can be used throughout Europe.

What is the significance of "Energiepark Wunsiedel" for the new hydrogen strategy?

The energy park will be the ideal location for the electrolyser. All material flows will be able to be utilized (hydrogen, oxygen, and waste heat) so that none of the energy is lost. In addition, the stored hydrogen will be available at any time to generate electricity again, for example via hydrogen-compatible cogeneration units. In this way, fluctuating renewable energy sources suddenly become a controllable power plant. Surpluses are to be stored in the form of hydrogen and released again in case of renewable energy shortages.

Interview: Christian Wiffler

■ Fig. 1: View of the city centre of Wunsiedel (Aerial photograph: Franz X. Bogner).



Prospects for research & practice



■ Fig. 2: Wunsiedel Energy Park will combine renewable energy sources, an electrolysis plant (power-to-gas plant still under construction) for the production of "green" hydrogen, combined heat and power plants, and industrial production (wood-pellet production) (Photo: SWW Wunsiedel).

The goal that the district of Wunsiedel in the Fichtelgebirge has set itself is ambitious: Together, players from politics, business, and society are seeking to develop our region into a model of sustainable, decentrally-organized energy supply. In doing so, high-tech, ecology, and business make up a three-pronged attack. The vision is comprehensive decarbonization that integrates different forms of generation, storage, and use of renewable energy sources according to regional needs. To achieve this, innovative impetus from research must be combined with many years of practical experience. This provides numerous starting points for cooperation with the University of Bayreuth:

- It would be well worthwhile to review our regional natural gas network to see under what conditions it can be used for the transport of hydrogen. To do this, we need analytical methods that can determine the level of investment required. At the same time, material science aspects must be resolved. In particular, what materials should be used in the future expansion of our energy infrastructure to achieve comprehensive hydrogen capability?
- In the long term we aim to replace natural gas heating systems with heating systems based on "green" hydrogen. If excess photovoltaic energy is generated in summer, it can be stored as hydrogen and used to generate electricity and heat over the winter months. To continuously simulate these interlinked technical processes using the example of Wunsiedel, and to continuously

evaluate the data thus obtained, would be of great assistance to future planning.

- Innovative strategies are also required for the production of renewable energies. This includes agricultural photovoltaics, for example. How can the farming of land be optimally combined with the use of sunlight as energy? To link established techniques of agriculture with renewable energy production, and to further develop them in combination, is definitely a future-oriented field of research. This would also be an opportunity to counteract urban encroachment of rural areas.
- Characteristic for our "WUNSiedler Weg – Energie" is the simultaneous development of battery and hydrogen technology, which we intend to interlink more closely. The modular energy storage system SIESTORAGE, built by Siemens in Wunsiedel, uses high-performance lithium-ion batteries. With the signing of the LOI (Siemens, Rießner Gase, SWW Wunsiedel GmbH and the City of Wunsiedel) for the planning and construction of a PEM electrolysis plant and WUN H2 GmbH, founded in 2020, the basis for the construction of a power to gas plant, which will further advance the "Hydrogen Initiative Wunsiedel" has been put in place. The interaction of these two key energy technologies holds great potential for future contacts with the University of Bayreuth – both with the Bavarian Centre for Battery Technology (BayBatt), founded in 2018, and with working groups in hydrogen research.

It is a unique constellation in Germany: the University of Bayreuth with its interdisciplinary focus area of "Energy Research and Energy Technology", and the adjoining region of Wunsiedel, where new approaches to decarbonisation are being put into practice in exemplary fashion. Here, when it comes to the transfer of knowledge from energy research, we can act like a "large-scale laboratory", which in turn will impact science with the wealth of experience it amasses.

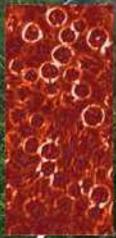
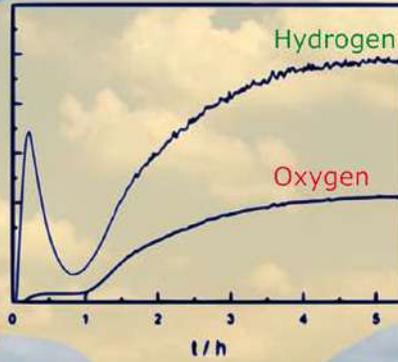
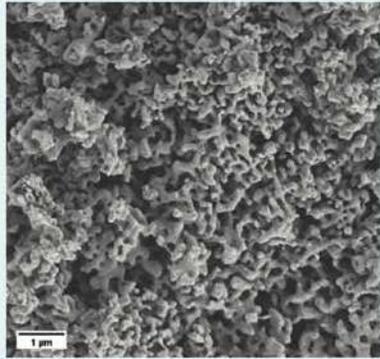
The prospects for cooperation with university research are not limited to energy technology challenges. Further tangents are also appearing in law and economics. For example, exactly how could energy industry law provide the necessary legal framework to integrate a rural, decentralized energy industry into a European integrated network? SWW Wunsiedel GmbH, the University of Bayreuth and other partners have recently started working together in the IT project "SiZero", which is funded by the Bavarian State Ministry of Economic Affairs, Regional Development and Energy. Together we committed to increasing IT security in the areas of transport and traffic, food, water, and energy in a sustainable way.

AUTHOR



■ Marco Krasser is Managing Director of SWW Wunsiedel GmbH.

SUSTAINABLE PRODUCTION



■ Jana Timm
Roland Marschall

Harvesting hydrogen with sunlight

Photoelectrochemical water splitting with nanostructured semiconductor electrodes

■ Photoelectrochemical hydrogen production under solar radiation is a promising process for a sustainable hydrogen-based economy (Image: Jana Timm / Roland Marschall).

One of the most pressing challenges facing our society today is to replace traditional carbon-based fossil fuels with alternative energy sources whose use does not contribute further to climate change. In the face of this, the European Union's Renewable Energy Directive was comprehensively revised in 2018. It set the EU member states an ambitious target: from 2021 they are to work together to ensure that by 2030, renewable energy will account for 30 percent of the EU's gross final energy consumption.

The most promising way towards renewable fuels is to use the energy of sunlight or wind to split water into oxygen and hydrogen. The energy remains stored in the chemical bonds of these reaction products, and can be retrieved when needed – especially when solar radiation is weak and there is little wind. If hydrogen is produced in this way, it is a "green" fuel, one whose production and combustion does not produce carbon dioxide. It is thus a clean fuel for fuel cell vehicles and can even be used for chemical conversion reactions that require hydrogen. Until now, however, this hydrogen has been produced using fossil fuels.

Photovoltaic cells connected to water electrolyzers exhibit the highest efficiency when it comes to using light energy for splitting water and "storing" it in the chemical bonds of the reaction products. But this technology is currently still held back by very high costs. Worldwide demand for renewable energy hence cannot yet be met in this way.

Water splitting via "artificial photosynthesis"

One promising alternative to convert solar energy into hydrogen, however, is water splitting on the surface of semiconductors or semiconductor electrodes. This process is called photocatalytic or photoelectrochemical water splitting. Photocatalytic water splitting was first reported in an article published in 1972, which described water splitting on the surface of the semiconductor TiO₂ (titanium dioxide).¹ In this process light energy is converted into electrical charge within the semiconductor material itself. The carriers of the negative charge are electrons (red in Fig. 1), while the carriers of the positive charge are called holes (green in Fig. 1). In a suspension, the

Photocatalysis vs Photoelectrochemistry

Fig. 1

Water splitting by photocatalysis: The energy of sunlight absorbed by the semiconductor (grey) generates a positive charge (green) and a negative charge (red) in its interior, charge carriers are electrons or holes (red or green). On the surface of the semiconductor a release of electrons (oxidation) takes place at the electron donor (D). Water is converted to oxygen and hydrogen protons. At the electron acceptor (A), electrons are taken up (reduction): protons become hydrogen.

Water splitting by photoelectrochemistry: The negative charge generated inside the semiconductor is transferred to the working electrode. From here it is transferred to the counter electrode, where hydrogen is produced by reduction. On the surface of the semiconductor, however, hydrogen protons and oxygen are produced by water oxidation.

Illustrations: Roland Marschall

negative charges are then transferred to electron acceptors (A), the positive charges to electron donors (D). In the case of water splitting, these processes

and oxygen. In thermodynamics, this is generally referred to as an "uphill reaction". Here, energy is fed into a reaction system and stored in it. Such a process also takes place in nature when plants convert carbon dioxide and water into sugar and oxygen during photosynthesis, so that the energy is stored in these products. Therefore, the splitting of water into hydrogen and oxygen can also be called artificial photosynthesis.

"The more sunlight a semiconductor absorbs, the more electrons and holes are available for photocatalytic or photoelectrochemical water splitting."

result in the irradiated solar energy being stored in the products oxygen and hydrogen. However, this process has the disadvantage that the two gases must be physically separated from one another by means of complex processes to prevent an explosive gas mixture being generated.

An alternative process that avoids this problem is photoelectrochemical water splitting. Here, the products hydrogen and oxygen are spatially separated right from the beginning. On the surface of the semiconductor, which functions as a photoanode, water is converted by the release of electrons into oxygen and protons (oxidation). Hydrogen, on the other hand, is produced on the surface of a counter electrode in the photoelectrochemical cell, which functions as a cathode. Here, the protons are converted into hydrogen by accepting electrons (reduction). The cell consists of two sections separated by a proton-conducting membrane.² A reference electrode helps to determine the actual photovoltage.

In photocatalytic and photoelectrochemical reactions that split water, the energy originating from sunlight is stored in the chemical bonds of hydrogen

Light absorption by semiconductor materials: critical for the efficiency of water splitting

Theoretically, the more light energy is converted into hydrogen, the greater the efficiency of water splitting by sunlight. Actually, this is mainly influenced by the colour of the semiconductor used, which in turn depends usually on its band gap. For example, titanium dioxide (TiO₂) is a white powder, which means that it does not absorb visible light. Yet it does absorb ultraviolet light, that component of sunlight that causes sunburn if we stay in the sun too long. Because we humans cannot see UV light, TiO₂ is visible to us as a white material. Plants, on the other hand, appear green to us because they absorb visible light. Visible light accounts for about 50 percent of sunlight, while UV light accounts for between three and five percent of sunlight. As a result, white semiconductors cannot absorb as much sunlight as plants.

The more sunlight a semiconductor absorbs, the more electrons and holes are available for photocatalytic or photoelectrochemical water splitting, and the greater the amount of light energy that can be converted into hydrogen. For this reason, many ma-

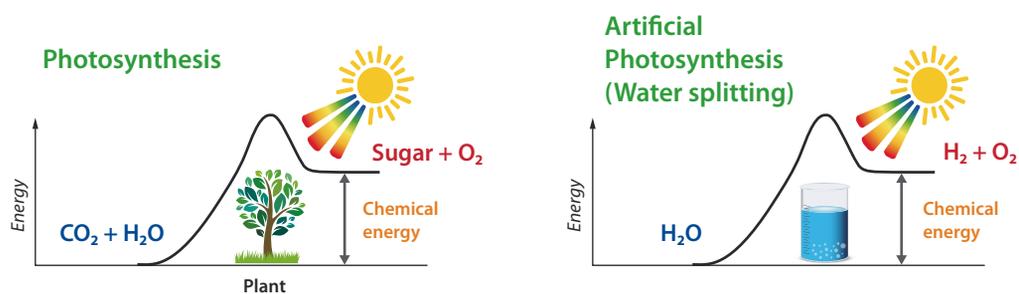
AUTHORS



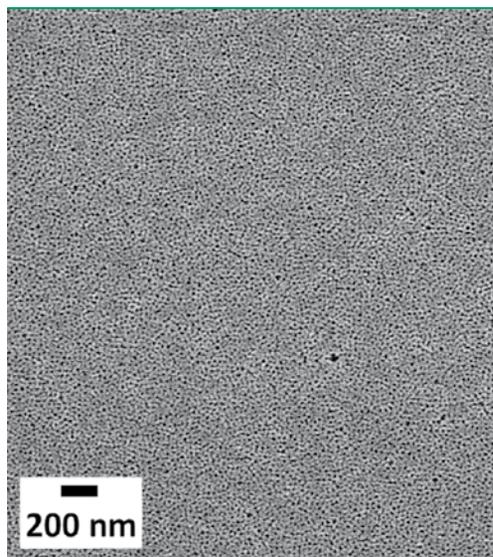
■ Prof. Dr. Roland Marschall is the Chair of Physical Chemistry III at the University of Bayreuth.



■ Dr. Jana Timm is Academic Counsellor at the Physical Chemistry III research group at the University of Bayreuth.



■ Fig. 2: Left: Principle of natural photosynthesis. Plants absorb the energy of sunlight and thus convert carbon dioxide and water into sugar and oxygen. The light energy is stored in the sugar as chemical energy. Right: Principle of water splitting as "artificial photosynthesis". In photocatalysis and photoelectrochemistry, water is converted into hydrogen and oxygen with the help of a semiconductor that absorbs the energy of sunlight. The light energy is stored as chemical energy in the chemical bonds of the hydrogen and oxygen molecules (Graphs after A. Kudo, Y. Miseki: Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* (2009), 38, 253-278. DOI: 10.1039/B800489G).



terials scientists are looking for semiconductors that are highly efficient with regard to their absorption capacity. This is one of the research focuses of the working group of Prof. Dr. Roland Marschall at the University of Bayreuth.

With the aim of finding highly efficient alternatives to titanium dioxide, several semiconductors like bismuth vanadate (BiVO_4), tantalum nitride (Ta_3N_5), and iron(III) oxide (Fe_2O_3), in particular, have recently been investigated in detail:

- Bismuth vanadate is a yellow-coloured semiconductor that can absorb a wide spectrum of visible light. In recent years, the efficiency of this semiconductor material has been considerably optimized – especially by managing to accelerate electron transport in the photoanodes.³ However, this material contains the rare element bismuth, so its application on an industrial scale is not expected in the long term.
- This also applies for the dark red tantalum nitride. The metal tantalum contained in it is relatively rare, and the material also has the disadvantage that – like many other nitrides and oxynitrides – it is not stable over long periods due to photo-corrosion.
- α -iron(III) oxide, in contrast to tantalum nitride and bismuth vanadate, has the advantage that it does not contain any other metal than earth-abundant, low cost iron. It is a powder reddish-orange in colour, and its mineral name is hematite. It is often used in photoelectrochemical cells for oxygen production at the photoanode, but unfortunately it is not ideal for hydrogen production at the photocathode. Other disadvantages include low electrical conductivity, a short diffusion length for holes, and a low absorption coefficient, so that relatively thick layers of the material are needed to absorb light effectively. Consequently, there are numerous research groups around the world working on refining this inexpensive and readily available material by means of nanostructuring it into a semiconductor suitable for water splitting. At the same time, alternative ferrous materials are also being researched for their suitability.

In recent years, it has been found that mixed oxides containing iron with the formula MFe_2O_4 ($\text{M} = \text{Ca}, \text{Mg}, \text{Zn}$) can be used for the splitting of water with sunlight, and are therefore an alternative to

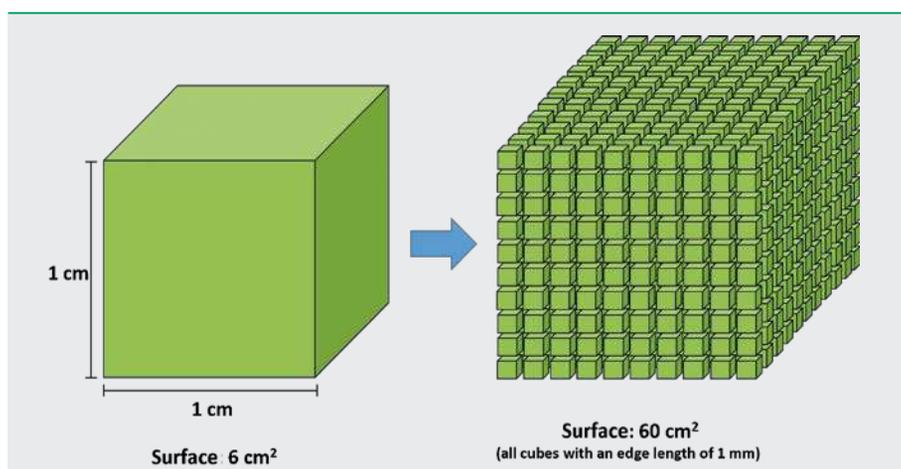
■ Fig. 3: Highly porous thin film of zinc ferrite (ZnFe_2O_4), which is well suited as photoanode for photoelectrochemical hydrogen production (Photo: © Wiley-VCH. First published in K. Kirchberg et al.: Mesoporous ZnFe_2O_4 , Photoanodes with Template-Tailored Mesopores and Temperature-Dependent Photocurrents. *ChemPhysChem* (2018), 19 (18), 2313-2320, reprinted with kind permission of the publisher).

■ Fig. 4: Model of the cubic crystal structure of ferrites with embedded metal compounds in the museum of the Tokyo Institute of Technology (Photo: Masao / wikimedia commons / CC-BY-SA-4.0).

■ Fig. 5: Iron(III)-oxide in powder form (Photo: BXXXD / wikimedia commons / CC-BY-SA-3.0-migrated).



titanium dioxide. Like iron(III) oxide, they are orange to dark red in colour, meaning they can absorb about half of the sunlight irradiation. Moreover, these mixed oxides contain inexpensive elements that are commonly found on Earth, which is very important for sustainable hydrogen production. Calcium ferrite (CaFe_2O_4) has ideal properties for hydrogen production at the photocathode, while zinc ferrite (ZnFe_2O_4) and magnesium ferrite (MgFe_2O_4) are suitable for the photoanode of a photoelectrochemical cell.



■ Fig. 6: Surface enlargement by structuring (Illustration: Roland Marschall).

Increase in efficiency by enlarging semiconductor surfaces

In addition to light absorption, there is another important property of semiconductors that significantly influences their activity in photocatalytic or photoelectrochemical water splitting. In both cases, the splitting of water takes place on the surface of each individual semiconductor particle. Hence, the greater the surface area of a particle, the greater the number of reactions that can take place. As in other areas of catalysis research, one of the main goals of water splitting research is to increase the surface area of the semiconductor nanoparticles. This way, more surface reactions can take place per gram of semiconductor material. This is another focus of Prof. Dr. Roland Marschall's research group.

Let us assume that a semiconductor is in the shape of a cube with each side measuring 1 cm resulting a surface area of 6 cm^2 , all of which is available for photocatalytic or photoelectrochemical water splitting. If this cube is divided into 1,000 smaller cubes, each

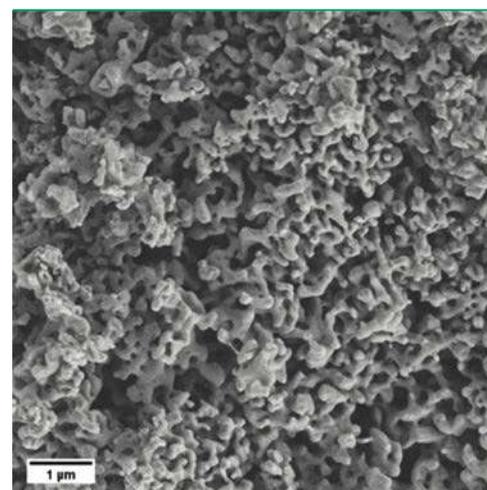
with a side length of 1 mm, the result is a surface area of $1000 \times 6 \text{ mm}^2 = 6000 \text{ mm}^2 = 60 \text{ cm}^2$. The smaller the cubes become, the greater the surface enlargement. In fact, various chemical synthesis techniques can now be used to produce cubes with a side length of just a few nanometers. If a cube with a surface area of 60 cm^2 were to be divided into even smaller cubes with a side length of only one nanometer (1 nanometer = 0.0000001 cm), a specific surface area of $60,000,000 \text{ cm}^2$ would be obtained.

Zinc ferrite (ZnFe_2O_4) and magnesium ferrite (MgFe_2O_4) can be processed into nanostructured thin films, and used in this form as photoanodes of very high porosity.⁴ The good absorption of visible light that characterizes these materials is combined with the advantages resulting from the nanostructuring of large surfaces. This surface then functions as a working electrode (photoanode) where oxygen is produced, while hydrogen is produced at the counter electrode (cathode).

Calcium ferrite CaFe_2O_4 is even more interesting. This oxide also absorbs visible light and is composed of elements that are particularly common in the earth's crust. In the form of thin layers, it is almost ideal for hydrogen production.⁵

Forward-looking innovation in Bayreuth

Recently, a promising development has emerged from cooperation within the University of Bayreuth, in which the research groups of Prof. Dr. Roland Marschall (Physical Chemistry), and of Prof. Dr. Josef



■ Fig. 7: Highly porous, sponge-like structured calcium ferrite for photoelectrochemical hydrogen production (Image: Roland Marschall).

Since July 2020, Dr. Jana Timm has received a research grant from the Max Buchner Research Foundation. In her new project, she deals with proton-conducting inorganic-organic hybrid materials. The aim is to use these hybrid materials as additives in fuel cell membranes and thus increase the efficiency of the energetic use of hydrogen. The membrane is an important component in a polymer electrolyte membrane (PEM) fuel cell. It has the function of transporting protons from the anode of the fuel cell to the cathode, and at the same time must be gas-impermeable. Inefficient proton transport significantly reduces the efficiency of the PEM fuel cell. The development of performance-enhancing additives therefore plays a key role for the efficient use of "green" hydrogen and thus also for a sustainable future.



■ Fig. 8 and 9: Dr. Jana Timm at the electrochemical test apparatus. Right: Synthesis of inorganic-organic hybrid materials (Photo: Christian Wjßler).

Breu and Prof. Dr. Birgit Weber (Inorganic Chemistry) all participated. For the first time, it has been possible to produce an extremely porous calcium ferrite powder with a sponge-like structure by microwave synthesis at moderate temperatures. It has very large pores, each with a diameter of several hundred nanometers, and phase-pure crystalline pore walls. This material is capable of absorbing more than 50 percent of sunlight and is therefore eminently suited for photoelectrochemical hydrogen production from solar radiation. The hydrogen produced this way would be a carrier of sustainable, green energy, and thus fuel for a hydrogen-based economy.⁶



■ Fig. 10: Photoelectrodes for the production of "green" hydrogen (Photo: Jana Timm).

RECOMMENDED READING

A. Bloesser et al.: A Novel Synthesis Yielding Macroporous CaFe_2O_4 Sponges for Solar Energy Conversion. *Solar RRL* (2020), DOI: 10.1002/solr.201900570.

- 1 A. Fujishima, K Honda: Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature* (1972), 238, 37-38. DOI: 10.1038/238037a0.
- 2 R. Marschall et al.: Composite proton-conducting polymer membranes for clean hydrogen production with solar light in a simple photoelectrochemical compartment cell. *International Journal of Hydrogen Energy*, Vol. 37, 4012-4017. DOI: 10.1016/j.ijhydene.2011.11.097.
- 3 Fatwa F Abdi et al.: Efficient solar water splitting by enhanced charge separation in a bismuth vanadate-silicon tandem photoelectrode. *Nature Communications* (2013), 4: 2195. DOI: 10.1038/ncomms3195.
- 4 R. Marschall: Nanostrukturierte Oxide. Funktionelle Materialien für die elektrochemische Energiespeicherung und -wandlung. *SPEKTRUM – das Wissenschaftsmagazin der Universität Bayreuth* (2019/1), 22-25; K. Kirchberg et al.: Mesoporous ZnFe_2O_4 Photoanodes with Template-Tailored Mesopores and Temperature-Dependent Photocurrents. *ChemPhysChem* (2018), 2013. DOI: 10.1002/cphc.201800506.
- 5 K. Kirchberg, R. Marschall: Sol-gel synthesis of mesoporous CaFe_2O_4 photocathodes with hierarchical pore morphology. *Sustainable Energy Fuels* (2019), 3, 1150. DOI: 10.1039/C8SE00627.
- 6 See recommended reading. The interdisciplinary research team has investigated in detail the process of microwave synthesis and the magnetic properties that play a role in this process.

SUSTAINABLE PRODUCTION

■ Thomas Scheibel
Muhammad Shakir Bin Zainuddin
Tim Schiller

Spider silk for the *Energiewende*

Photocatalytic hydrogen
production with novel
hybrid systems

■ *Electrospinning process: A syringe is mounted on a holder, then a cannula is placed on the syringe. A syringe pump pushes the syringe plunger downwards, causing the spinning solution to be extruded. Under the syringe there is an earthed laboratory lift (aka "labboy"). A piece of black paper serves as a collector surface. The black colour makes it easier to identify the electrospun fibres that have been produced (Photo: Christian Wißler).*

The technologies for producing hydrogen in industry today are still largely based on processes in which fossil fuels – mainly natural gas or oil-based – are processed. This applies to both steam reforming and catalytic reforming, which in this respect, make no contribution to energy production from renewable sources. Moreover, these processes not only release hydrogen, but also lead to the emission of the greenhouse gases carbon monoxide (CO) and carbon dioxide (CO₂). The situation is completely different with the electrolysis of water, a comparatively inexpensive resource. In view of the goal of a sustainable energy economy, this is a much more attractive way to produce hydrogen. However, the energy required to split water into its component hydrogen and oxygen is very high. Therefore, research today is being challenged to develop the most energy-efficient and cost-effective ways of electrolyzing water. In particular, high-performance catalysts are needed to initiate, accelerate, and control the necessary chemical reactions.

Metal-semiconductor photocatalysts

It has long been known that semiconductors such as titanium dioxide (TiO₂) can have a photocatalytic effect. When irradiated with ultraviolet light, they are able to oxidize water and thus produce oxygen. The resulting protons can be converted into hydrogen in a second reaction with free electrons. The discovery that there may be great potential for the catalysis of these reactions at the interface between metals and semiconductors has been met with great interest in the scientific community. Of particular interest in this context are titanium dioxide nano-particles on which gold nanoparticles have been placed. Physical processes at the interface between the two particles cause these nanocomposites to be photocatalytically active even in the visible light spectrum.

Recent research has shown that the larger the area of contact, the more efficient such photocatalysts become. If titanium dioxide and gold are combined in one particle, "Janus nanoparticles" are formed, which have two faces, as it were. On the one hand, they have the properties of a semiconductor, on the other hand, those of a metal, depending on which "side" you look at. As a result, higher efficiency can be achieved with these particles in photocatalytic hydrogen production than with the nanocomposites that have been tested as photocatalysts up to now, which have a core/shell structure.¹

Recyclable lattice materials

Most of the photocatalysts used to date have the disadvantage of being difficult to recycle. However, for economic reasons alone, ease of recyclability is

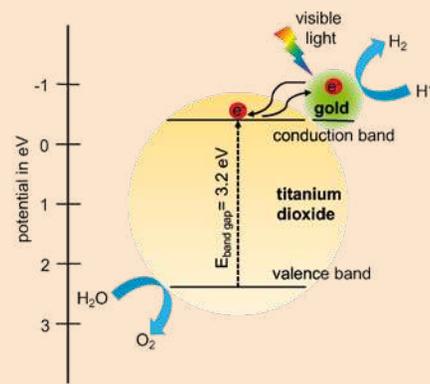
"For the first time, we have succeeded in creating a highly organized hybrid material to which titanium dioxide and gold particles can be attached in a controlled and scalable manner. This hybrid material represents a water-splitting catalyst."

an important prerequisite for large-scale technical applications. For this reason, research today is increasingly focusing on large-area membranes that are structured in such a way as to form a framework for the positioning of photocatalytic nanoparticles. These materials are generally easy to reuse, and greatly differing examples have already proven that they are indeed suitable for the efficient photocatalytic production of hydrogen.

Photocatalytic water splitting is an economical, environmentally friendly, and emission-free method of producing hydrogen using sunlight. By absorbing UV or visible light, the electrons of the valence band of a photocatalyst are excited and transit to the energetically higher state of the conduction band. This change creates positively charged "holes" in the valence band. This state is called the "photo-excited state". The distance between valence band and conduction band is called band gap. In photocatalysis, the holes and the electrons serve as oxidizing and reducing agents to produce oxygen and hydrogen.

For hydrogen production, the conduction band should be lower than the hydrogen production level (0 eV = electron volt), while at the same time the valence band should be more positive than the oxidation level of water (1.23 eV). This results in a band gap of 1.23 eV, which is the minimum required for hydrogen production. Titanium dioxide has a band gap of 3.2 eV, much larger than the required 1.23 eV, and is therefore very well suited for hydrogen production. The band gap of 3.2 eV means that mainly UV light

can be absorbed, so that visible light remains almost unused. However, light absorption can be improved by means of so-called surface plasmon resonance. Noble metals such as gold are usually used for this purpose because they can be excited by visible light. This extends the wavelength range of the absorbed light and thus increases the efficiency of photocatalysis and hydrogen production – but only if the two materials can be brought into direct contact with each other.



■ Fig. 1: The principle of photocatalytic water splitting (Illustration: Tim Schiller).

■ Fig. 2: Muhammad Shakir Bin Zainuddin dissolving eADF4(C16) (spider silk) in hexafluoroisopropanol (HFIP), a strong protein denaturing agent. The solution appears yellowish due to the interaction between the originally white spider silk powder and the colourless HFIP (Photo: Christian Wiffler).

Based on these promising findings, the optimization of lattices has become an important research topic. A good lattice should be mechanically and chemically stable, flexible, and cost-effective. It should be possible to place semiconductor and metal nanoparticles on it in such a way that their surfaces are easily accessible and that the desired catalytic processes can be initiated without hindrance. Various materials have now been successfully tested for such lattice materials: cellulose fibre, cotton fibre, but also silk thread produced by silkworms.²

However, there is one problem that has not yet been resolved. In the synthesis of such membrane systems, the arrangement of the titanium dioxide and metal nanoparticles is very difficult to control. It would be advantageous to use lattice materials whose production would allow the precise determination, in advance, of which photocatalytic nanoparticles will dock to defined parts of the lattice. The materials could then be specifically structured in such a way to subject the nanoparticles to the best possible conditions at their respective positions for using incident light to efficiently split water. In this respect, researchers have recently made significant progress. For example, it has been shown that hybrid materials have clear advantages over purely inorganic or purely organic materials. However in general, the "pre-programming" of the lattices and their precisely controlled loading with nano-photocatalysts is still in its infancy.

■ Fig. 3: Artificial spider web in a laboratory of the Biomaterials research group (Photo: UBT).



Novel hybrid materials on the basis of spider silk

This is exactly the point from which current research work at the Biomaterials research group at the University of Bayreuth sets out. Over the last two decades, interdisciplinary research groups have achieved substantial success in the artificial production and modification of spider silk proteins. Innovative developments have opened up a wide range of application fields, from textiles and cosmetics to the biomedical production of artificial tissue.³ Building on this, Bayreuth researchers have for the first time attempted to use spider silk proteins as an organic lattice material for the photocatalytic production of hydrogen.⁴ Titanium dioxide and gold nanoparticles are meant to form a stable organic-inorganic hybrid material in combination with this lattice material.

From the outset, the Bayreuth research work was geared to

- modifying silk proteins in such a way as to allow the stable positioning of titanium dioxide or gold nanoparticles at predefined sections of these proteins,
- and to producing lattices out of the modified proteins on which the photocatalytic nanoparticles are distributed in exactly this pre-programmed way.

For this research approach, it is crucial that it not be necessary to subsequently modify the already existing proteins of spider silk. Instead, the spider's silk genes are specifically redesigned and complemented with information for new properties, and subsequently introduced into *E. coli* bacteria. The

bacteria then produce proteins that contain "docking possibilities" for photocatalytic nanoparticles at exactly these pre-programmed sites. In this way, it has been possible for the first time to create a highly organized hybrid material to which titanium dioxide and gold particles can be attached in a controlled and scalable manner, while remaining in close contact with each other. This hybrid material represents a water-splitting catalyst. The architecture of the material reflects, on a much larger scale, the pairwise coupling and interaction of titanium dioxide and gold particles, as is characteristic of the catalytically efficient "Janus nanoparticles".

Genetic combinations

In order to be able to produce this hybrid material, it was first of all important to create two new variants of silk proteins. On the one hand, proteins with defined sections for the stable placement of gold particles, and on the other hand, proteins with defined sections for the stable placement of titanium dioxide particles. To enable the binding of titanium dioxide particles, the short titanium-binding peptide QPYLFATDSLK was incorporated into the spider silk protein eADF4(C16). The Bayreuth scientists achieved this on the genetic level by linking a nucleotide sequence encoding the peptide to the gene of the silk protein. The gene modified in this way was inserted into *E. coli* bacteria, which now produced the spider silk protein "eADF4(C16)-TiO₂-bp": This is the chemical name for the well-established protein eADF4(C16), which now additionally contains the titanium-binding sequence – and is thereby equipped with pre-programmed binding sites for the semiconductor titanium dioxide.

For the production of a silk variant that allows the binding of gold particles, an analogous process was initially chosen. However, this caused the problem that so-called inclusion bodies formed in the bacteria. These crystal-shaped accumulations of incorrectly folded proteins hindered the constant production of the spider silk protein "eADF4(C16)-Au-bp" containing the gold binding peptide



■ Fig. 4: Biomimetic spider silk (Photo: UBT).
 ■ Fig. 5: Dissolving of polymers under constant stirring (Photo: Christian Wißler).
 ■ Fig. 6: After dilution, the spinning solution is drawn into a syringe (Photo: Christian Wißler).

■ Fig. 7: Electrospinning process: Sometimes the material solidifies too quickly and blocks the cannula opening. In this case, the solidified tip can be pinched off with tweezers to free the cannula (Photo: Christian Wißler).

■ Fig. 8: Electrospinning process: A drop grows at the cannula opening. If you now place a sufficiently high voltage difference between the cannula and the labboy, a Taylor cone is created, at the tip of which a stream of spinning solution is directed towards the labboy. In flight, the solvent evaporates from the liquid stream, so that only the solidified fibres land on the black paper (Photo: Christian Wißler).

WQVQVEVQVEVQVQVQVWV. In response, the Bayreuth scientists developed an alternative strategy to produce a suitable silk variant. A cysteine residue was incorporated into the protein at a selected site. This cysteine residue is able to bind gold nanoparticles, which are specially coated for this purpose, in a controlled manner.

The new hybrid material: A structured film with nano-photocatalysts

On this basis, it is now possible to synthesize the desired hybrid material with alternating titanium dioxide and gold particles. The two silk variants are first processed into a structured film: The material for the base layer consists of positively charged proteins of the "gold-binding" silk variant. Negatively charged proteins of the "titanium dioxide binding" silk variant are then applied in strips to the base layer. Now there is nothing to stop the targeted mineralization of the films with titanium dioxide and gold nanoparticles. These particles find a stable position exactly where they are supposed to be, implementing the structure pre-programmed into the film.

Extensive experiments in the Bayreuth laboratories, which were carried out together with a cooperation partner at the University of Potsdam, have clearly shown that these hybrid film systems are ideally suited as catalysts for the splitting of water. Moderate irradiation with light is an indispensable prerequisite for this to happen. In order to make these

■ Fig. 9 (left below): Electrospinning process: Backlighting helps to identify the Taylor cone, the point of origin of the spun thread (Photo: Christian Wißler).

■ Fig. 10 (right below): Tim Schiller modifying films of spider silk protein with gold nanoparticles (Photo: Christian Wißler).



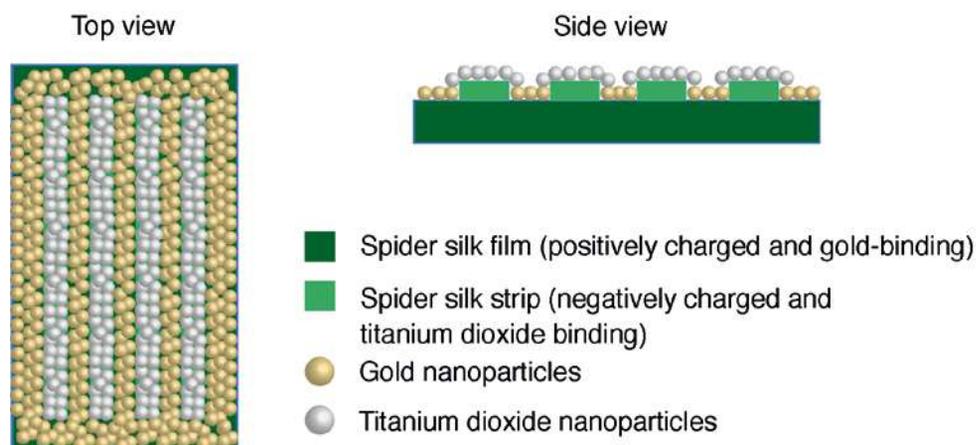
2D methods scalable, Janus fibres are made from spider silk by means of electric spinning. One side of these fibers has the titanium dioxide binding properties, the other side has the gold binding properties. With the help of these Janus fibers it is then possible to produce flow membranes that will enable continuous hydrogen production. The new "bio-inspired" material based on spider silk thus opens the door to producing photocatalytically active membranes for the production of "green" hydrogen, which could soon prove to be the key fuel of the 21st century.

Numerous detailed questions are currently being examined more closely in Bayreuth. An important goal is to understand the connection between the arrangement of the inorganic nanoparticles in the film system and the respective photocatalytic efficiency. It will then be possible to regulate hydrogen production as required and to increase it beyond the level of efficiency achieved to date.



■ Fig. 11: Light microscopic image of the structured spider silk membrane: the positively charged protein forms the base film to which the negatively charged protein has been applied in strips. The spider silk protein in the strips has been marked with a fluorescent dye (green) to make it more visible (Image: Thomas Scheibel).

■ Fig. 12: The structure of the new hybrid film system based on spider silk (Illustration: Thomas Scheibel).



AUTHORS



■ Prof. Dr. Thomas Scheibel is the Chair of Biomaterials at the University of Bayreuth.



■ Muhammad Shakir Bin Zainuddin is a doctoral researcher at the Biomaterials research group at the University of Bayreuth.



■ Tim Schiller is completing his Master's degree in Biochemistry and Molecular Biology at the University of Bayreuth.

- 1 S. Rawalekar, T. Mokari: Rational design of hybrid nanostructures for advanced photocatalysis. *Advanced Energy Materials* (2013), 3(1), 12-27. DOI: 10.1002/aenm.201200511; Z. W. Seh et al.: Janus Au-TiO₂ photocatalysts with strong localization of plasmonic near-fields for efficient visible-light hydrogen generation. *Advanced Materials* (2012), 24(17), 2310-2314. DOI: 10.1002/adma.201104241.
- 2 S. Krüger et al.: *Bombyx mori* silk/titania/gold hybrid materials for photocatalytic water splitting: combining renewable raw materials with clean fuels. *Beilstein Journal of Nanotechnology* (2018), 9, 187-204. DOI: 10.3762/bjnano.9.21.
- 3 K. Spiess, S. Wohlrab, T. Scheibel: Structural characterization and functionalization of engineered spider silk films. *Soft Matter* (2010), 6(17), 4168-4174. DOI: 10.1039/B927267D; J. Petzold et al.: Surface Features of Recombinant Spider Silk Protein eADF4(k16)-Made Materials are Well-Suited for Cardiac Tissue Engineering. *Advanced Functional Materials* (2017), 27 (36), 1701427. DOI: 10.1002/adfm.201701427.
- 4 The research work was carried out in cooperation with scientists at the University of Potsdam.

SUSTAINABLE PRODUCTION

■ Rhett Kempe

Sustainability₃

Chemical reactions for the
production of hydrogen

■ 3D model of hydrogen molecules (H_2) (sst).

The sustainable use of the resources of our planet, especially of the available chemical elements, is essential for life on earth. It is also a central prerequisite for high living standards in future generations, and is closely linked to other important global challenges, such as climate protection. Chemistry is the science that deals with the transformation of substances, and based on its findings, the chemical industry provides the material basis for many products of daily life, or manufactures these products itself. It is therefore "at the coalface" of the sustainable use of our (elemental) resources.

At the University of Bayreuth, the Inorganic Chemistry II – Catalyst Design research group is concerned with the development of a "New Sustainable Chemistry". It is working towards ensuring that carbon-containing products that we need or use every day, such as medicines or plastics, are produced from renewable resources such as biomass – and not, as has been the case up to now, from finite fossil sources of the element such as coal, oil, or natural gas. This does not, of course, mean that carbon-containing products for daily use should be produced from potential food products, as is currently (and irresponsibly) the case with fuels such as "bio-diesel". Rather, the aim is to use biomass which has not been usable as a source of carbon to date, but is available in large quantities, and is unsuitable as food.

Of particular interest here is the vegetable material lignocellulose, which is contained, for example, in straw, rice husks, and waste from the paper industry. These waste products can be converted into alco-

hols – compounds that by definition contain an OH group. The alcohols obtained from these waste materials are referred to here as "bioalcohols". The central question now is: How can we convert the bioalcohols into all the important carbon-containing products that we have learned to appreciate in our everyday lives, and on which we are in some cases even dependent? The challenge here is to leave the classical pathways to carbon-containing products, and to pursue "New Sustainable Chemistry" instead (Fig. 1).

Alcohol chemistry – a key to sustainable hydrogen production

This is exactly where the Bayreuth catalyst research at the Inorganic Chemistry II research group comes into play. With the aim of efficiently and selectively converting alcohols, catalysts, small molecular machines, and nanomachines are being designed that are capable of carrying out the respective chemical reactions over and over again. One focus in recent years has been the production of aromatic N-heterocycles. These are cyclic compounds whose rings contain both nitrogen and at least one other chemical element. They are important components in many medicines.¹ Moreover, chemical reactions in which hydrogen is produced have been key to the production of these molecules. For example, about 66 litres of hydrogen are produced when only 80 grams of pyridine is synthesized.² Pyridine is an example of a heterocyclic motif that occurs in about 7,000 pharmacologically active substances.

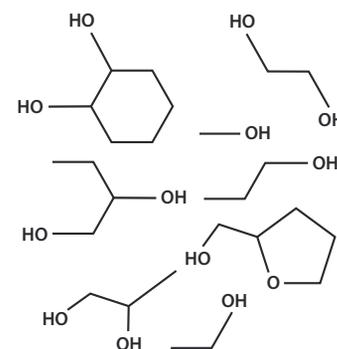
■ Fig. 1: In classical "petroleum chemistry", crude oil is converted into olefins, chemical compounds with a C-C double bond, to produce the all-important carbonaceous products (left). The central challenge of the "New Sustainable Chemistry" is to "invent" the chemical reactions which will make these products accessible on the basis of alcohols (right) (Photos: sst, Illustration: Rhett Kempe / Andreas Gaube).



Lignocellulose



Alcohols



■ Fig. 2: Within the framework of "New Sustainable Chemistry", carbon atoms are taken from CO₂ in the air to produce carbon-containing products for daily use. This process produces hydrogen, an important energy carrier, and combines chemistry with nature (Illustration: Rhett Kempe).

CO₂ (diluted in air)

Nature & Chemistry

Carbonaceous products



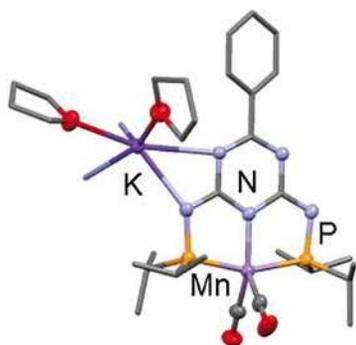
AUTHOR



■ Prof. Dr. Rhett Kempe is the Chair of Inorganic Chemistry II – Catalyst Design at the University of Bayreuth.

However, alcohols are not very reactive: There are relatively few reactions that they will willingly undergo. A core problem of "New Sustainable Chemistry" has therefore been to get that "lazy" alcohol "going". If a suitable catalyst is added, it can extract hydrogen from the alcohol. This chemical reaction is called dehydrogenation.³ When hydrogen is removed from the alcohol, it is transported to the catalyst. Chemical compounds are formed which readily undergo a variety of reactions. At this point, there are various options for how to proceed. Since 1932, it has been known that the catalyst can simply pass the hydrogen on to another chemical compound, to again – as one would expect from a catalyst – mediate the dehydrogenation step. Unfortunately, the hydrogen is "lost" in the process. In the laboratories of the Bayreuth Catalyst research group, however, catalysts have been developed which do something different: namely, release the hydrogen as an H₂ molecule, i.e. as a gas.

The "New Sustainable Chemistry" being used here, is thus sustainable in two respects: Renewable resources are used instead of petroleum, and hydrogen is generated on the basis of alcohol chemistry. Because in chemistry, multiplication is indicated by a lowered appended number, we could well call this *Sustainability*₂. This concept is particularly interesting because it combines nature and chemistry to produce carbonaceous products. The "raw material" used in this process is ultimately carbon dioxide (CO₂) from the air, where as a persistent greenhouse gas, it can have climate-damaging consequences (Fig. 2).



■ Fig. 3: Structure of a manganese catalyst: N = nitrogen (light blue); P = phosphorus (orange), K = potassium (violet). Grey atoms represent carbon and red atoms represent oxygen. The central manganese atom (Mn) is shown in light violet (Illustration: Rhett Kempe).

Bayreuth research success: On track for sustainable catalysts

One unresolved problem with regard to the sustainability aspect, was until recently the catalyst. The best catalysts used in the production of aromatic N-heterocycles from alcohols with the release of hydrogen had been based on the metal iridium (Ir). However, iridium is very rarely found in the earth's crust. Consequently, research at Inorganic Chemistry II was aimed at replacing it with a much more common metal such as cobalt, iron, or manganese. Replacing rare chemical elements used in key technologies with abundant elements is generally considered an important means of conserving the earth's resources. With its work on manganese (Mn), the third most common transition metal in the earth's crust, the Bayreuth working group has hit the jackpot.⁴ Manganese proved to be highly suitable for replacing iridium in hydrogenation and dehydrogenation catalyses.

This research result came as a great surprise to the experts, as it was not known until 2016 that hydrogen could be catalytically activated with Mn compounds at all. Indeed, very well defined Mn complex compounds are necessary for this. Recently, the Bayreuth research group was able to define what such Mn catalysts look like, and how they work.⁵ An Mn catalyst can react with hydrogen and split it into H⁺ (proton) and H⁻ (hydrid) (Fig. 3). In this process, the hydride is "parked" on the metal while the proton migrates to the ligand. When the hydrogen is released from alcohols, this process is reversed, or chemically speaking, inverted. In this process, the proton and the H⁻ ion are removed from the alcohol, "parked" on the catalyst, and then brought together. The result is gaseous hydrogen. With this innovative process, Bayreuth's catalysis research has proven to be sustainable with regard to the catalyst metal as well – and thus in a third respect: The leap to *Sustainability*₃ has been achieved.

Prospects

In the 20th century, catalysis developed into a technology that is present in almost all areas of the economy and society. As sustainable catalysis, it will be a key technology of the 21st century, and indispensable in facing global challenges. It will potentially make a vital contribution to a hydrogen-based way of life.

- 1 S. Michlik, R. Kempe: A sustainable catalytic pyrrole synthesis. *Nature Chemistry* (2013), 5 (2), 140-144. DOI:10.1038/nchem.1547.
- 2 S. Michlik, R. Kempe: Regioselectively functionalized pyridines from sustainable resources. *Angewandte Chemie International Edition* (2013), 52 (24), 6326-6329. DOI: 10.1002/anie.201301919.
- 3 The term is often mistakenly used in the media to refer to the removal of water – instead of hydrogen.
- 4 N. Deibl, R. Kempe: Manganese-Catalyzed Multicomponent Synthesis of Pyrimidines from Alcohols and Amidines. *Angewandte Chemie International Edition* (2017), 56 (6), 1663-1666. DOI:10.1002/anie.201611318.
- 5 F. Freitag, T. Irrgang, R. Kempe: Mechanistic Studies of Hydride Transfer to Imines from a Highly Active and Chemoselective Manganate Catalyst. *Journal of the American Chemical Society* (2019), 141 (29), 11677-11685. DOI:10.1021/jacs.9b05024.

A model of Sustainability₃

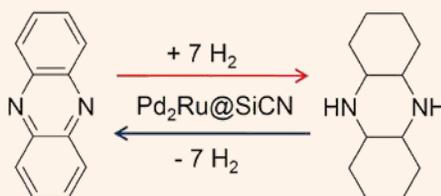
Hydrogen storage with a powerful catalyst

New technology for storing hydrogen will be a central component of a sustainable energy economy, generating a growing share of the energy required from renewable sources such as the sun and wind. The process of storing this share must therefore be made as efficient and sustainable as possible. Liquid Organic Hydrogen Carriers (LOHC) offer a promising solution in this regard. They are organic compounds that can absorb and release hydrogen. Notable examples of these are the already mentioned N-heterocycles: small molecules consisting of carbon rings which contain nitrogen atoms instead of carbon atoms at certain points. Belonging to this family of molecules is N-ethylcarbazole (NEC). Under suitable temperatures and pressures, it is capable of binding and releasing 12 hydrogen atoms. Both chemical reactions are initiated and controlled by a catalyst.

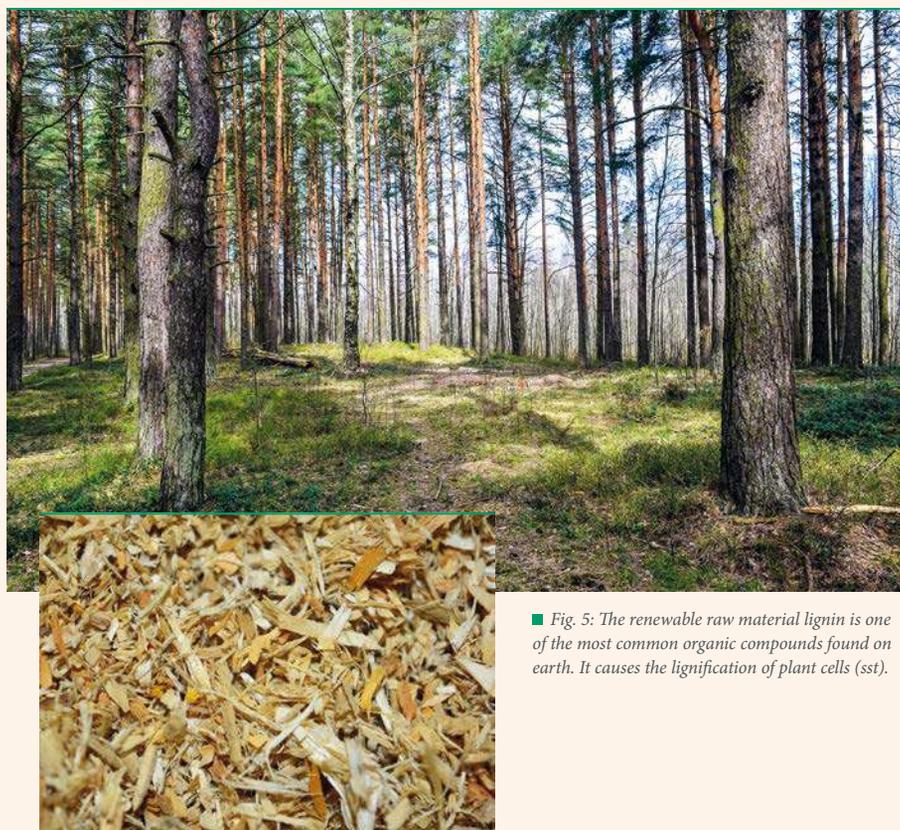
A research team at the Inorganic Chemistry II – Catalyst Design research group has succeeded in developing a catalyst that makes far better use of the storage potential of NEC molecules than other compounds. The new catalyst contains two metals, palladium (Pd) and ruthenium (Ru), which have been applied to a silicon carbon nitride (SiCN) backbone. The chemical formula thus reads: Pd₂Ru@SiCN. With this compound, it is possible to bind an unusually high number of hydrogen atoms to NEC molecules and to release them again if necessary.

NEC molecules, and other liquid organic hydrogen carriers that have been used for hydrogen storage so far, have ultimately all come from fossil sources such as coal and oil. But with the new catalyst, the Bayreuth research team has for the first time been able to produce a hydrogen carrier of this type from a renewable raw material. This material is lignin: a waste product of wood processing that has to date found hardly any industrial use, and is not suitable for food production, either. It can be used to produce phenazine without any great technical effort. Phenazine molecules consist of three chained carbon rings, with two carbon atoms in the middle ring being replaced by nitrogen atoms. Pd₂Ru@SiCN makes it possible to bind 14 hydrogen atoms in a phenazine molecule and to release them at any time.

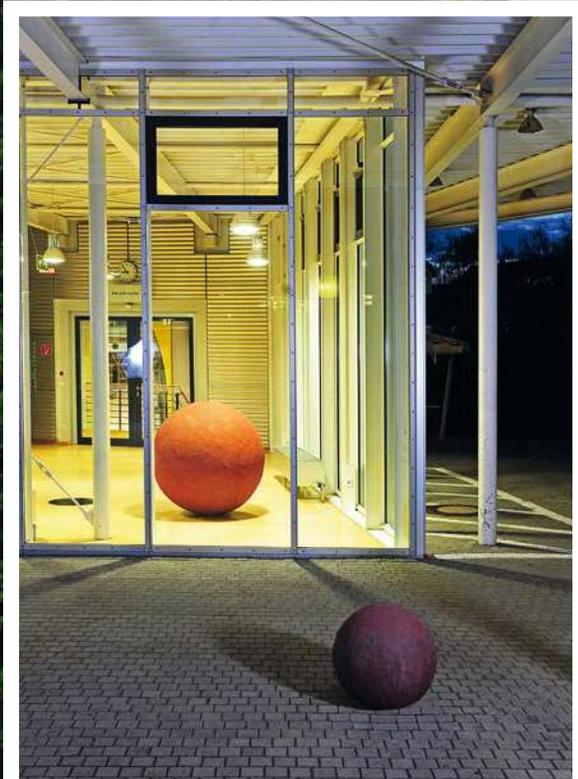
This system of hydrogen storage thus even improves on the performance achieved with NEC. While the hydrogen bound in NEC accounts for a maximum of about 5.8 percent by weight of the entire molecule, phenazine achieves a figure of 7.2 percent. Phenazine therefore provides an ideal medium for hydrogen storage in the 21st century: It comes from a plant-based raw material that is available in large quantities and in no way competes with the growing global demand for food.



■ Fig. 4: Hydrogen loading and unloading of a phenazine molecule with the new catalyst Pd₂Ru@SiCN (Illustration: Rhett Kempe).



■ Fig. 5: The renewable raw material lignin is one of the most common organic compounds found on earth. It causes the lignification of plant cells (sst).



"Connecting the inside to the outside"

In 1994, the Audimax was opened on the campus of the University of Bayreuth: a modern building complex with large areas of exterior glass designed by the architectural firm Dürschinger of Fürth. In 1999 a floor sculpture was installed in the upper light-flooded foyer of the building and to its exterior. It takes up the circular arc as the architectural leitmotif of the building, and was created by the award-winning artist Gisela Kleinlein, born in Nuremberg in 1955.

About her installation on campus, the artist says: "When you get closer to the building of the Audimax, you can see a reddish brown sphere located under the canopy next to one of the supporting columns. Behind it, in the interior, close behind the disc, there is another sphere, with a diameter more than twice as large. Next to it, in turn, the parquet flooring seems to sport a circular opening. What appears at first glance to be a yawning hole, turns out, in fact, to be a reflective, black disc, set level into the floor. The trio look as though they belong together, and yet the parts seem isolated. Reflections in the expanse of window glass lead to the superposition and pervasion of these circular shapes, connecting the inside to the outside."