





May 2018
Position Paper

Artificial Photosynthesis

State of Research, Scientific-Technological Challenges and Perspectives

German National Academy of Sciences Leopoldina | www.leopoldina.org acatech – National Academy of Science and Engineering | www.acatech.de Union of the German Academies of Sciences and Humanities | www.akademienunion.de

Imprint

Publishers

acatech – National Academy of Science and Engineering (lead institution) acatech Office: Karolinenplatz 4, 80333 München

German National Academy of Sciences Leopoldina Jägerberg 1, 06108 Halle (Saale)

Union of the German Academies of Sciences and Humanities Geschwister-Scholl-Straße 2, 55131 Mainz

Editor

PD Dr. Marc-Denis Weitze, acatech

Translators

Paul Clarke (FITI) & Charlotte Couchman (FITI), Lodestar Translations

Design and typesetting

unicommunication.de, Berlin

ISBN: 978-3-8047-3645-0

Bibliographic information of the German National Library

The German National Library lists this publication in the German National Bibliography. Detailed bibliographic data is available online at http://dnb.d-nb.de.

Recommended citation:

acatech – National Academy of Science and Engineering, German National Academy of Sciences Leopoldina, Union of the German Academies of Sciences and Humanities (Eds.) (2018): Artificial Photosynthesis. Munich, 74 pages.

Artificial Photosynthesis

State of Research, Scientific-Technological Challenges and Perspectives

Contents

Abst	tract	and s	ummary of recommendations	4
1.	Int	roduc	tion	8
	1.1	Move	away from fossil resources and global changeover to a CO ₃ -neutra	I
		energ	y supply	9
	1.2	Energ	y supply in Germany	10
	1.3	Biolog	gical photosynthesis	14
	1.4	Artific	cial photosynthesis	16
	1.5	Previe	ew of the following sections	19
2.	Sta	te of ı	research and current challenges	20
	2.1	Biolog	gical, modified and hybrid photosynthesis	21
		2.1.1	Advantages and drawbacks of biological photosynthesis	21
		2.1.2	Modified photosynthesis	22
		2.1.3	Hybrid photosynthesis	26
	2.2	Sub-p	rocesses of artificial photosynthesis	28
		2.2.1	Light absorption and charge separation	28
		2.2.2	Catalysts and efficiency of chemical sub-processes	32
		2.2.3	Water oxidation and O ₂ evolution	32
		2.2.4	Proton reduction, H ₂ evolution	35
		2.2.5	CO ₃ reduction	37
		2.2.6	Ammonia production	43
	2.3	Artific	cial photosynthesis – systems integration	44
		2.3.1	Separate PV-driven electrolysis systems	44
		2.3.2	Integrated photovoltaics/electrolysis systems	46
		2.3.3	Photoelectrocatalysis on semiconductor surfaces	
		2.3.4	Artificial leaves	
		2.3.5	Systems integration in a nutshell	
	2.4	Altern	native approaches	
		2.4.1	Use of visible light for chemical synthesis	
		2.4.2	Synthetic motor fuels from solar thermochemical conversion	
	2.5	Summ	, nary	

3.	State of research and social context	56
	3.1 Research activities and funding programmes	. 56
	3.1.1 Germany	. 56
	3.1.2 Europe	. 57
	3.1.3 Worldwide	. 58
	3.2 Challenges from the viewpoint of industry experts	60
	3.3 Social aspects – ethics and communication	
	3.3.1 Ethical issues around technology assessment and technological futures .	. 62
	3.3.2 Communication and participation	. 64
	3.4 Summary	. 66
4.	Recommendations	67
5.	References	73
Parti	icipants in the project	77
App	endix	79

Abstract and summary of recommendations

Maintaining an energy supply while minimising impact on the environment and climate is one of the greatest social and scientific challenges of our times. Coal, oil and natural gas have to replaced by $\rm CO_2$ -neutral fuels and valuable products if the effects of climate change are to be mitigated. There is one important prerequisite: renewable energy carriers can only contribute to climate protection if they can be produced sustainably.

Artificial photosynthesis is one possible approach. Photosynthesis is a process which produces chemical energy carriers and organic valuable products using sunlight as the sole energy source. In biological photosynthesis, plants, algae and bacteria use the energy from the sunlight to produce biomass from carbon dioxide and water, while artificial photosynthesis yields products such as hydrogen, carbon monoxide, methane, methanol or ammonia, as well as more complex substances, capable of replacing fossil fuels and resources. These energy-rich substances can be transported, stored and subsequently used in the energy and resource system. Successful use of artificial photosynthesis on a large scale would bring about a considerable reduction in anthropogenic CO₂ emissions since fewer fossil resources would have to be extracted and combusted.

Solar production of fuels and valuable products from the limitless supplies of water and air components (CO₂ and nitrogen) can thus make a contribution to the energy transition and climate protection. There are various fields of research and technological developments in this con-

text but the focus of the present study is on artificial photosynthesis:

- Modified biological photosynthesis: fuels and valuable products are produced by genetically engineered photosynthetic microorganisms. This approach is particularly suitable for producing relatively complex substances such as carboxylic acids. This technology does not take the roundabout route via biomass, which is a central feature of the now well established production of biofuels or biopolymers from maize or other energy crops.
- Combining biological and nonbiological components to create hybrid systems: This makes use of renewably generated electricity for the electrolytic production of hydrogen and carbon monoxide which are converted into fuels and valuable products by microorganisms in bioreactors.
- Power-to-X technologies: These processes use electricity from renewable sources off the grid for the electrochemical synthesis of fuels or valuable products. These include, for instance, hydrogen, ethylene or, in multistage processes, methane (natural gas), alcohols or hydrocarbon-based plastics.
- ergy is converted with the assistance of catalytic processes and used for producing fuels and valuable products. Production takes place in completely integrated systems such as for example "artificial leaves" or by directly combining photovoltaic and electrolysis systems. The advantage of this approach is that the substances produced can be stored, stockpiled and transported.

The scientific basis for artificial photosynthesis has been thoroughly investigated over the last two decades. Building on these foundations, highly promising test systems have already been developed in German and international projects which have primarily investigated and optimised sub-reactions of the overall processes. Various fuels and valuable products can now successfully be produced using sunlight as the sole energy source while completely dispensing with fossil starting materials. While the first relatively large power-to-X plants have already begun test operation, artificial photosynthesis in contrast still largely remains at the level of basic research. Suitable systems are so far still at the laboratory prototype stage which means that a reliable cost-benefit analysis and an economically justifiable outlook for the future are as yet not possible.

The progress which has been made in recent years means that large-scale industrial production of "solar fuels and valuable products" is now entering the realm of the possible. Industry experts see scalability of the existing approaches as being the essential challenge. Interfaces and connection points to existing technologies, for example for efficiently combining photovoltaic and electrolysis systems, are becoming apparent. However, large-scale industrial use of artificial photosynthesis and an associated move away from a fossil energy supply can only be successful if the opportunities and challenges presented by this new technology are widely debated across society from an early stage.

Recommendations by the Academies

The fuels and valuable products produced by artificial photosynthesis can help to replace fossil resources in future. Artificial photosynthesis can make a major contribution to making the energy transition a reality. The following recommendations from the German Academies of Sciences to the worlds of politics, science and business and to society as a whole suggest how this might be achieved:

1: Inclusion of new technologies for sustainable production of fuels and valuable products in future scenarios

If energy supply needs in the year 2050 are to be met entirely or at least largely without fossil fuels, wind and solar systems will play a central role, but their output varies. The energy supply could be secured if large quantities of fluctuating solar and wind energy were stored for an extended period in the form of non-fossil fuels (chemical energy storage). Artificial photosynthesis offers a further method for also obtaining chemical valuable products from the limitless supplies of air components (CO₂ and nitrogen) and water using renewable energy sources. Solar production of fuels and valuable products from water and CO₂ should therefore in future be included to a greater extent in national and global plans for energy production and climate protection.

2: Continuation of wide-ranging basic research

In Germany, research into the sustainable production of fuels and valuable products is taking place in numerous individual projects and interdisciplinary research groups. Depending on the project, researchers are addressing different issues, for example investigating new light absorbers and developing catalysts and processes in synthetic biology. Other projects, for instance, are researching how CO₂ can be used for producing plastics, how pilot plants might be constructed and controlled or how sustainable materials cycles can be economically modelled. This diversity makes sense and should be retained. Basic research could in this way enable "game-changing" scientific and technical innovations.

3: Stronger coordination between basic and industrial research

If fuels and valuable products are to be produced sustainably using artificial photosynthesis technologies, research and development projects will have to be better coordinated and interlinked. Such coordination could be provided by existing bodies such as the collaborative research projects organised by the Federal Ministries, excellence clusters or research centres, for instance along the same lines as the "Kopernikus" energy transition projects. Since it remains unclear how largescale industrial systems can be optimally planned and set up, industrial research teams should also be involved in this process from an early stage. Only in this way will it be possible to identify clear economic prospects for the production of non-fossil fuels and valuable products while taking account of societal and legislative constraints.

4: Focus on systems integration and evaluation of the cost benefits of highly integrated artificial photosynthesis systems

Artificial photosynthesis technologies are the link between the conversion of solar energy and the production of fuels and valuable products. Integration in a device or compact system could make it possible to produce the substances more efficiently and cost-effectively. Numerous individual components for artificial photosynthesis, some of which already perform very well, are already known and have been thoroughly investigated in the laboratory. Nevertheless, research and development of these systems is still at an early stage. Above all, it is unclear how key individual processes can be sensibly combined and integrated into the overall system. Power-to-X technologies are based on the same key chemical processes, but use electricity from the power grid as their energy source. The technical implementation of power-to-X has been more thoroughly researched than has the

application of artificial photosynthesis. In order to investigate how and where artificial photosynthesis might be a meaningful complement or alternative to power-to-X technologies, the Academies recommend an approximately ten year research and development phase for integrated laboratory systems and pilot plants, followed by a critical evaluation.

5: Evaluation of the potential of artificial photosynthesis

There are scientific, technological, economic, ethical and societal dimensions to the reorganisation of the energy and resource system. It will require a wide-ranging discussion between scientists, engineers, economists and social scientists and representatives from industry. The goal is to make a realistic assessment of the potential of artificial photosynthesis in terms of scalability, energy efficiency, process engineering and costs before promising approaches are further developed for large-scale industrial application. In the light of intense international competition and the seriousness of the aim, this assessment should be carried out with care to make sure that highly promising research and development projects are not prematurely brought to an end.

6: Intense dialogue within society about artificial photosynthesis in the context of the energy transition

The transformation of the energy system into a system based on renewable energy concerns every group in society. Therefore, citizens should early be made aware of this new technology which, in the long-term, could replace fossil energy carriers. Obtaining "renewable" fuels and valuable products by artificial photosynthesis plays a major role in this context. Given the current early stage of development of artificial photosynthesis, there is a need for this technology to be discussed objectively, transparently and without any preconceptions. It is particularly important to provide information about aspects

such as security of supply, the availability of natural resources and climate impact. There is a need not only for communication of the scientific and technical principles and current research results but also for a clear explanation of the economic and environmental interrelationships. Information communicated via media channels can be helpful in raising the profile of this issue in society as a whole. In addition to the media, scientists, together with other stakeholders, will in future also have to maintain stronger direct contact with civil society organisations. If the public is involved in decision-making processes from an early stage, it will be possible to clarify the conditions which have to be met to ensure acceptance of these new technologies. The Academies can helpfully assist this social dialogue by providing discussion for aand exchange platforms.

1. Introduction

Securing a sustainable energy supply is one of the central challenges facing science and technology. Today, wind and solar energy are already being used for generating power, and the development of technologies for efficiently and affordably storing the energy from sunlight will in future very probably become more significant. Plants and phototrophic microorganisms have mastered this conversion via biological photosynthesis, in which carbohydrates are obtained from water (H_2O) and carbon dioxide (CO_2) by means of sunlight. Molecular oxygen (O_2) is here liberated into the atmosphere as a secondary product.

The goal of this position paper is to explain developments in artificial photosynthesis technologies for the production of fuels and valuable products. These are, in principle, even on a large industrial scale, an alternative to the use of fossil fuels and can therefore, in the long term, make a significant and sustainable contribution to mitigating the effects of climate issues. The starting point of the analysis is biological photosynthesis, in which, with the assistance of sunlight and the release of oxygen, organisms split water and then convert CO₂ into biomass. Modifications to biological processes are initially discussed and then hybrid systems which combine natural and synthetic components are considered. This position paper above all focuses on photochemical processes which are inspired by nature and primarily consist of synthetic components. These systems are known as "artificial photosynthesis"1 the primary goal of which is

German makes use of the term "Künstliche Photosynthese".

to use solar energy for the climate-neutral production of fuels and chemical products from readily available starting materials (water, carbon dioxide and nitrogen).²

The idea of using sunlight directly instead of fossil resources and catalytically converting carbon dioxide is not in any way new.3 "Artificial photosynthesis" has in preceding years already been examined by various international organisations and generally evaluated as highly promising, for instance by the Royal Society of Chemistry4, the European chemical sciences organisation EuCheMS⁵ and the European Commission⁶. The present position paper updates and supplements publications by the Academies on related topics, including Biotechnological energy conversion (2012)7, Bioenergy: possibilities and limits (2012)8 and Jointly shaping technology. Early public involvement based on the example of artificial photosynthesis (2016)9. The Academies' position paper "Combining sectors – options for the next phase in the energy transition" (2017)10 sets out major considerations on this issue with regard to the energy transition.

² This position paper does not address the conversion of biomass into bioenergy, which was the subject matter of earlier studies by the Academies (acatech 2012a, German National Academy of Sciences Leopoldina 2013) and is again being tackled in the Academies' ESYS project (https://energiesysteme-zukunft.de/projekt/ arbeitsgruppen/).

³ Ciamician 1912.

⁴ The Royal Society of Chemistry 2012.

⁵ European Association of Chemical and Molecular Sciences (EuCheMS) 2016.

⁶ Directorate-General of Research and Innovation (European Commission) 2016.

⁷ acatech (ed.) 2012a.

⁸ German National Academy of Sciences Leopoldina 2013.

⁹ acatech 2016.

¹⁰ acatech et al. 2017.

Definition: artificial photosynthesis

Artificial photosynthesis serves to produce chemical energy carriers and valuable products using sunlight as the sole energy source in integrated apparatuses and systems. The particular strength of this approach lies in the provision of renewable energy stored in material form which can be stockpiled and transported. This is achieved by mimicking a central principle of the biological model: combining light-induced charge separation with catalytic processes for the production of energy-rich compounds.

1.1 Move away from fossil resources and global changeover to a CO₂-neutral energy supply

Between 1973 and 2014, the annual world energy demand doubled from 4,661 million tonnes of oil equivalent to 9,425 million tonnes11 and is expected to double again by 2050. Rising energy demand has previously mainly been met by an expansion in the use of fossil fuels, i.e. oil, natural gas and coal. Use of non-fossil energy resources (hydroelectric power, nuclear energy, wind/solar electricity, bioenergy and other renewable energies) is, however, also growing strongly worldwide and now accounts for 14 per cent of total consumption worldwide (see figure 1-1 A). In addition to being used as fuels, oil and natural gas are in particular also used as starting compounds in the chemicals industry for producing valuable products such as polymers or fertilizers. However, in comparison with energy use (combustion), which constitutes 97 per cent of fossil energy carrier consumption, this proportion is very small (see figure 1-1 B).

While the availability of oil and natural gas beyond 2050 can be predicted only with difficulty, it may relatively reliably be assumed that coal extraction could meet humanity's energy demand for

some centuries. 2 Consequently, a general move away from using fossil fuels during the 21st century is not absolutely necessary due to exhaustion of their sources. However, unpredictable trends in prices, inadequate security of supply in the event of unfavourable geopolitical developments and ecotoxicological consequences (for example airways diseases due to nitrogen oxides, carcinogenic aerosols, exposure to fine particulates etc.) are significant risk factors which are linked to the use of fossil fuels and the associated emissions.

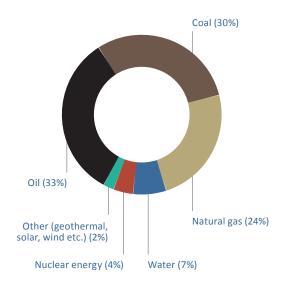


Figure 1-1 A: World supply of commercially traded energy carriers for 2016. At present fossil energy carriers (oil, natural gas and coal) provide more than 85 per cent of the world's primary energy supply.¹³

¹² Federal Institute for Geosciences and Natural Resources (BGR) 2016, p. 91.

¹³ BP 2017, p. 9.

¹¹ International Energy Agency 2016, p. 28.

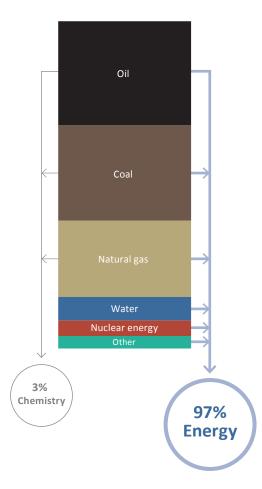


Figure 1-1 B: Worldwide, only 3 per cent of fossil fuels are used for direct conversion into valuable products in the chemicals industry while the remainder of these fossil resources formed over millions of years is burnt.¹⁴

The most important reason for moving away from using fossil energy carriers is today considered to be climate issues. Burning fossil energy carriers is associated with huge emissions of CO_2 into the world's atmosphere, ¹⁵ which are considered to be the primary cause of global climate change. According to current science and research, there is a causal link between the rise in CO_2 content in the atmosphere caused by burning fossil fuels and a global

The link between $\mathrm{CO_2}$ emissions from anthropogenic processes and the resultant climate change is today also largely accepted worldwide at a political level. This acceptance found its expression in the Paris Agreement, which came into force on 4 November 2016 and sets goals for reducing $\mathrm{CO_2}$ emissions.¹⁷

1.2 Energy supply in Germany

The Paris Agreement provides for the avoidance of any net anthropogenic CO₂ emissions in the second half of this century in order to keep the average increase in global temperature to well below 2 degrees Celsius. Industrialised nations such as Germany are intended to achieve such "CO₂ neutrality" sooner than are current emerging and developing countries. The German government's "Climate Protection Plan 2050" is guided by this mission statement and sets the goal of Germany being largely neutral in greenhouse gas emissions by 2050.

rise in temperatures (see figure 1-2).¹⁶ This climate change is a genuine danger with serious local and global impacts, including environmental, economic and humanitarian disasters.

¹⁶ A detailed scientific assessment of the extensive data set relating to climate change has been carried out under the auspices of the Intergovernmental Panel on Climate Change (IPCC). In addition to CO₂, further "greenhouse gases" are contributing to global climate change. Their contribution is, however, smaller overall and in part likewise associated with the use of fossil fuels, such as for example methane emissions from the extraction and transport of oil and natural gas or the formation of nitrogen oxides from burning fossil fuels. Cf. Intergovernmental Panel on Climate Change (IPCC) 2014.

^{17 &}quot;In order to achieve the long-term temperature goal of holding the increase in the global average temperature to well below 2°C, Parties aim to undertake rapid reductions in greenhouse gas emissions in accordance with best available science, so as to achieve a balance between anthropogenic emissions by sources and removals by sinks of greenhouse gases in the second half of the 21st century." Cf. Paris Agreement, cited from European Commission 2017.

¹⁸ Federal Ministry for the Environment, Nature Conservation, Construction and Nuclear Safety (BMUB) 2016.

¹⁴ Seitz 2013, p. 23.

¹⁵ International Energy Agency 2016 for numerical values.

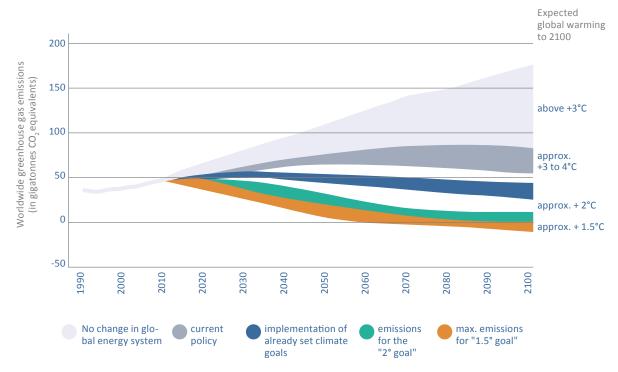


Figure 1-2: Alternative scenarios for net CO₂ emissions up to year 2100. Implementation of climate goals which have already been set (in particular by the Paris Agreement) makes it 80 per cent probable that the increase in global temperature will be held below 2 degrees Celsius.¹⁹

In particular the government will endeavour to ensure that by 2050 the use of fossil fuels in Germany is the exception. In the light of the level of Germany's primary energy consumption (sum of all energy carriers used for heating, industrial production, transport, agriculture etc.) this is a necessary goal which will demand significant effort.

As in the past, primary energy consumption in Germany is primarily met by fossil energy carriers, accounting for 80 per cent in 2015 (see figure 1-3, left). Taking electricity in isolation, there has been a considerable increase in provision by renewable energies in particular over the last ten years. Above all, an expansion in photovoltaics, wind power and bioenergy for electricity generation in Germany has led to a continuous rise in the production of "renewable electricity", which now (2016) accounts for over 30 per cent of annual electricity output. In

a highly populated industrial nation, this extraordinary development supported by a legal framework (Germany's Renewable Energy Sources Act (EEG)) has also attracted much attention internationally and serves as a model for the world. The public perception of the significance of electricity generation by wind, water and sun is, however, often overestimated: the high proportion of these renewable energy sources relates only to the electricity sector, but not to transport fuels and heating, which means that it only accounts for 4 per cent of Germany's overall primary energy consumption (see figure 1-3, right).

In future, the majority of electricity will probably be provided by wind power and photovoltaics (PV). There is a need for easily storable energy carriers so that even a gap of several weeks with little wind and sunshine can be bridged. Over half of the renewable energy sources currently in use are based on the conversion of biomass, with the combustion of wood continuing

 $^{19\} After\ http://climateactiontracker.org/global.html.$

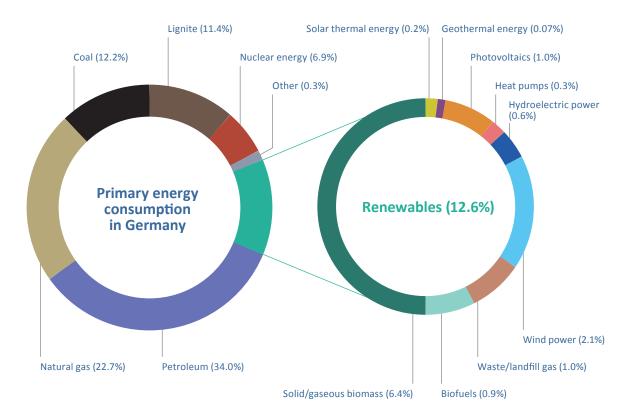


Figure 1-3: Primary energy consumption in Germany by type of generation.

Currently, 12.6 per cent of total German energy consumption originates from renewable sources.²⁰

to make a major contribution. Biomass is the direct product of biological photosynthesis. Any further expansion of bioenergy in Germany is limited by various factors: low efficiency of photosynthetic energy conversion by crop plants, limited availability of usable agricultural land and unfavourable life cycle assessments together with a desire to achieve autonomy in the supply of agricultural products, which already requires feedstuffs imports from third countries.²¹

A bundle of measures and developments will very probably be required to check the use of fossil fuels and achieve the CO₂ goals set for Germany. Energy economies and replacing fossil fuels with further developed renewable electrical energy will be able to make a significant contribution to reducing CO₂ discharges. As this position paper will demonstrate below, fuels

and valuable products produced with the assistance of renewable energy sources could replace fossil resources and thus, quite possibly from 2030, make a significant contribution to resolving energy and climate issues. This approach would permit the storage of fluctuating solar energy on a large scale as fuels and raw materials such as hydrogen, methanol or ammonia reach energy densities unachievable for example in battery storage²² (see box). Moreover, substances such as methane or methanol are relatively simple to include in existing energy and valuable material systems, on both the energy supply side and consumption side.

²⁰ Federal Ministry of Economics and Energy, 2017.

²¹ German National Academy of Sciences Leopoldina 2013.

Comparison of energy storage densities

Fuels such as coal, petrol, propane, methane or hydrogen store energy which is liberated again on combustion. This energy can be stated in quantity terms as net calorific value²³ in relation to either the weight (in kilograms) or volume of the substance (in litres or cubic metres) (see table 1-1). Conventional fossil fuels such as petrol and diesel are characterised by a high energy density in terms both of volume (per litre) and of weight (per kilogram). The storage density of gases such as methane or hydrogen is particularly high relative to the weight thereof (per kilogram). The necessary storage or tank volume, however, depends on the pressure of the gas (for example 200 bar in a present day car gas tank) or whether it is stored in liquid form at low temperatures. Hydrogen in particular has excellent storage density per kilogram, but the volume required for storage at the current pressure of 200 bar is comparatively high.

Table 1-1:²⁴ Energy storage density for various fuels and comparison with storage battery. The numerical values relate solely to the fuel and do not include the volume and weight of the storage vessel (tank). The reference quantity stated is in each case the fuel required to heat 10 litres of tap water to boiling point (heating from 15°C to 100°C), which corresponds to an energy requirement of around 1 kWh.

	Energy per unit weight (per kilogram)		Energy per unit volume (per litre)	
Energy stored by:	Energy or net calorific value per kilogram	Weight for boiling 10 litres of water	Energy or net calorific value per litre	Volume for boiling 10 litres of water
Petrol	12.5 kWh	80 g	9.2 kWh	0.1 L
Methane (natural gas) – 200 bar pressure tank	14 kWh	70 g	2.2 kWh	0.5 L
Hydrogen - liquid gas tank	33 kWh	30 g	2.4 kWh	0.4 L
Hydrogen – 200 bar pressure tank	33 kWh	30 g	0.6 kWh	1.7 L
High performance battery cell ²⁵	0.25 kWh	4,000 g	0.7 kWh	1.4 L

^{23 &}quot;Gross calorific value" is sometimes used instead of "net calorific value". The former also takes account, in addition to the energy released directly during the combustion process, of the thermal energy of the hot combustion products, in particular water and CO₂. The gross calorific value is thus always larger than the net calorific value, usually by approx. 10 per cent.

 $^{24\,}$ Data from various sources, compiled by H. Dau.

²⁵ No technology-independent values could be stated for electrical battery storage. The values stated here relate to specific, particularly high-performance battery cells (24 cm³ cells, Tesla model 2170), without taking account of the weight or space required for arranging and controlling the temperature of for example 3,000 to 5,000 such cells in a car.

1.3 Biological photosynthesis

In natural photosynthesis, sunlight serves as the energy source for splitting water (H_2O) and converting atmospheric carbon dioxide $(CO_2, 0.04 \text{ percent by volume})$ into biomolecules, for example into carbohydrates $([CH_2O]_n)$ (see figure 1-4).

Some 3 billion years ago biological photosynthesis began to develop starting from bacteria and leading to the formation of chloroplasts in higher organisms such as algae and plants. This system which has developed by evolution is very capable of meeting the requirements of biological functions but has its limits in (bio)technological applications (see section 2.1). Biological photosynthesis converts incident sunlight into biomass at an efficiency of

less than 1 per cent.²⁶ At an efficiency of 0.7 per cent, a net amount of some 7 kWh of solar energy per m² averaged over the year can be captured by biological photosynthesis in Germany. Germany's entire area of agricultural land (167,000 km²) thus captures less than 1,200 billion kWh per year in biomass, which corresponds to around 30 per cent of Germany's primary energy consumption of 3,750 billion kWh per year. Since only a proportion of the biomass is technically usable, a multiple of Germany's total area would be required to meet its national primary energy requirement by biological photosynthesis.

Biological photosynthesis is now well understood biochemically, structurally and functionally.²⁷ The process proceeds in two spatially and temporally tightly co-

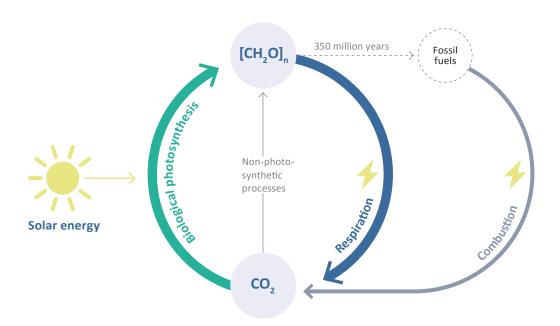


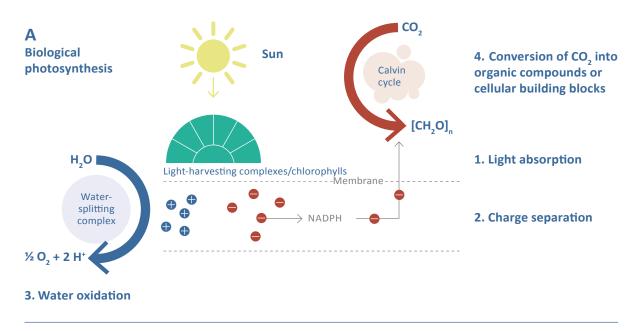
Figure 1-4: Biological photosynthesis in the global carbon cycle. Globally, biological photosynthesis by bacteria, algae and plants converts a net amount of approx. 450 gigatonnes of CO_2 into biomass each year (green arrow on the left). This corresponds to around 95 per cent of natural CO_2 emissions (blue arrow on the right). The missing 5 per cent to achieve equilibrium is converted into biomass via non-photosynthetic biological processes (thin arrow, centre). In addition to natural CO_2 emissions, humanity is responsible for around 32 gigatonnes of CO_2 per year from the combustion of fossil fuels (grey arrow on the right), some of which remains in the atmosphere, thus raising the CO_2 concentration²⁸ (diagram: T. Erb).

²⁶ German National Academy of Sciences Leopoldina 2013, p. 24.

²⁷ Blankenship 2014, Umena et al. 2011.

²⁸ Intergovernmental Panel on Climate Change (IPCC) 2013, p. 471.

15



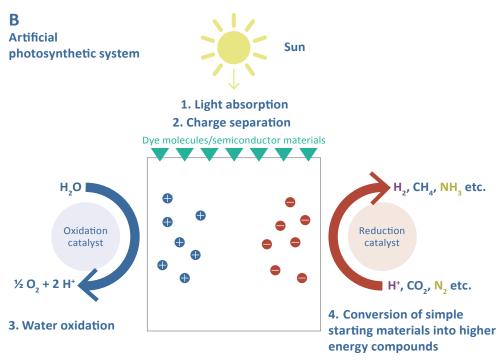


Figure 1-5: Biological photosynthesis (A) and artificial photosynthetic system (B). Sunlight induces charge separation (2) via chlorophyll molecules (A) or via light-absorbing materials or dye molecules (B). This is combined with water splitting (water oxidation) (3). In the case of biological photosynthesis, the electrons and protons from water splitting are used in the reduction of carbon dioxide and thus in the synthesis of biomass (A) while in the case of artificial photosynthesis they are used in the production of higher value, reduced compounds from simple precursor molecules (B). These are higher energy compounds which can be used as fuels and valuable products (4) (diagram: T. Erb).

ordinated sub-stages: the light reaction and the dark reaction. During the multistage light reaction, the energy from sunlight is absorbed and then used to split water and provide electrons (reducing equivalents) from this reaction. The likewise multistage dark reaction utilizes this chemical energy to convert CO₂ into biomolecules (see figure 1-5 A, right). Biological photosynthesis is a complex catalytic process involving more than thirty protein components with numerous metal centres, cofactors and pigments (chlorophylls and carotenoids) for light absorption and energy conversion.

Elucidation of the individual molecular steps involved in biological photosynthesis inspired the development of artificial photosynthesis systems. Conceptually, both biological and artificial photosynthesis systems can be reduced to common basic processes (see figure 1-5 A and B). The mode of action of biological photosynthesis is in principle also reproduced in artificial systems, but their technical implementation does, however, in part differ significantly from the biological model (see section 2.3).

1.4 Artificial photosynthesis

Artificial photosynthesis serves to produce chemical energy carriers and valuable products using sunlight as the sole energy source. The particular strength of the system is that it provides renewable energy stored in material form. It is not expedient in this context to attempt to "replicate" the huge complexity of the biological machinery. It also unnecessary to do so since many alternative materials and production methods which biological cells do not have at their disposal are available to science and engineering for artificial photosynthesis.

In recent decades, many and varied approaches have been developed for storing solar energy in material (chemical) form, the majority of which follow the general concept for artificial photosynthesis shown in figure 1-5 B. In a first step, absorption of visible light leads to charge separation. The resultant negative charges (electrons) are used to form energy-rich compounds such as hydrogen, methanol or ammonia from precursors such as water, carbon dioxide or nitrogen. These are processes involving complex mechanisms for which catalysts are required. On the other hand, the light-driven reaction results in an accumulation of positive charges (electron holes). There is only one feasible way of refilling these holes on a large industrial scale: since no other oxidisable compound is present in sufficient quantity overall, it is necessary, as in the biological process, to master the oxidation of water to oxygen, for which purpose catalysts are again necessary.

The wide variety of systems for storing solar energy in material form may in principle be differentiated into two approaches, it being as yet unclear which will be implemented industrially:

- **Direct approaches:** Light absorption, primary charge separation and material reactions here proceed in integrated manner in a single object, for example in "artificial leaves" in which the catalysts for producing the valuable products and for oxidizing water are applied directly onto the semiconductors of a "solar cell".²⁹
- Multistage approaches: While the individual steps do indeed proceed at a common location, in a large scale industrial plant, they are spatially separated, for example by combining conventional solar cell technology with electrolysers.

The resultant products are either used directly (for example hydrogen as a fuel) or, in combination with downstream reactions, are converted into energy carriers such as methane, methanol or formic acid (figure 1-6). Industrial and biological systems can also be combined into multistage "hybrid systems" in order to obtain higher value products. One example of this is obtaining isopropanol bioelectrochemically from hydrogen and oxygen produced using solar energy by reducing ${\rm CO}_2$ with the assistance of hydrogen oxidizing bacteria. 30

²⁹ Marshall 2014.30 Torella et al. 2015.

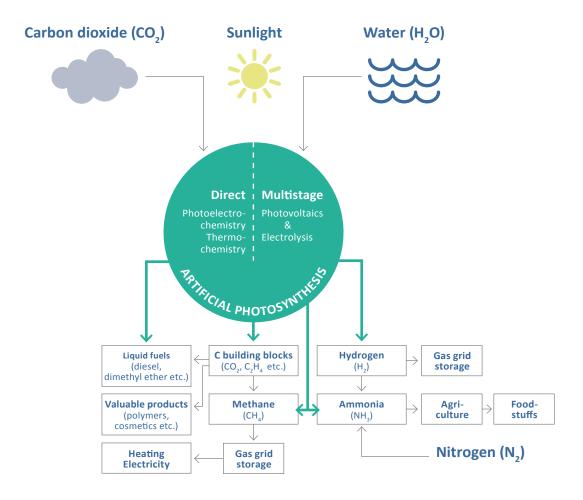


Figure 1-6: Possible role of artificial photosynthesis in the global energy and natural resource system. A number of fuels and resources such as hydrogen, ethylene, methane or also ammonia are directly obtainable (green arrows) by means of various direct and multistage approaches to artificial photosynthesis. These products can then be directly used, stored or input, using well-established processes, into the energy and natural resource system (grey arrows). The feature common to all routes is that they all start from sunlight, water and CO₂. It is vital to ensure that, despite the use of carbon-containing compounds, which is advantageous for many applications, a carbon cycle is created so that an overall completely CO₂-neutral material balance is obtained (diagram: R. van de Krol and Ph. Kurz³¹).

Whatever form artificial photosynthesis may take, its products have to fit in with the global energy and resource system (figure 1-6).

Interim conclusion:

Using direct or multistage artificial photosynthesis pathways, it could in the long term become possible to produce most fuels and valuable products on a large scale from non-fossil starting materials (in particular CO₂) by means of solar energy. Artificial photosynthesis here differs in several central points from the generation of solar

electricity by means of photovoltaics (which is already carried out on a large scale; see table 1-2). Unlike photovoltaics (which is already carried out on a large scale), artificial photosynthesis is still largely at the basic research stage. The results to date, however, have shown on the basis of pilot projects that artificial photosynthesis could in principle make a major contribution to sustainably supplying society with various fuels and valuable products. Developing and evaluating such reaction systems is therefore viewed as a central scientific and technological challenge worldwide and work is being intensified accordingly.

1.5 Preview of the following section in the position paper

Section 2 below explains the state of research into solar production of fuels and valuable products and discusses the resultant challenges facing practical implementation of the systems in question on a large industrial scale. In addition to artificial photosynthesis, which is the primary focus of this position paper, section 2.1 also describes progress with regard to increasing yields in biological photosynthesis, primarily by genetic modification, for the direct production of fuels and valuable products. Advantages and drawbacks of the biological system are explained and new hybrid approaches, which combine biological components with electrochemical modules, are presented.

Table 1-2: Comparison of solar electricity/photovoltaics and artificial photosynthesis.

	Solar electricity/photovoltaics	Artificial photosynthesis	
	Solar energy ► electricity	Solar energy ► fuels and valuable products	
Energy conversion	Market-ready technologies: silicon solar cells, dye-sensitised solar cells, voltage converters, grid feed-in	Major need for development: photoprocesses, catalysts for high synthesis specificity and efficiency, equipment and systems integration	
	Electricity storage entails major additional costs	Energy stored in non-fossil fuels or valuable products	
	Various types of battery for storing electrical energy in existence, greater capacity and materials development still necessary	Various tank types for storing gaseous and liquid fuels and valuable products are in existence	
Energy storage	Due to low energy storage density (high weight and bulk), currently primarily used for small-scale (mobile electronics) and medium-scale (cars, domestic PV systems) applications; cost reductions are enabling initial large-scale use in the MWh range	Thanks to high energy storage density, readily usable in medium-scale (cars, trucks) and large-scale (GWh range, stockpiling for national demand over months) applications	
	High energy efficiency (low energy losses)	Energy efficiency achievable in practice still unclear, but tends to be lower than with electrical energy storage in batteries	
	Complete replacement of fossil fuels problematic (aircraft and shipping traffic, petrochemicals)	Potential for complete replacement of fossil fuels and resources in all fields	
	Technological feasibility unclear for bat- tery storage of large volumes of electri- cal energy (storage via pumped-storage power station is, however, possible and power-to-X option)	No fundamental technological problems (similar storage and safety technologies as for fossil fuels; optimisation required for hydrogen)	
	Electrical line systems	Gas and liquid fuel lines (pipelines), goods transport (tanker trucks, cargo ships)	
Energy transport	Mature technologies (optimisation required for long-distance transport and "smart power grids")	Completely and partially mature technologies (completely mature, for example, for non-fossil methane as a natural gas replacement, partially mature, for example, for hydrogen or alcohols such as methanol)	

Building on the biological models, section 2.2 introduces the central sub-processes of artificial photosynthesis and the catalysts involved, namely light absorption, water oxidation with associated oxygen formation, proton reduction to form hydrogen ($\rm H_2$) and reactions of carbon dioxide ($\rm CO_2$) or nitrogen ($\rm N_2$) which yield organic carbon compounds or ammonia.

Section 2.3 puts the components of artificial photosynthesis together to form complete systems. For instance, the electrolysis used to obtain reducing power can be carried out by either a separate photovoltaic system or an integrated system. New photoelectrocatalysis systems, which are also known as "artificial leaves", can replace photovoltaics. Above and beyond the electrochemical production of hydrogen, other highly promising processes include those which enable direct use of CO₂. Section 2.4 finally describes two alternative approaches to artificial photosynthesis: using solar energy for chemical synthesis and the production of fuels or valuable products at high temperatures (over approx. 1,000°C) in solar-thermal reactors.

Section 3 examines artificial photosynthesis from the standpoint of its significance to society and ongoing research activities, with section 3.1 firstly describing German research activities and funding programmes before setting them in the context of international initiatives. Section 3.2 outlines industrial perspectives on the development potential of artificial photosynthesis. In order to involve society as a whole in these new technologies from an early stage, section 3.3 discusses general issues of technology assessment, environmental ethics and the options for social dialogue.

Finally, section 4 sets out six recommendations which are intended to indicate how dynamic development of a highly promising field of research might be pursued and supported.

2. State of research and current challenges

Photosynthetic processes in plants, algae and bacteria, which have been thoroughly investigated and are today well understood, serve as a model for the development of artificial photosynthesis. When it comes to the technical implementation of the two sub-processes, the light and dark reactions, development has progressed to different stages. Photovoltaic solutions have been achieved for the light reaction which match the natural process in terms of photon yield. It has not yet been possible to identify a catalytic solution for the technical implementation of the dark reaction which is competitive with the natural system. It is in principle possible to split water into hydrogen and oxygen and to form hydrocarbons and carbon monoxide (CO) from CO, with the assistance of photovoltaic processes, but the direct conversion of atmospheric CO2, which, at a content of 0.04 per cent by volume, is present at very low dilution in air, into higher value products still lags far behind the biological model. With regard to water splitting and CO₂ conversion, research and development in artificial photosynthesis are pursuing the following common objectives:

- energy efficiency to ensure that as much as possible of the absorbed solar energy is stored in the resultant products,
- selectivity to ensure that few undesired secondary products are produced,
- robustness to ensure that the systems can ideally be operated for years at constant output without replacement of components,
- scalability to ensure that the systems can be used on an industrial scale,

- extensive freedom from dependence on rare and/or toxic components,
- economic viability, in terms of both capital costs and energy return on investment, and
- safety both in terms of risks to the population and the environment and in terms of stability of energy supply.

The various approaches to the solar production of fuels and valuable products from water and air components (CO₂ or nitrogen) which are currently being pursued are presented in greater detail below (cf. table 2-1):

- Modified biological photosynthesis: Targeted production of fuels and valuable products by genetically engineered photosynthetic microorganisms. The technology concept presented here differs fundamentally from the long-established production of biofuels by the conversion of biomass into biogas, biodiesel or bioalcohol.
- Combining biological and non-biological components to create
 hybrid systems: Using renewably
 generated electricity in bioreactors for
 producing fuels and valuable products
 by microorganisms and their enzymes.
- Power-to-X: Using renewable electricity from the power grid for synthesizing fuels or valuable products, such as electrolytic production of hydrogen or ethylene or, in multistage processes, conversion into methane, alcohols or polymers.
- Artificial photosynthesis: Combining the conversion of solar energy with catalytic processes for producing fuels and valuable products in a single,

completely integrated system, such as in an "artificial leaf" or by directly combining photovoltaic and electrolysis modules.

The sub-processes for obtaining the desired product in power-to-X and artificial photosynthesis are in principle identical, including with regard to the use of syn-

thetic catalysts, but the solar energy is put to a different use in each case. While artificial photosynthesis integrates the capture of sunlight with the production of fuels and valuable products in one apparatus or system, power-to-X involves conveying solar electricity via the power grid to the location where fuels and valuable products are produced.

Table 2-1: Approaches to the solar production of fuels and valuable products from water and air components.

		Energy source: Sun		
		Charge sepa- ration by leaf pigments	Charge separation by semiconductors/pigments	PV modules or other sources of solar electricity
Production of fuels/valuable	Enzymes	Modified biological photosynthesis		Hybrid systems
products by:	Synthetic catalysts		Artificial photo- synthesis	Power-to-X

2.1 Biological, modified and hybrid photosynthesis

2.1.1 Advantages and drawbacks of biological photosynthesis

The principles of biological photosynthesis have already been explained in section 1.3 and figure 1-5 A. Biological photosynthesis systems have a series of advantages over artificial systems. They are capable of repairing and replicating themselves and, over the course of evolution, have adapted themselves to extreme locations such as arid and very cold and hot areas. They are also highly flexible with regard to varying light conditions.

A further advantage of biological photosynthesis over artificial systems is its ability to store the energy from sunlight in the long term by reducing atmospheric CO_2 . This takes place in the dark reaction of biological photosynthesis, in which atmospheric CO_2 is converted into valuable multi-carbon compounds. A comparable conversion of atmospheric CO_2 into high-

er energy carbon compounds has not yet been achieved in artificial photosynthesis systems. This entails the development of stable, inexpensive and environmentally compatible catalysts which, like the biological systems, bind the low atmospheric concentrations of CO₂ (0.04 per cent) and reduce them to higher quality products with elevated specificity and high conversion rates.

In addition to the conversion of CO₂ by the Calvin cycle⁵ in plants, algae and bacteria which has long been known, six further CO₂ metabolic pathways have in recent years been discovered in microorganisms and their molecular detail has in part already been elucidated.³² This newly discovered biological diversity has revealed previously unknown catalytic principles of CO₂ binding and reduction which can be used as a model for the development of new CO₂ conversion processes in artificial photosynthesis (see section 2.1.2).

³² Berg 2011; Erb 2011; Fuchs 2011.

In terms of the use of sunlight, biological systems are characterised by a relatively low conversion efficiency of light energy into chemical energy. While the theoretical maximum efficiency of the light reaction is around 10 per cent,33 the actual efficiency in crop plants on an annual average basis is typically less than 1 per cent, while values of 3 per cent have been achieved in microalgae in a photobioreactor.34 A further disadvantage for (bio)technological applications is that the solar energy in biological photosynthesis is primarily stored in the form of biomass. Biomass is a chemically complex mixture of individual substances which are suitable for nutrition (for example grain starch) and for heating (for example wood) but cannot straightforwardly be introduced into the industrial value chain. Ongoing research is developing strategies for modifying natural photosynthesis or creating hybrid photosynthesis systems which more efficiently and selectively produce the desired fuels and valuable products (see figure 2-1 A).

2.1.2 Modified photosynthesis

Modified photosynthesis should be taken to mean the modification of photosynthetic organisms using the methods of genetic engineering and/or synthetic biology (see figure 2-1 B).35 The approaches of synthetic biology are particularly promising in this respect because not only do they bring about incremental improvements in biological processes, for example by optimising individual components, but they endeavour to create new biological solutions which do not exist in nature in this form, for example by implementing completely new metabolic pathways for CO_a conversion in photosynthetic organisms (see box with figure 2-2 A and 2-2 B, p. 24/25).

Approaches to boosting the efficiency of the light reaction are currently primarily focused on targeted modifications of the light-harvesting and photosynthesis apparatus by

- direct intervention in the dynamic regulation of the photosynthesis apparatus which has made it possible to achieve a 20 per cent increase in biomass formation in tobacco plants³⁶,
- reducing the ratio of light-harvesting complexes to photosynthetic reaction centres which has already led to a fivefold increase in synthesis output³⁷, and
- directly channelling photosynthetic energy into the production of hydrogen or other products³⁸.

It remains to be determined how much photosynthetic energy can be extracted for directly obtaining valuable products and how much is necessary for maintaining the cell's essential vital processes. It has been estimated that up to 70 per cent of the energy provided by photosynthesis can flow directly into the production of valuable products.³⁹

³³ Dau/Zaharieva 2009.

³⁴ Blankenship et al. 2011; Long et al. 2015.

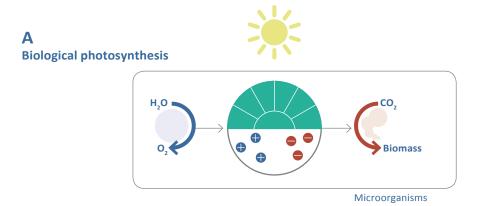
³⁵ Orta et al. 2011.

³⁶ Kromdijk et al. 2016.

³⁷ Bernat et al. 2009.

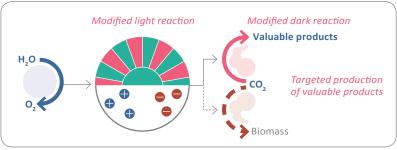
³⁸ Rögner 2013.

 $^{39~\}mathrm{M}.$ Rögner, personal communication.



B Modified photosynthesis





Modified microorganisms

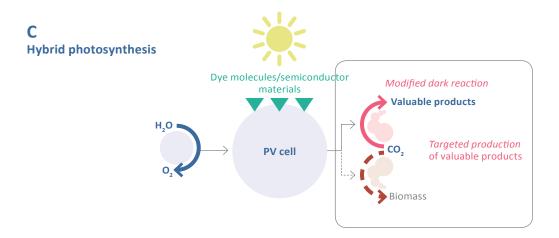


Figure 2-1: Comparison of biological, modified and hybrid photosynthesis:

(A) The starting point is a biological photosynthetic organism. (B) In modified systems, organisms are modified by molecular methods in order to boost the efficiency of photosynthesis. The points of attack are primarily an improved light reaction and, in relation to the dark reaction, more efficient CO₂ reduction and the targeted production of valuable products. (C) In hybrid systems, a chemical-physical process (for example photovoltaically driven hydrogen production) combined with CO₂-reducing organisms (C, on right in box) (diagram: T. Erb).

Implementation of new metabolic pathways for CO₂ fixation

Two examples are intended to clarify the new approach taken by synthetic biology to equip biological systems with new characteristics for CO_2 conversion. Figure 2-2 A: Designing and creating artificial metabolic pathways for more efficient CO_2 reduction.⁴⁰ Figure 2-2 B: Reprogramming the photosynthetic microalga Synechocystis for targeted production of valuable products from CO_2 ⁴¹

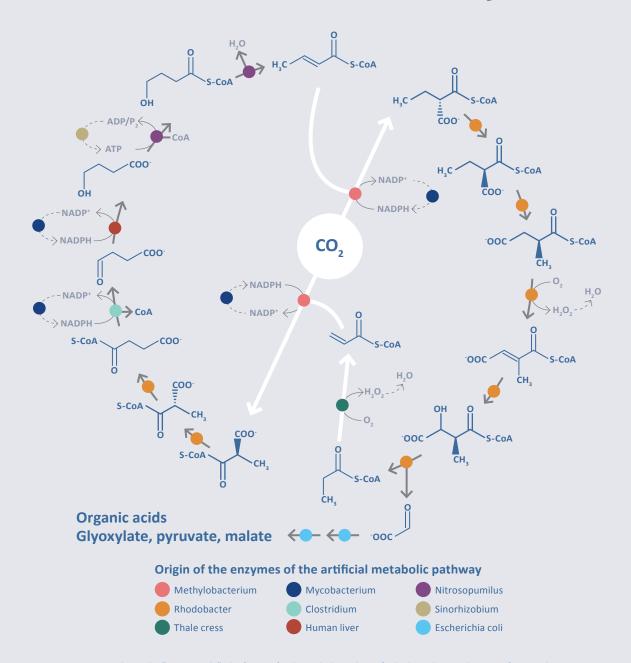


Figure 2-2 A shows the "CETCH cycle", the first artificial metabolic pathway for biological ${\rm CO}_2$ reduction. After initial planning on the drawing board, it was built in the laboratory from individual biological "Lego bricks". The CETCH cycle consists of 17 different enzymes which originate from a total of nine different organisms (marked in colour). Three of these enzymes were customised with computer assistance to catalyse a specific reaction. Theoretical calculations have shown that the CETCH cycle requires only 24 to 28 light quanta per reduced ${\rm CO}_2$ molecule. Compared with the natural dark reaction in plants and algae (approx. 34 light quanta per ${\rm CO}_2$), the artificial metabolic pathway thus requires up to 20 per cent less light energy. This designer metabolic pathway is already functional in the test tube and further testing is now focusing on implementing it in photosynthetic organisms (diagram: T. Erb).

⁴⁰ Schwander et al. 2016.

⁴¹ Oliver et al. 2013; Oliver et al. 2014.

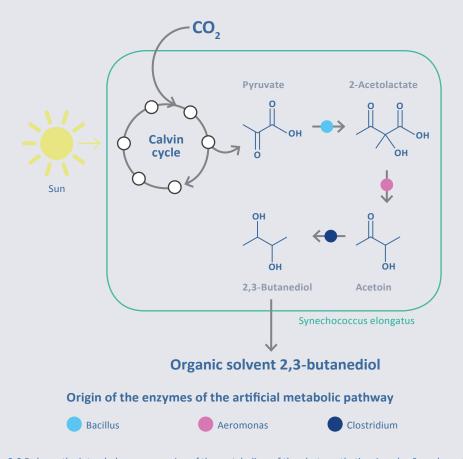


Figure 2-2 B shows the intended reprogramming of the metabolism of the photosynthetic microalga Synechocystis to obtain 2,3-butanediol from ${\rm CO_2}$. 2,3-Butanediol is an organic solvent which is used in industrial manufacturing, for example for producing paints. It is also used as a starting material for producing methyl ethyl ketone, another important industrial solvent, and butadiene, a basic building block of synthetic rubber. An artificial metabolic pathway comprising three reactions was established in Synechocystis in order to produce butanediol in this microalga. Various enzymes were tested in order to identify the best three-component combination which is composed of enzymes from the bacterial genera Bacillus, Aeromonas and Clostridium. Using the artificial metabolic pathway, Synechocystis produces butanediol from ${\rm CO_2}$ at a rate of approx. 10 ${\rm \mu g/L}$ per hour, at a maximum yield of 2.8 ${\rm mg/L}$. However, a substantial further increase in yields of butanediol in Synechocystis will have to be achieved for the industrial production (diagram: T. Erb).

There is considerable further potential for increasing photosynthetic yields by improving the dark reaction. The conventional CO₂-reducing metabolic pathways with ribulose bisphosphate carboxylase (RuBisCO) as the key enzyme are relatively inefficient in comparison with the recently discovered alternative CO₂ metabolic pathways of some microorganisms. Furthermore, a proportion of the captured CO₂ is lost in the dark reaction of plants and microorganisms, which results in a loss of up to 30 per cent of the provided energy. ⁴² It is hoped to combat these losses by targeted modification of CO₂-convert-

ing enzymes and metabolic pathways.⁴³ A series of approaches are being pursued:

- Replacement of the CO₂-converting enzymes in plants and algae with microbial enzymes or specifically modified variants with increased catalytic efficiency,⁴⁴
- Establishing CO₂ concentration mechanisms in plant and algal cells which minimise the effects of photorespiration and promise increases in yields of up to 30 per cent, and

⁴³ Erb/Zarzycki 2016.

⁴⁴ Greene et al. 2007; Kreel/Tabita 2015; Lin et al. 2014; Occhialini et al. 2016.

Creating new higher efficiency CO₂-reducing metabolic pathways from scratch.⁴⁵

In addition to the above-stated approaches which have the aim of improving the light and dark reactions, further experiments are focusing on deriving individual valuable products from the metabolism of photosynthetic organisms in a targeted manner. This is achieved by modifying the metabolism of photosynthetic organisms by genetic/synthetic biology in such a way that a higher value product is preferably formed in larger quantities. Such products are above all hydrogen,46 biofuels and carboxylic acids⁴⁷ which can be used as fuels or valuable products in the chemicals industry. The goal of initial experiments is to implement the dark reaction in biotechnologically well established microorganisms in order to create new CO₂-reducing production strains for biotechnology and hybrid photosynthesis systems (see section 2.1.3).48

Furthermore, coupling specific enzymes, the oxidoreductases, with natural photosynthesis enables the use of recombinant cyanobacteria for the photocatalysed, enantioselective reduction of C=C-bonds, i.e. for asymmetric syntheses. Such products have already been obtained on the gram per litre scale using whole cells.⁴⁹

2.1.3 Hybrid photosynthesis

Hybrid photosynthetic systems are a combination of biological and non-biological components. The goal of such systems integration is to power the reduction of ${\rm CO}_2$ by light. Most hybrid systems combine a photovoltaic process with a biological dark reaction sequence. For instance, water and carbon dioxide are reduced to hydrogen (${\rm H}_2$), carbon monoxide (CO)

or formic acid by electrolysis powered by photovoltaically generated electricity. Microorganisms are then capable of synthesising organic valuable products from these natural resources (see for example figure 2-3 A).

Siemens and Evonik are currently implementing a combination of electrolysis and fermentation in a pilot plant which initially produces hydrogen and carbon monoxide by electrolysis. In the next step, these gases are fermented to yield acetic acid and ethanol (figure 2-3 B) before being converted into butanol and hexanol in further fermentation steps.⁵⁰ The products are in turn starting materials for speciality polymers and nutritional supplements. Production capacities of up to 20,000 tonnes per year are envisaged.51 This hybrid system is capable of achieving sunlight conversion efficiencies of approaching 10 per cent. The system does, however, have to be operated with almost 100 per cent CO, i.e. atmospheric CO, (0.04 per cent) would have to be concentrated with considerable energy input (at least 20 kJ/mol). The plan is in fact to use power station waste gases.

⁴⁵ Schwander et al. 2016; Bar-Even et al. 2010.

⁴⁶ Rögner 2015; Rumpel et al. 2014.

⁴⁷ Larkum et al. 2012; Banerjee et al. 2016, p. 432.

⁴⁸ Antonovsky et al. 2016.

⁴⁹ Köninger et al. 2016.

⁵⁰ Haas et al. 2018.

⁵¹ http://corporate.evonik.de/de/presse/pressemitteilungen/Pages/news-details.aspx?newsid=72462.

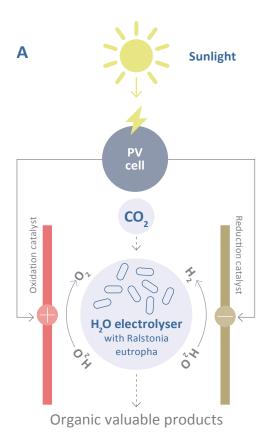
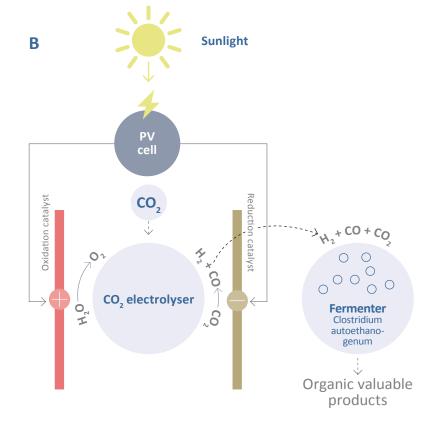


Figure 2-3 A shows the photovoltaically driven electrolysis of water to yield H₂ and O₂, which are then utilised in the same reaction vessel by the hydrogen oxidising bacterium Ralstonia eutropha to reduce CO₂ into valuable products such as isopropanol.52 The hydrogen oxidising bacterium is capable of growing with H, and O, as sole energy source and CO₂ as sole carbon source. Genetic engineering is capable of constructing strains of bacteria which can be used in this process to produce organic valuable products such as isopropanol, C4 and C5 alcohols or also the biopolymer polyhydroxybutyrate in targeted manner. The hydrogen oxidising bacterium can withstand the cobalt-oxide-phosphate ("CoPi") electrocatalysts and tolerates high concentrations of reactive oxygen species. On a laboratory scale, organic compounds were produced using atmospheric CO₂ (0.04 per cent) at a sunlight conversion efficiency of almost 10 per cent, which far surpasses the conversion efficiency of natural photosynthesis. This hybrid, bioelectrochemical system is moreover highly stable and reduces CO, at a largely constant rate for over five days. The present system is still limited by a low electrolysis current density (1 mA/cm²) and this would have to be increased one hundred fold for industrial use.53

Figure 2-3 B shows a hybrid system which is already somewhat closer to achieving the goal of higher current density. It consists of a photovoltaically operated CO, electrolyser which is equipped with a silver-based gas diffusion cathode and is active at an electrolysis voltage of 3.5 volts with a current density of 300 mA/cm². CO yield amounts to 80 per cent, the remaining 20 per cent of the electrons flowing into the reduction of protons to H₂. At higher voltages, the proportion of H₂ rises and energy conversion efficiency drops. The gases CO and H, formed in this CO, electrolyser are passed, together with unreacted CO₂, into a separate fermenter. This "syngas" mixture is converted at almost 100 per cent efficiency by the bacterium Clostridium autoethanogenum into acetic acid and ethanol.54



⁵² Diagram after Liu et al. 2016.

⁵³ Larkum et al. 2012.

⁵⁴ Diagram after Haas et al. 2018, figure 1, p. 33.

2.2 Sub-processes of artificial photosynthesis

During the production of fuels and valuable products, it is often necessary to transfer both reducing equivalents (e-, electrons) and protons (H+, positively charged hydrogen atom nuclei) from one substance to another with input of external energy. Such processes are known in chemistry as "proton-coupled electron transfers". In artificial photosynthesis, the necessary energy originates from the absorption of sunlight. In this manner, it is possible to form not only hydrogen as an energy-rich synthesis product, but also carbon-based fuels and valuable products, such as methane (CH₄) from the reduction of CO₂ or ammonia (NH₂) as an energy carrier or artificial fertiliser by reducing atmospheric nitrogen (N_o). In contrast with this wide variety of possible products, water, similarly to biological photosynthesis, is the sole source of the electrons and protons required for forming fuels and valuable products. The reactions in question can in general terms be stated as follows:

$$H^+/CO_2/N_2 + H_2O \xrightarrow{Solar} H_2/CH_4/NH_3 + O_2$$

As indicated by the colour of the letters, the light-driven electron transfer reactions of artificial photosynthesis thus always consist of two parts or "half reactions": the oxidation of water as a source of electrons and protons to yield O_a and the reduction of H+, CO2, N2 etc. as electron and proton sinks to yield H₂, CH₄ or NH₃. The desired products are produced by means of the reduction reactions. In the simplest case, they could be combined with oxygen back into the starting compounds accompanied by release of heat ("thermal use"). These compounds are, however, also valuable raw materials: ammonia, for instance, is used as a fertiliser in agriculture.

2.2.1 Light absorption and charge separation

As shown in figure 2-4, the initial processes in photosynthesis are light absorption and charge separation. In artificial systems, these can in principle proceed via light-absorbing pigment molecules or in the solid state (photovoltaics, usually with semiconductors). In biological photosynthesis, "leaf pigments" are responsible for light absorption and charge separation, the best known being the green chlorophyll molecules.

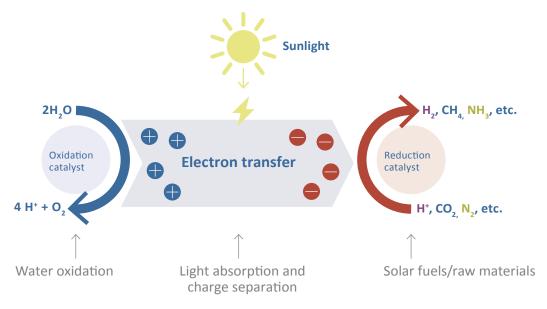


Figure 2-4: Overview of artificial photosynthesis sub-processes. After light absorption and charge separation (section 2.2.1), catalytic water oxidation (2.2.3) and reduction of CO_2 , H⁺ and/or N_2 lead to fuels and valuable products (2.2.4 to 2.2.6) (diagram: Ph. Kurz).

For some decades, development has therefore focused on synthetic, molecular dyes which can be used in a similar manner to chlorophylls for light-induced charge transfer. Thanks to the wide variety of synthetically accessible compounds, this approach has a series of advantages:

- Because their structures can very often be varied in a highly systematic way, important characteristics such as colour, solubility or redox potentials of dye molecules can be tailored to requirements. As a result, the ability to accept or release electrons can now be adjusted virtually at will and in a predictable manner.
- Most of the molecules are truly small which means that a large number can be packed in per unit volume, so ensuring a very good "light yield".
- Light absorption characteristics can furthermore be improved in targeted manner by arranging further molecules as an "antenna system" around a central pigment.
- Complicated syntheses even allow dye molecules to be directly bound to catalytically active units for product formation in order, ideally, to achieve a directional electron flow determined by the overall molecule.

It must, however, be noted that many molecular dyes are not yet sufficiently stable for use in catalysis systems, in particular in aqueous solution. They are often broken down after just a few days or even sooner due to unwanted secondary reactions.

Apart from biological photosynthesis, the best known process for using solar energy is photovoltaics. Photovoltaic elements consist of semiconducting solid materials such as silicon which absorb light and convert it into electrical energy, i.e. current and voltage. The practical utility of a photovoltaic technology is defined by its combination of efficiency, costs and relia-

bility. High efficiency in converting solar energy into electrical energy is important in order to ensure the highest possible output of electricity per unit area of module.

The fundamental process in semiconductor solar cell operation is the absorption of a photon, which lifts an electron with a negative charge out of the valence band of the semiconductor into the conduction band and leaves behind an empty place, a "hole", with a positive charge in the valence band. In the case of a photon with an energy exactly corresponding to the band gap of a semiconductor, this can proceed with 100 per cent efficiency, the energy of such a photon being directly converted into electrical energy. The semiconductor is transparent to lower energy photons which are not absorbed. Photons with an energy higher than the band gap lead to the production of "hot" photons with energy high in the conduction band which then quickly release their additional energy to thermal oscillations, or phonons. Ultimately, therefore, only the energy of the band gap can be harvested from these higher energy photons as well. For these two reasons, the maximum efficiency of a semiconductor ideally adapted to the solar spectrum is 33 per cent. Silicon, which is currently the semiconductor material most widely used for solar cells, with its band gap of 1.2 eV is very close to this optimum and should ideally be capable of achieving efficiencies of up to 29 per cent.

An electron-hole pair is initially bound by electrostatic attraction, as an "exciton" is being formed. The latter has to be separated in order to avoid harmful recombination and to collect the charge carriers in external contacts. Covalent semiconductors such as Si or GaAs have a high dielectric constant which effectively shields the electrical charges of opposing polarity from one another. In covalent semiconductors, the binding energy of an

exciton is therefore close to the thermal energy of a few meV. In organic semiconductors, in contrast, this shielding is significantly weaker and exciton binding energy can easily amount to 0.5 eV and above. This energy has to be applied on collection of the charge carriers at the external contacts and is therefore lost from the energy yield. In perovskites (mineral compounds of calcium, titanium and oxygen), the incorporated heavy elements such as lead ensure that the dielectric constant is high, resulting in low exciton binding energies. These materials are accordingly currently receiving considerable scientific interest with regard to new PV structures.

A third step which follows the fundamental processes is the necessary transport of the charge carriers to the contacts for negative charges (electrons) and positive charges (holes), the mobility of the charge carriers here in turn playing a significant role. In this case too, crystalline covalent semiconductors are orders of magnitude better than other materials, for example organic compounds or also perovskites.

Silicon photovoltaics⁵⁵ currently hold the largest, and still growing, market share of all photovoltaic technologies (around 95 per cent).56 Thanks to intense research and development work over recent decades, crystalline silicon solar cell efficiency has been raised from around 1 per cent to over 25 per cent. In addition to a typical module efficiency of approx. 20 per cent, silicon photovoltaics have the advantage over other technologies of high reliability and low price. Long-term studies on silicon modules have revealed that the output of the modules declines only slightly over a period of more than 20 years, so that long-term stability is adequate. Today's global mass production of silicon solar cells has resulted in a dramatic drop in production costs and so also in

the costs of PV generated electricity. The most recent auctions for electricity from large PV plants resulted in final electricity prices of below 2 €cent/kWh. Ongoing developments of interest in silicon solar cell technology have the goal of increasing efficiency while ensuring costs continue to fall as far as possible, for example by passivating the rear side ("PERC" technology⁵⁷) or by using a thin film of amorphous silicon with particularly good passivation characteristics in what is known as heterojunction technology. The current world record of 26.2 per cent efficiency has been achieved by applying these measures.58 Further increases in efficiency beyond 30 per cent are anticipated from combinations with other semiconductor materials with a larger band gap.

Thin-film photovoltaic systems⁵⁹ contain components consisting of thin semiconductor layers. As a result of largescale production at relatively low temperatures, thin-film solar cells are particularly inexpensive to manufacture. One central disadvantage, however, is their relatively low efficiency. The rapid fall in prices over recent years of modules with crystalline Si-solar cells, which are inexpensively manufactured in gigawatt scale plants, have largely offset the cost advantage of thin film-technology. Perovskite solar cells are one particularly remarkable example of the potential of thin-film photovoltaics; within just a few years of their discovery, it has proved possible to achieve efficiencies of over 20 per cent with the assistance of organic/inorganic hybrid materials.60 The current disadvantages of this technology is its lower stability and low reliability in comparison with silicon photovoltaics. Challenges also remain with regard to scalability.

⁵⁷ The architecture of a Passivated Emitter and Rear Cell essentially enables improved light yield in the rear region of the cell, which in turn increases electron yield.

⁵⁸ Yoshikawa et al. 2017.

⁵⁹ Zeeman and Schropp 2012.

⁶⁰ Yang et al. 2017.

The currently most efficient photovoltaic cells are based on heterostructures of a number of high purity semiconductor layers and achieve efficiencies of over 45 per cent⁶¹ (in combination with optical lenses which concentrate the sunlight onto the solar cell to create *concentrator photovoltaics*).⁶² However, such high efficiency photovoltaics have particularly high material and production costs and are therefore not yet competitive despite their great potential.

Last but not least, there are also dye-sensitised solar cells, which are often also known as "Grätzel cells", after their inventor, and which have been developed in recent decades from laboratory curiosities to market maturity.63 In these cells, in contrast with most photovoltaic modules, light is absorbed by molecular dyes. However, in a Grätzel cell, these are not in solution, but are instead immobilised on inexpensive, conductive materials. After excitation by light, the pigments "contacted" in this manner inject electrons into the conducting layer from where they flow towards consumers. Reactions coupled with this process on a counter-electrode and the electron flow mediated via a liquid electrolyte complete the Grätzel cell circuit. Efficient charge transport through the entire system and, most particularly, the long-term stability of the molecular dyes are problems which are vet to be solved. In recent years, however, major breakthroughs have been made which mean that it might in future be possible to benefit to a greater extent from the identifiable advantages of dye-sensitised solar cells, namely favourable price, processing in almost any desired colour and shape and good energy conversion efficiency.

Despite the fundamental differences among the various approaches in terms of the materials used (molecular dyes versus semiconducting solids), some central challenges remain to be solved in future, specifically in the case of integrated systems where photovoltaic systems are directly combined with catalysts:

- Light absorption must create a sufficient potential difference so that the desired chemical process can take place. The theoretical minimum for light-driven splitting of water into H, and O, is approx. 1.23 volts. Under real conditions, however, the catalyst overpotentials always have to be added to this voltage such that, depending on catalyst quality and the necessary current density, potential differences of 1.5 to 2.5 volts are required.⁶⁴ The light-absorbing substances used should be capable of efficiently utilising as much as possible of the visible spectrum of sunlight. Together, the first two requirements mean that a combination of absorbers will generally be used. This can be achieved, for example, in the form of antenna or tandem systems which may also consist of different materials.
- Photophysical characteristics must be good. Key parameters here are high absorption coefficients, good charge separation efficiencies, i.e. quantum yields, low recombination of charges once separated and, in particular for large molecular systems, directional charge transfer which leads to the product with as few secondary reactions as possible.
- The absorbers used must have very good photostability, so they must not undergo any decomposition reactions despite extremely reactive intermediates arising after photoexcitation.

⁶¹ Dimroth et al. 2016.

⁶² Philips and Bett 2014.

⁶³ O'Regan and Grätzel 1991.

2.2.2 Catalysts and efficiency of chemical sub-processes

Artificial photosynthesis differs from using solar energy for generating electricity in that the primary purpose of light absorption and charge separation is not to generate electrical energy but to drive chemical processes. In most cases, this can only happen with the assistance of catalysts which are in direct electrical contact with the light absorption unit. The characteristics of the catalysis systems fundamentally determine the energy efficiency of the particular chemical reaction (see box p. 33).

2.2.3 Water oxidation and O_2 evolution

Water oxidation is a key process in artificial photosynthesis, as it is for biological photosynthesis, because it is the process by which both electrons and protons are obtained from water as an almost limitless natural resource. Oxygen (O₂) is liberated as a secondary product in accordance with the following reaction equation:

$$2 \text{ H}_{2}\text{O} \rightarrow 4 \text{ e}^{-} + 4 \text{ H}^{+} + \text{O}_{2}$$

In relation to the scientific and technological challenges, three variants can be identified which are characterised by different "electrolyte solutions", i.e. they differ in terms of the selection of the ions dissolved in the water.

Alkaline water oxidation (high concentration of OH⁻ in the electrolyte, pH >13)

Readily available, inexpensive metals can be used as catalysts here, the catalytically active phase (surface layer) of which is an oxide or hydroxide. Systematic investigations have revealed low overpotentials for example for nanostructured nickel-iron mixed oxides ($\eta < 0.25 \text{ V}$ at 10 mA/cm²). Many available large scale industrial systems are based on nickel steel sheets (in sodium or potassium hydroxide solution at temperatures of 60 to 80°C) and here too only low overpotentials are necessary in con-

tinuous operation for current densities of $> 500 \text{ mA/cm}^2$.

The requirements which apply to the catalyst material differ in the case of direct coupling of the photoreaction, water oxidation and reductive product formation. Since the dimensions of the photomaterial (for example multilayer silicon solar cells) permit comparatively large catalyst surface areas, current densities of 10 to 50 mA/cm² are sufficient even at maximum sunlight intensity. In this case, it is usually thin catalyst layers (thickness in the nano- and lower micrometre range or nanoparticles) which are used.

Acidic water oxidation (high concentration of H^+ , pH < 1)

Acidic water oxidation is primarily carried out using high-performance PEM electrolysis technology which can take the form of a compact "sandwich" of anode, cathode and proton-conducting polymer membrane. In this way, extremely high current densities (> 1 A/cm²) can be achieved in a space-saving and robust structure which moreover, unlike the alkaline electrolyser, can be started up and shut back down again within minutes. This concept has already been successfully trialled in combination with wind power systems and, in the context of artificial photosynthesis, is of interest in particular for relatively small, distributed systems for combining photovoltaic systems with fuel production. However, due to the tendency of almost all oxides to dissolve in acidic media, virtually only iridium oxide has so far been used as the water oxidation catalyst in PEM electrolysers. Since iridium is an extremely rare and thus costly element, the use of such catalysts can only be considered to be a stopgap technology.

Neutral water oxidation (low concentration of both H^{+} and OH^{-} , moderate pH values)

Water oxidation in the neutral pH range would appear to be attractive on safety

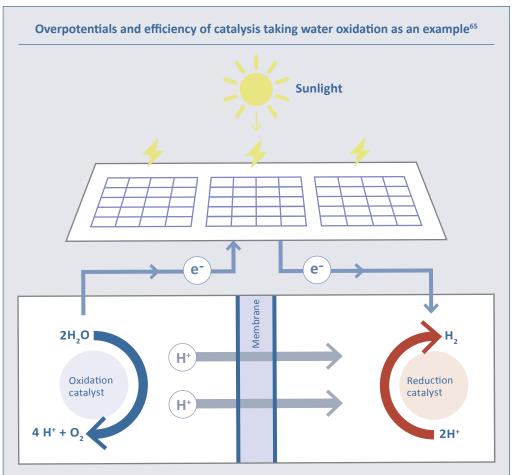


Figure 2-5: Half reactions of electrically driven water splitting (diagram: Ph. Kurz).

If it is to be possible for water oxidation (see figure 2-5, left), for example, to proceed on the electrode, the applied potential must be more positive than the equilibrium potential ($E^0_{H2O/O2}$) of approx. +1.23 volts (versus RHE, potential or electrical voltage relative to a reversible hydrogen electrode). In fact, however, no reaction yet proceeds at this value because an overpotential (η) is necessary in order to achieve acceptable reaction rates or electrode currents for water oxidation. The electrode potential E required for industrial application is obtained as the sum of the equilibrium potential of the respective half reaction (in this case of water oxidation) and the overpotential according to:

$$E = E^{0}_{H2O/O2} + \eta$$

In the case of catalysis on electrode materials, η is in each case stated for a current density of relevance in the respective system (for example 10 milliamperes or 1 ampere per cm²).

In energy terms, the overpotential η is the energy which is lost on the electrode during the electron transfer process, since it is mainly released in the form of heat. The task of catalysts or catalytically active electrode materials is to keep the overpotential required for high conversion rates or current densities as low as possible, this applying to both half reactions of the process. One major research and development task in the field of artificial photosynthesis is thus to develop suitable catalysts for both the oxidation and the reduction half-reactions. The characteristics of the catalyst material largely determine both the energy efficiency and the chemical selectivity of the system.

grounds (avoidance of strong acids and bases). As things stand today, near-neutral conditions are essential for water oxidation in conjunction with electrocatalytic CO₂ reduction, since the introduction of gaseous CO₂ into the electrolyte normally gives rise to a hydrogencarbonate solution with a pH of between 5 and 10. However, at comparable overpotentials, the current intensities which have so far been achieved are usually several orders of magnitude below those of alkaline or acidic water oxidation, even in the case of electrolytes which are actually highly conductive and which buffer pH effects. The reasons for this are so far only partially understood.

State of research and development

In principle, no further scientific or technological breakthroughs are necessary in order to be able to combine alkaline or acidic water oxidation on a large industrial scale with the generation of "green" electricity. Overall, a system of two structural units directly connected to one another (see figure 2-5) would then be used: 1) generation of renewable electricity (e.g. by solar cells) and current/voltage conversion to create appropriate electrolysis voltages; 2) water oxidation and for example hydrogen formation in an electrolysis unit connected to the electricity module.

Further development is, however, still required. For instance, alkaline oxidation requires the development of high-performance hydroxide ion (OH-) exchange membranes in order to enable more compact and inexpensive systems in particular for distributed fuel production. In the light of the advantages of existing PEM systems, there is great interest in the development of iridium-free catalyst materials for acidic water oxidation. There is moreover an urgent need for efficient catalysts for neutral water oxidation in order to permit the (electro)catalysis of CO₂ reduction in an aqueous medium. And finally, photomaterial and water oxidation are often directly coupled using nanostructured catalyst films, the long-term stability of which is not as yet satisfactory and requires further experimental investigation. Furthermore, attention must be paid to critical corrosion or dissolution processes which could possibly be remedied by dynamic "self repair".⁶⁶

2.2.4 Proton reduction, H, evolution

Of the reactions which need to be controlled for the production of "solar fuels", the formation of hydrogen is indisputably one of the simplest. A glance at the reaction equation reveals that, in formal terms, four fundamental particles (two protons and two electrons) are combined to yield $\rm H_2$, the lightest stable chemical molecule that exists.

Formation of H_2 : 2 H⁺ + 2 e⁻ + energy \rightarrow H₂

Combustion of H_2 : 2 $H_2 + O_2 \rightarrow$ 2 $H_2O + energy$

Hydrogen reacts with oxygen from the air, liberating considerable energy, to form water, so the waste gas is non-toxic. This combustion reaction is already in routine use in hydrogen fuel cells (or more spectacularly in rocket engines) for ${\rm H_2}$ -based energy generation and is a well-established technology for both stationary and mobile applications. Today, however, hydrogen is used less as an energy storage means than for chemical synthesis (refineries, ammonia production, organic chemistry). At least two major challenges still face the large scale industrial use of hydrogen:

The energy density of gaseous H₂ is low (relative to its volume). At present, compressed gas tanks at high pressure (> 500 bar) or high-throughput pipelines are used for transport so that relatively large volumes of H₂ (and thus relatively large quantities of energy) can be moved.

When combined with air, gaseous H₂ forms an explosive mixture, in a similar way to natural gas or petrol vapour. Different safety requirements therefore have to be met for hydrogen as an energy carrier than for example for coal or oil.

Nevertheless, the above-stated applications mean that hydrogen is already an "everyday" industrial product. Germany alone produces over 50 billion cubic metres of gaseous H₂ per year.⁶⁷ Currently, however, more than 80 per cent of the hydrogen produced worldwide is obtained from fossil fuels, primarily by steam reforming of natural gas. Since this production route involves the formation of more than one equivalent of CO₂ for every four H₂ molecules produced, hydrogen is at present thus anything but a "green" fuel.

Electrolysis processes are an alternative way to produce hydrogen (see box p. 36). In this case, the above-stated $\rm H_2$ formation reaction takes place in aqueous solution on the surface of electrodes. If the necessary electrical energy originates from renewable sources, the resultant hydrogen obtained from water and for example solar or wind-generated energy is actually "green". Such electrolytic production of $\rm H_2$ is, however, not yet economically viable (even when using "fossil electricity") and therefore accounts for only approx. 5 per cent of current global output volumes. 68

Furthermore, hydrogen formation is a two-electron/two-proton process in aqueous solution. If high reaction rates and low energy losses are to be achieved, catalysts must be used for the hydrogen evolution reaction (HER). One catalyst material which has been used for this purpose for over 150 years is platinum metal, on which $\rm H_2$ can be formed very quickly and virtually without energy loss at overpotentials of $\eta \approx$ -50 to

-100 mV. Platinum electrodes have to date been used for HER in commercially available electrolysis systems⁶⁹ to produce hydrogen, in particular for reactions in an acidic solution using the polymer membrane process ("PEM electrolyser").

Despite its excellent characteristics and stability, the noble metal platinum could very probably never be the HER catalyst for large-scale production of "solar hydrogen" because the terrestrial abundance of this element is too low and it is already very costly due to its use in other catalytic processes. Accordingly, scientists have been working for years on the development of alternatives to conventional platinum catalysts and considerable progress has already been made:

Thanks to the findings of nanotechnology, instead of solid platinum electrodes it is now possible to prepare minute, finely divided metal particles just a few nanometres in size and stabilise them on suitable support materials. While such catalysts are indeed still based on platinum, the quantity of noble metal required can be distinctly reduced in this way. In biological systems, the HER is very efficiently catalysed by specific proteins (known as hydrogenases) which contain iron and nickel centres as the catalytic site.70 Synthetic molecular catalysts, in particular based on these two metals, which are very inexpensive in comparison with platinum, have been developed by analogy with such proteins. Some of the reaction mechanisms of the HER have been elucidated in detail, so enabling rational optimisation of the catalyst molecules.71 As a result, noble metal-free homogeneous catalysts for the HER are now known which have very high conversion rates but as yet inadequate long-term stability. It has been possible to develop worthwhile alternative materials for heterogeneous HER catalysis

⁶⁷ These and further figures for H_2 production from: Bertau et al. 2013.

⁶⁸ Ursua et al. 2012.

⁶⁹ For example the new "SILYZER" from Siemens (Siemens 2015b).

⁷⁰ Lubitz et al. 2014.

⁷¹ Coutard et al. 2016.

Electrolysis of water

Combining photovoltaics and water electrolysis means that solar energy can be used to produce hydrogen from water. Electrolysis is a tried and tested technology which has been in use for decades. Water electrolysis involves using electrical currents to split water into hydrogen and oxygen. The efficiency of water electrolysis is above 70 per cent. Industrial plants make use of a 25 to 30% potassium hydroxide solution while the temperature is around 70 to 90 degrees Celsius in order to reduce cell resistance. A membrane is used for electrolysing water. The electrode material used may be for example ruthenium oxide hydrates (anode) or platinum (cathode), but also more readily available materials such as nickel.

High-temperature steam electrolysis (at 800 to 1,000°C) on solid electrolytes is currently also being investigated. The elevated operating temperature means that the necessary voltage can be reduced from approx. 1.90 to 1.30 volts.⁷² Obtaining hydrogen from electrolysis allows the CO₂-intensive gas reforming process to be replaced, so greatly improving the emissions balance of industrial processes. Another application could be direct use as fuel for fuel cell powered vehicles.⁷³

If "excess" electrical energy from wind power or photovoltaic systems is to be stored using water-splitting, the systems must be able to respond quickly to rapid fluctuations in electricity production. The Linde Group, Siemens and Stadtwerke Mainz have established the world's largest "power-to-gas" plant of this kind.⁷⁴ It uses a highly responsive PEM high-pressure electrolysis system which is particularly well suited to high current densities and is capable of quickly responding to the major peaks in electricity production from wind and solar systems. A proton-conducting membrane (PEM) in the electrolyser separates the zones in which oxygen and hydrogen are formed.⁷⁵ Three electrolysis units split water into hydrogen and oxygen. The PEM electrolysers⁷⁶ supply hydrogen at a pressure of up to 35 bar which means that it does not need to be pressurised further in order to permit further processing or storage.

based on inexpensive metals, in particular alloys of the metals iron, cobalt or nickel. The latter are already in routine use in alkaline electrolysers. Ionic compounds such as molybdenum sulfides are, however, now also achieving acceptable rates of catalysis. However, work is still required on rate of reaction, energy efficiency (η currently mainly above around -200 mV) and stability before industrial use of these readily available platinum alternatives will be possible.

Hydrogen is certainly a target molecule of interest for artificial photosynthesis. In industrialised nations such as Germany there is already strong demand for H₂ in the chemicals industry, and technologies for making use of hydrogen in energy applications are likewise well established. However, if large volumes of "solar hydrogen" are to be produced via artificial photosynthesis, further development effort is required, in particular to make the already known noble metal-free catalysts more efficient, durable and reactive.

⁷² Sunfire GmbH has delivered a high-temperature steam electrolysis system based on solid electrolytes with an input power of 150 kW.

⁷³ Siemens 2015a.

⁷⁴ The research project includes investment of some € 17 million and half the funding was provided by the Federal Ministry for Economic Affairs and Energy as part of the "Energy Storage Funding Initiative".

⁷⁵ Siemens 2015c; Siemens 2015a.

⁷⁶ Siemens 2015b.

2.2.5 CO, reduction

Together, the chemical sub-processes of water oxidation (see section 2.2.3) and proton reduction (see section 2.2.4) permit the formation of hydrogen (H2), the simplest chemical energy carrier. Selectivity and product specificity are generally not a problem, since solely H_oO is oxidised in aqueous solutions and specifically protons (H+) are reduced to yield molecular hydrogen (H₂).⁷⁸ In addition to "cold combustion" in fuel cells (for electricity generation), hydrogen can also be put to direct thermal use in engines, generators and heating systems, the latter without any fundamental technical differences from the use of fossil fuels. Light-driven hydrogen formation therefore can be and generally is classified as one possible kind of artificial photosynthesis, even if, unlike natural photosynthesis and cellular respiration, CO₂ conversion is not involved in either the production or use (combustion) of hydrogen.

Artificial photosynthesis does, however, also include the synthesis of carbon-containing compounds which are generally easier to transport, store and use. It is therefore to be expected that obtaining non-fossil fuels and valuable products from water and CO₂ will become increasingly significant in future artificial photosynthesis systems. In addition to the light-driven reduction of carbon dioxide which is possible in principle, it is also possible to use conventional chemical reduction of CO₂,⁷⁹ electrons being indirectly transferred to CO₂, for example by means of the already industrially established gas phase reaction of carbon dioxide with gaseous H, which could originate, for example, from light-driven water splitting (cf. figure 1-6).80,81

Direct electrocatalytic CO_2 reduction in solutions using solid catalyst electrodes is discussed in the following section. Photoelectrocatalytic CO_2 reduction by direct combination of photoactive semiconductor materials and catalysts is not separately discussed since, with regard to the catalyst materials, the same principles and issues as in purely electrocatalytic CO_2 reduction will very probably be of significance.

Direct electrocatalytic CO, reduction

A typical system for electrocatalytic CO₂ reduction contains a water-oxidising catalyst electrode (see section 2.2.1) and an electrode for CO₂ reduction. In contrast with the ready availability of water, specific steps must be taken to supply the "raw material" CO₂. This is achieved by a usually aqueous solution having its concentration of CO₂ increased in the surroundings of the reduction electrode, typically by introducing the CO₂ into the solution under pressure in gaseous form. Reactions then proceed in the solution which can in general be described by the following equation:

$$iCO_2 + jH^+ + j\{e^-\} \rightarrow C_1H_xO_y + kH_2O$$

While in biological photosynthesis it is usually sugar molecules containing six carbon atoms which are formed (for example glucose, C₆H₁₂O₆), the products in direct electrocatalytic CO₂ reduction are (so far) primarily compounds with just one or two carbon atoms (C₁ or C₂ products).82 Particularly frequent C, products are the gases methane (main component of natural gas, CH₄) and carbon monoxide (CO) and, to a lesser extent, the liquids formic acid (or formate, HCOO-) and methanol (CH₂OH). Particularly frequent C₂ products are the gas ethylene (C₂H₄) and ethanol (C₂H₂OH). In virtually every case, however, hydrogen (H_o) also occurs as a further, in this case unwanted,

⁷⁸ Hydrogen peroxide might occur as a further reaction product, but this potentially valuable product is not normally formed to any great extent. When carbon-based electrode materials are used, unwanted secondary reactions can lead to oxidation of the carbon with formation of CO₂.

⁷⁹ Klankermayer et al. 2016.

⁸⁰ van de Krol/Parkinson 2017.

⁸¹ The Sabatier and Fischer-Tropsch processes are reactions which can be used on a large industrial scale to reduce CO_a to yield methane and many further hydrocarbons.

secondary product. Normally, two to five reaction products predominate, the range of products being dependent on the catalyst material and the overpotential. One of the causes of the low specificity is that the equilibrium potentials (redox potentials) for the formation of hydrogen and the various carbon-containing reaction products are very similar (see figure 2-6). High CO specificity has for example been achieved for silver-based catalyst electrodes (> 85 per cent of the reducing current leading to CO formation), the ratio between the carbon monoxide and hydrogen gases which are formed being controllable via the overpotential.83 Accordingly, "synthesis gas" (with H₂:CO ratios ranging from 1:1 to 3:1 depending on application) can be obtained in a targeted manner and used in the gas phase synthesis of methane and further carbon-containing fuels and valuable products using established industrial processes. Good specificity for direct methane formation (80 per cent of current used) has been reported for a copper-based catalyst.84 Using other electrodes enables the formation of C₂ products, in particular ethylene and ethanol, it being possible for the proportion of the reducing current for ethylene formation to exceed a value of 30 per cent. Electrocatalytic ethylene formation using CO2 from waste gases could be of economic interest even in the relatively near future due to the comparatively high market price of this chemical industry intermediate (see also 3.2). In addition to complex nanostructured metal-based catalyst electrodes, new carbon-based materials are also showing great promise. 85

Research and development into scalability
Electrocatalytic or also directly photoelectrolytic CO₂ reduction is of great interest both for the direct formation of fuels and valuable products and for the production

of synthesis gas. Apart from possible exceptions such as ethylene formation from waste gas CO₂, the transition to industrially significant large scale systems can only be undertaken in the long term. Relatively extensive basic research and development work remains to be done. Systematic investigation of catalytic mechanisms, which has so far not been carried out to a particularly great extent, may play an important part here. Possible success in terms of industrially significant systems will also depend on unpredictable, but potentially game-changing, discoveries. There is, however, a general need for research and development in CO₂ reduction with regard to the following points:

- · product specificity,
- boosting energy efficiency (to > 50 per cent),
- direct or indirect combination with systems for using "dilute" atmospheric CO₂ (instead of using prepurified CO₂ from coal combustion or from cement and steel manufacturing) and
- new catalyst systems for forming longchain carbon compounds (C_{i>2} products).

CO, as raw material

For almost a century now, CO₂ has been used as a starting material for the production of urea (output in excess of 200 million tonnes per annum in 2016).⁸⁶ More recently, applications in the plastics sector (for example (poly)carbonates) have come into use (see figure 2-7). There are, however, no further major industrial applications, which is above all attributable to the thermodynamic stability of CO₂ and the associated huge energy requirements.

As a reliable and renewable carbon source, carbon dioxide is a C1 building block which is of interest for the production of energy carriers and valuable prod-

⁸³ Hatsukade et al. 2014. 84 Manthiram et al. 2014.

⁸⁵ Zhu et al. 2016.

⁸⁶ http://www.ceresana.com/de/marktstudien/chemikalien/harnstoff-urea/.

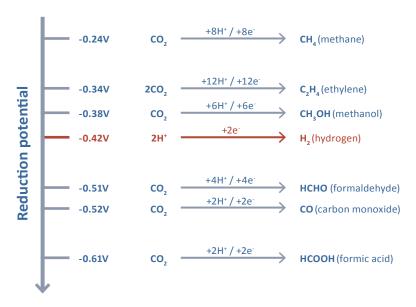


Figure 2-6: Reduction potentials for important reaction products of CO₂ reduction at neutral pH (potentials versus normal hydrogen electrode). However, if the respective reactions are actually to proceed at high rates (current densities), substantially more negative electrode potentials (i.e. high overpotentials) must in general be applied with currently known electrocatalysts. All the potentials of the electrocatalytic CO₂ reductions shown are furthermore close to the equilibrium potential of H₂ formation (also shown in red), which is why product specificity and suppression of H₂ formation with the lowest possible overpotentials are among the central tasks facing catalyst development (diagram: Ph. Kurz).

ucts. The central challenge facing the use of carbon dioxide on a large scale is providing the raw material CO₂ inexpensively and energy-efficiently. A fundamental distinction must be drawn between capturing CO_o from combustion or industrial waste gases (which typically contain 5 to 15 percent CO₂) on the one hand and from the ambient air (containing only 0.04 percent CO₂) on the other.87 The latter process of Direct Air Capture (DAC)88 is distinctly more complex due to the approx. 300 times lower CO₂ concentration in ambient air. Using highly concentrated CO₂ from waste gases can only be a stopgap or transition technology for the large-scale production of carbon-based fuels and valuable products by artificial photosynthesis; in the long-term, it will be necessary to use CO₂ from the ambient air.

The associated challenges are comparable with those facing CCS (Carbon Capture and Storage) processes. Unlike this latter process, artificial photosynthesis makes use of the CO₂ carbon as a raw material (CCU: Carbon Capture and Utilisation).⁸⁹ Technologies are being developed in the course of work on CCS/CCU for capturing ⁹⁰, purifying⁹¹ and storing CO₂.

Increasing the concentration of CO₂ requires energy. The theoretical (thermodynamic) minimum energy input for concentrating CO₂ from ambient air amounts to approx. 20 kJ/mol (126 kWh per tonne of CO₂). If, for example, this CO₂ is converted into methanol, 726 kJ/mol (enthalpy of combustion) of energy can be stored (4580 kWh per tonne of "fixed" CO₂), which would amount to an energy input of 2.75 per cent of the stored energy. In actual industrial systems for concen-

⁸⁷ While CO₂ capture from the air (0.04 per cent) may appear very complex, these systems could easily be scaled because they are potentially universally usable. BECCS (Bio-Energy with Carbon Capture and Storage) is currently being investigated by the "Bioenergy" Working Group of the ESYS project (https://energiesysteme-zukunft.de/projekt/arbeitsgruppen/).

⁸⁸ Sanz-Perez et al. 2016.

⁸⁹ Fischedick et al. 2015

⁹⁰ For example from combustion gases by absorption or membrane capture.

⁹¹ CO₂ purity is important for catalytic processes.

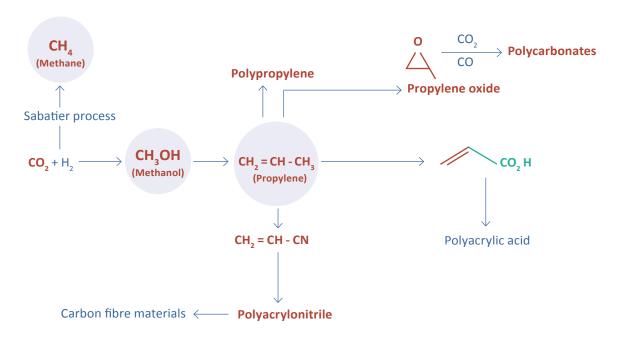


Figure 2-7: Chemical utilisation of CO, as a carbon source for industrial plastics (diagram: M. Beller).

trating CO₂ before the step of CO₂ conversion into methanol, the energy required for concentration could be for example five times higher, which would raise the energy input to 14 per cent of the chemically stored energy. (This value would be somewhat lower, approx. 11 per cent, for methane formation and slightly higher for other substances such as ethanol.)

Research is currently being carried out into the development of improved chemical technologies for concentrating CO₂.92 Pilot plants for concentrating CO₃ from ambient air have already been built, some in the context of company startups, so the technology can be considered technically feasible. Costs for future systems (including investment and capital costs) per tonne of concentrated CO could amount to US\$ 100 to 200, but estimates are as yet unreliable (cost estimates ranging from US\$ 30 to 1,000 per tonne of CO₂).93 CO₂ can thus be used as a raw material, but using CO2 as a carbon source is an order of magnitude more costly than using coal.

In biological photosynthesis, CO₂ conversion proceeds without prior concentration. It would obviously be of great interest to develop artificial (chemical) systems which bypass the CO₂ concentration step or directly couple it with catalytic CO₂ reduction in order to reduce energy losses distinctly closer to the theoretical minimum. So far, only relatively little such "high risk – high gain" research is being pursued.

In addition, the energy required for recirculation must be provided from non-fossil sources and without generating additional CO₂. In general, "energy-rich" reagents (in the case of polycarbonates these are epoxides based on fossil resources) or costly reductive processes are required in order to convert CO₂ into other organic fine or bulk chemicals, materials or fuels.⁹⁴

Direct or indirect CO, reduction

Possible scenarios for new large scale industrial conversions of CO₂ into bulk products include direct reduction with hydrogen to yield methane, methanol or al-

⁹² Olfe-Kräutlein et al. 2016, p. 8.

⁹³ Sanz-Perez et al. 2016.

kanes. Numerous homogeneous and heterogeneous catalysts are known for such transformations.95 Complete reduction to methane can be successfully carried out with the assistance of nickel-based catalysts, while methanol is produced using copper-based catalysts. Heterogeneous materials, which are suitable for industrial applications after further optimisation, are predominantly used for these two products. Formic acid derivatives of CO can be produced both with molecularly defined complex catalysts and with nanostructured heterogeneous catalysts. Industrial implementation of any of these processes will entail, in addition to optimisation of the catalyst systems, the availability of inexpensive reducing agents obtained from renewable energy sources.96

The conversion of CO₂ into methanol will be presented here by way of example. The process has been put into commercial operation in a geothermally powered demonstration plant in Iceland (Carbon Recycling International). The methanol obtained can be used for producing both motor fuel and chemical products. There could thus be a prospect of large scale industrial production of acetic acid (using the Monsanto process from methanol and CO) and the conversion of methanol into propylene using the MTP process. Propylene in turn is widely used as a starting material for a series of organic materials (see figure 2-7) ranging from polypropylene (material) via polyacrylic acids (inter alia superabsorbents in hygiene products) to polyacrylonitrile (PAN) fibres. The latter are the basis not only for modern textiles ("Dralon") but also for carbon fibres which are used in the production of lightweight materials in the automotive sector and for wind turbines for energy generation. Oxidation of propylene to yield propylene oxide provides access to further important polymeric materials for

cosmetics, foodstuffs and medical products and the production of polyurethanes (PU). In principle, a major part of today's bulk chemicals can be made sustainably available in this way (see figure 2-7).⁹⁷

In addition to rapidly carrying out a sequence of processes (production of hydrogen from renewable energy and subsequent catalytic reduction of carbon dioxide), direct photo- and electrocatalytic conversions of carbon dioxide are of greater interest in the medium and long term because they can be more energy-efficient. Reductions of CO₂ to yield carbon monoxide (CO), formic acid derivatives, methane or ethylene are already known in principle. Which product is ultimately obtained depends on the catalyst or electrode used, these in turn determining not only selectivity but also the speed of reaction. Challenges for the future are here in particular the use of inexpensive, non-toxic metals and the development of systems with long-term stability.

2.2.6 Ammonia production

Ammonia (NH₂) is a very important commodity chemical and is also being discussed as an energy carrier. Ammonia is currently known in particular for its use as an agricultural fertiliser. However, virtually all industrial processes which result in nitrogenous compounds (for example nylon production) are also based on ammonia. The availability of this compound is therefore essential to humanity today. Some future scenarios, however, go even further and consider NH3 and ammonia derivatives such as hydrazine (N₂H₄) or aminoborane (H,BNH,) as also being potentially worthwhile carbon-free, molecular hydrogen carriers and fuels with a high energy density.98

97 Using CO, as a raw material for producing organic

chemicals cannot by itself prevent global climate change. Producing "solar fuels" based on carbon dioxide and renewable energy could, however, make a significant contribution to reducing CO₂ emissions.

⁹⁸ Lan/Tao 2014, Comotti/Frigo 2015.

At present, ammonia is produced industrially (global annual production around 200 million tonnes) almost exclusively on the basis of fossil resources (primarily natural gas) using the Haber-Bosch process; production is carried out in large plants worldwide (including in Germany).99 The second raw material for synthesising ammonia is air, 80 per cent of which consists of molecular nitrogen (N_o). Nitrogen is thus much more readily available than CO₂, but is also one of the most inert molecules known. The direct reaction with H₂ to yield NH₃ in the Haber-Bosch process thus requires high temperatures and pressures, which results in the process having a huge energy footprint. Industrial ammonia production is accordingly considered to be responsible for around 1 to 2 per cent of global CO₂ emissions. Developing alternative processes for a sustainable production of ammonia is therefore likewise a major technological challenge.

"Green" ammonia could, on the one hand, be synthesised by reacting sustainably produced hydrogen (for example from artificial photosynthesis) with No from the air in conventional Haber-Bosch plants. The primary problem to be solved in this case would be that of obtaining high purity nitrogen. In the Haber-Bosch process, the latter arises automatically as a secondary product of the upstream steam reforming of natural gas with air (by means of which the hydrogen for the process is usually obtained). Pure nitrogen, on the other hand, is currently obtained by air liquefaction (Linde process) which is itself very energy-intensive.

Electrochemical processes, on the other hand, are a less energy-demanding way of obtaining NH₃. Such processes theoretically have the potential to reduce energy consumption in ammonia production by around 20 per cent and to avoid

the high costs of high-pressure synthesis plants. 100 Both molecular and heterogeneous catalysts for the electrochemical reduction of $\rm N_2$ in solution are currently in development. 101

The production of ammonia as a fuel and valuable substance is therefore currently the least developed branch of artificial photosynthesis. In the light of its elevated potential for CO₂ savings and its major significance for the foreseeable future for feeding humanity, greater attention should however be paid to it as a possible target process for the conversion of solar energy.

2.3 Artificial photosynthesis – systems integration

The goal of artificial photosynthesis is to develop systems in which the processes of light absorption, charge separation and conversion of materials into fuels or valuable products are integrated to form a functional unit. Such systems will ultimately have to be scaled up for application to a number of square kilometres (light capture area) in size and gigawatts in power if they are to be able to produce bulk products such as hydrogen, methanol or ethylene at favourable prices in centralised plants. The apparatus should additionally have a service life of at least ten years in order to recoup the initially required investment in energy and capital. Large devices of this type do not yet exist, but there are smaller scale demonstration devices operated by various research groups. Most of these are for splitting water to produce H₂,102 some for reducing CO₂¹⁰³ or combinations of the two, for ex-

¹⁰⁰ Giddey et al. 2013.

¹⁰¹ In approaches involving an aqueous solution, it must be borne in mind that, although the concentration of nitrogen in air is very high in comparison with CO₂, the solubility of nitrogen in water is very low in comparison with the solubility of CO₂.

¹⁰² Ager et al. 2015.

¹⁰³ Schreier et al. 2015.

ample to produce higher alcohols.¹⁰⁴ Some current examples of such devices with an increasing degree of integration are presented below.

2.3.1 Separate PV-driven electrolysis systems

Probably the simplest structure for a system for artificial photosynthesis is a solar cell which drives an electrolysis cell (cf. section 2.2.4). Under operating conditions, typical silicon-based solar cells generate a voltage of 0.5 to 0.7 volts.

Accordingly, at least three series-connected silicon cells are necessary to generate the voltage of only a little below 2 volts which is conventionally required for electrocatalytic water splitting. Alternatively, the voltage of the solar cell(s) can also be raised by electronic voltage converters to the level required by the electrolyser. This conversion can proceed with high efficiency (over 90 per cent) but is associated with higher complexity and costs for the overall system. Another approach is solar

System efficiency in solar energy conversion

In photovoltaic modules, solar energy conversion efficiency is defined as the ratio between the total intensity of solar radiation incident on the module (W_{solar} in W/m^2) and the electrical power at solar module output ($W_{product}$ in W/m^2):

$$\Phi_{\text{solar}} = W_{\text{product}}/W_{\text{solar}}$$

For example, if in full sunlight (approx. 1,000 W/m²) the electrical output power is 180 W/m², the value of Φ_{solar} is 18 per cent, which is at present a typical value for a silicon-based photovoltaic module. The conditions and measurement protocols for determining Φ_{solar} are internationally standardised, so ensuring good comparability of this performance parameter. The same result is obtained if, instead of the powers ($W_{product}$, W_{solar}), Φ_{solar} is calculated by relating the power of the incident sunlight (E_{solar}) over one hour to the electrical energy ($E_{product}$) generated over the same period:

$$\Phi_{\text{solar}} = E_{\text{product}} / E_{\text{solar}}$$

In the above example of a typical photovoltaic module, $\rm E_{solar}$ would be one kilowatt-hour (kWh) and $\rm E_{product}$ 0.18 kWh.

If the solar energy is used to form fuels, the above equation for calculating Φ_{solar} can again be used but E_{product} then indicates the chemically stored energy. This can be defined in various ways, but the Φ_{solar} values obtained usually differ only slightly. It is simplest to define the chemically stored energy as a gross calorific value, i.e. as the energy which would be released again as heat on combustion of the substance produced using solar energy. Φ_{solar} is not necessarily a meaningful performance parameter for the production of specific valuable products for which the emphasis is not on chemical energy storage.

¹⁰⁴ Chong et al. 2016; Liu et al. 2016.

¹⁰⁵ If the substances produced are used as fuels in a fuel cell, Gibbs energy should be used to calculate $\Phi_{\rm color}$.

In photovoltaic modules, Φ_{solar} is only comparatively slightly dependent on sunlight intensity, temperature and season. This is not the case for solar energy use by plants, algae and cyanobacteria. For instance, the rate of photosynthesis is saturated at relatively high light intensities. The value of Φ_{solar} is thus substantially lower at maximum levels of sunlight than at a low sunlight intensity. Marked temperature dependency phenomena and major seasonal fluctuations also occur. The above equation for calculating Φ_{solar} can however still be used to obtain an indicative value for the efficiency of solar energy utilisation. This is achieved by relating the energy of the incident solar radiation over a full year to the energy of the fuel produced over one year. For crop plants, this would be for example the gross calorific value of the biomass harvested over the course of a year. The Φ_{solar} values obtained in this way are typically distinctly below 1 per cent. ¹⁰⁶

In artificial photosynthesis, the issue of light saturation as an adaptation between the characteristics of light absorption and primary charge separation on the one hand and the catalytic reactions on the other hand is being discussed. The role played by coordination of the sub-processes and light saturation in determining Φ_{solar} will have to be separately established for each newly developed artificial photosynthesis system.

Solar energy conversion efficiency must not be confused with quantum efficiency, which can reach values in excess of 90 per cent in both photovoltaic systems and biological photosynthesis. A high quantum efficiency is a necessary prerequisite but in no way a guarantee of a high Φ_{solar} value. Quantum efficiency alone is therefore of only subordinate significance in the assessment of technological performance.

cells which consist of a plurality of stacked absorber materials. Some such "tandem" solar cells generate voltages of over 2 volts and are thus capable of driving electrolysers for H_o production. One current example is a water splitting system developed at Stanford University which consists of a three layer solar cell of III-V semiconductors and two electrolysers with a polymer electrolyte membrane which operate at 80 degrees Celsius.107 The solar cell generates around 3 volts when irradiated with (48 times) concentrated sunlight which drives the two series-connected electrolysers. Over 48 hours of operation, the system achieved an average efficiency of 30 per cent and thus the highest value so far for photoelectrochemical water splitting.

Costs are the greatest challenge facing PV-driven electrolysis systems. All the

components (including the control electronics) have to be individually produced and then assembled with one another. In photovoltaics, such "system costs" in addition to material costs for the actual solar cell often account for over 25 per cent of the total cost of a module. A further challenge is that of transferring the waste heat from the solar absorber to the electrolysis modules, so making it utilisable for the electrochemical reactions.

2.3.2 Integrated photovoltaics/electrolysis systems

Some of the stated disadvantages of separate PV-driven electrolysis systems could possibly be overcome by combining light harvesting and electrolysis in a single apparatus. For example, the system costs (glass, frame, wiring) of such an integrated system would probably prove to be lower. As a result of the spatial vicinity of

light absorption and electrolysis, the heat evolved by the photoactive material could additionally be utilised to increase reaction rates. Moreover, the current density of such systems would be similar to the photon current and thus twenty to a hundred times lower than in the commercial electrolysers used in separate systems. Lower requirements are therefore placed on the catalyst, such that it is today already possible to use substantially less costly materials instead of noble metal-containing compounds.

Proofs of concept of such systems have already been provided, ¹¹⁰ although these have mainly been apparatuses with a small area. For instance, researchers at Forschungszentrum Jülich have recently reported an integrated electrolysis system with a size of around 50 square centimetres (see figure 2-8), in which commercial-

ly available nickel catalysts for forming $\rm H_2$ or $\rm O_2$ were applied to two series-connected silicon-based thin-film tandem solar cells. This small area assembly achieved an efficiency of 3.9 per cent, could be operated for forty hours without any major loss of activity and would in principle be scalable to substantially larger areas because it contains no rare or particularly costly individual components.

It goes without saying, however, that challenges still remain here: the relatively large active area of the apparatus makes it difficult to produce and to collect the gaseous products at high pressures (which would be desirable at least for H₂ as a fuel). Moreover, as shown, membranes are necessary for separating the two sub-processes and these are neither inexpensive nor stable over extended periods.

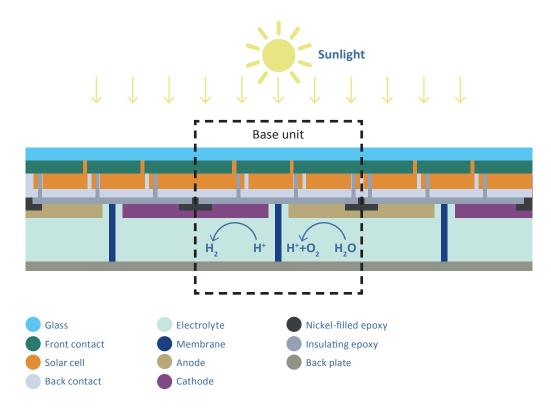


Figure 2-8: Integrated system for photoelectrochemical water splitting (explanations in the text, diagram after Forschungszentrum Jülich). 109

¹⁰⁹ Ager et al. 2015.

¹¹⁰ Turan er al. 2016.

2.3.3 Photoelectrocatalysis on semiconductor surfaces

The preceding sections have discussed light absorption and electrochemistry as separate processes. They can, however, also be combined by carrying out the electrochemical reactions directly on the surface of the light-absorbing semiconductor. The efficiencies of the processes which take place on such solid-liquid interfaces are in principle identical to those of photovoltaic systems. In contrast with PV systems, in which the interfaces have to be tailored to requirements, sometimes with not inconsiderable effort, during the production process, the semiconductor-electrolyte contacts are formed "automatically" on immersion of the semiconductor into the solution. This concept was first implemented in 1972 by Fujishima and Honda, specifically based on titanium dioxide (TiO_o) as photoelectrocatalyst material. However, only a very small proportion of the solar energy could be converted in this way because titanium dioxide absorbs only the UV range of the solar spectrum. A search was therefore then begun for alternative semiconductor compounds which were stable in water and had a smaller band gap in order to be able also to use visible light for charge separation. In most cases, these requirements are met by a combination of two semiconductor materials arranged one above the other in what are known as tandem cells in order to achieve a sufficient photovoltage despite the lower energy of visible photons. The band structure of the material should moreover match the redox potentials for water oxidation and reduction and the surface reaction kinetics should be rapid.

Although some highly promising materials for such cells have been known for many years, none of them has yet met all the requirements for industrial use. ¹¹² Bismuth vanadate (BiVO₄), for ex-

ample, has some advantages: this yellow pigment is very inexpensive, is stable in water at a neutral pH and exhibits very good light absorption characteristics. Indeed, with BiVO, and silicon as the semiconductor materials, efficiencies of 5 per cent have been achieved with a photoelectrochemical cell using solar energy for hydrogen production.113 However, the main drawback of the material is, as with TiO2, its excessively large band gap of 2.4 electron volts which limits the theoretically usable fraction of the solar energy to 9.3 per cent. A material which would be better in this respect (and still more inexpensive) would be the iron oxide haematite (Fe₂O₂), whose smaller band gap of 2.1 electron volts would allow to use 15 per cent of the solar energy. However, the electron-hole pairs produced by light recombine extraordinarily quickly in haematite so it is doubtful whether such high efficiencies could ever be achieved with this material.114

Two research routes are currently being pursued in order to overcome the limitations of known semiconductor materials for photoelectrodes. On the one hand, a search is being conducted for completely new materials with suitable band gaps and good chemical stability. A virtually unlimited number of combinations of elements is generally possible and it is to be expected that broadly directed materials research (for example in the context of the "Materials Genome Initiative"115) will allow the identification of new, highly suitable materials. Traditional trial and error searches are today increasingly being replaced by computer-assisted processes and automated high throughput methods and these have already made it possible to track down several highly promising new absorber

¹¹³ Abdi et al. 2013.

¹¹⁴ Carbon nitrides or polymers may also be used in addition to metal-containing materials.

¹¹⁵ https://www.mgi.gov/content/materials-project.

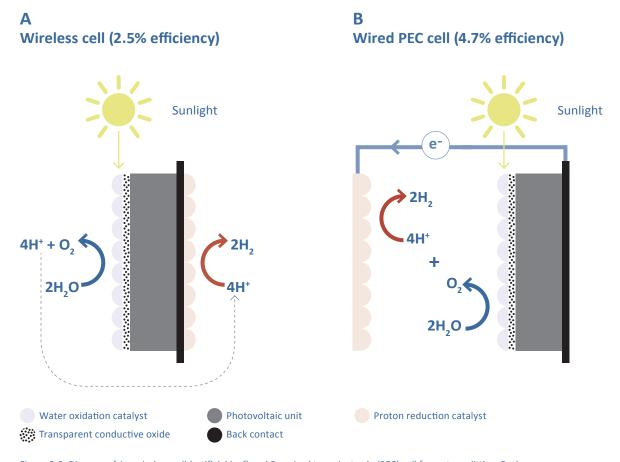


Figure 2-9: Diagram of A a wireless cell (artificial leaf) and B a wired two-electrode (PEC) cell for water splitting. Both approaches use identical light absorbers and catalysts. 116

materials for further study. 117 Alternatively, various already known materials could be combined in order to get closer to the desired characteristics. For instance, ultra-thin (< 100 nanometre), electrically conductive protective layers for semiconductor surfaces have been developed which prevent direct contact between the semiconductor and solution and so increase from minutes to days the service life of for example copper oxide photocathodes or photoanode materials which are susceptible to corrosion, such as Si, InP or GaAs.¹¹⁸ Another example is the functionalisation of semiconductor surfaces with electrocatalysts, which allows the low catalytic activity of some semiconductor surfaces to be significantly improved. Such catalysts are deposited as nanoparticles or covalently bonded molecules on the surface in the form of thin, inorganic layers. ¹¹⁹ In many cases, organic or inorganic layers are moreover capable of suppressing surface recombination of the semiconductor and thus considerably improve the photovoltage and efficiency of the system. ¹²⁰

Huge steps forward in knowledge have been made in recent years about the processes at the surfaces of semiconductor materials which have been coated with protective or catalyst layers. This is apparent, for example, from the recently developed concept of "adaptive interfaces". These are contacts which differ funda-

¹¹⁶ Diagram after Reece et al. 2011.

¹¹⁷ Yan et al. 2017.

¹¹⁸ Hu et al. 2015

¹¹⁹ Increasing semiconductor stability under reaction conditions is a further important motivation behind the search for new electrocatalysts.

¹²⁰ Zachäus et al. 2017.

mentally both from conventional semi-conductor-electrolyte interfaces and from "packaged" photovoltaic contacts in that their characteristics are influenced by the redox state of the catalyst layer applied onto them. ¹²¹ Further thorough investigations are, however, required in order to obtain a detailed understanding and improved production of such adaptive interfaces. This will also require the development of new investigatory methods, such as X-ray spectroscopy or electron microscopy measurements *during* photoelectrocatalysis using *in operando* or *in situ* techniques.

2.3.4 Artificial leaves

The currently most highly integrated artificial photosynthesis systems are "artificial leaves". They combine all the light-absorbing materials and catalytic centres in a single, sometimes paper-thin unit without external wires. One example, which was publicised in 2011 and met with considerable media interest, is shown schematically in figure 2-9. Although the conceptual simplicity of artificial leaves is attractive, they also have clear disadvantages. For instance, some of the substances participating in the reaction have to get from one side of the leaf to the

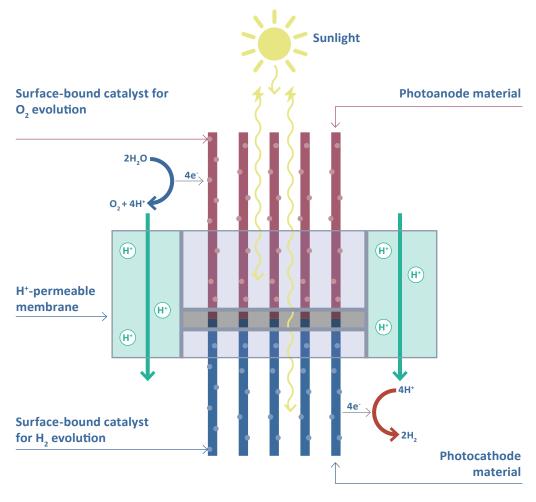


Figure 2-10: Artificial leaf concept in which light-harvesting nanowires are embedded in a proton-conducting membrane. ¹²²

¹²¹ Nellist et al. 2016.

¹²² After JCAP, cf. Marshall 2014, p. 24.

other, which considerably slows down the overall reaction. As a consequence, the leaf from figure 2-9 for example achieves only approximately half the system efficiency of the "wired" variant which is also shown. Ion-permeable membranes with directly integrated light absorbers and catalytic centres are an elegant solution to the problem of proton transport. Prototypes of this design have already been presented by the USA's JCAP consortium (see figure 2-10), but the practical implementation of such a system, which is very complicated to manufacture on a square kilometre scale, is a challenge which is yet to be solved.

2.3.5 Systems integration in a nutshell

The preceding sections have shown that the design of complete and efficient artificial photosynthesis apparatuses with long-term stability is still at an early stage and generally requires close collaboration between science and engineering, which is, however, currently still unusual in this field. It has nevertheless already been shown that bringing together the components, which are often very well understood as "individual parts" (see sections 2.1 and 2.2), is entirely possible and can result in functional overall systems. At the same time, it has become clear that systems integration is associated with new, sometimes very major, scientific challenges. Moreover, such apparatuses are currently produced in such small sizes and numbers that it has not yet been possible to estimate whether and to what extent integrated systems in the field of artificial photosynthesis actually have technological and/ or economic advantages over approaches such as coupling spatially separate photovoltaic and electrolysis modules.

2.4 Alternative approaches

Common features of the approaches to artificial photosynthesis presented up until this point are that, as an initial process, they all start from charge separation brought about by light absorption and they primarily convert small molecules such as water or carbon dioxide. The desired fuels and valuable products such as hydrogen, methane, polymers or pharmaceutical substances are then obtained on the basis of H₂O and CO₂. Two prominent alternative artificial photosynthesis concepts will be presented below. Both of them aim, once again, to produce compounds industrially using sunlight as the energy source. However, they differ fundamentally in at least one aspect of the process from the previously explained reaction sequences.

2.4.1 Use of visible light for chemical synthesis

Plastics, paints, medicines or plant protection products are produced by chemical syntheses. A considerable quantity of energy is always required for such synthesis reactions. In conventional syntheses, this process energy is provided by the starting materials (often substances which are obtained from fossil resources such as oil or coal) or supplied externally for example by heating the reaction mixture. Sunlight would here be an attractive alternative energy source for chemical syntheses.¹²³

However, most starting materials for chemical syntheses absorb virtually no visible light. Photocatalysts are therefore required which absorb solar energy and then provide this for example for redox reactions, in which, in contrast to the processes presented in sections 2.1 to 2.3, it is also possible to convert molecules with a very complicated structure (for example active pharmaceutical ingredients).

One particular advantage of photocatalysis resides in the selective excitation of the catalysts. Since the catalysts can only be excited in a targeted manner with light of appropriate energy, secondary

¹²³ Artificial illumination by LED could also be attractive here since this permits controllable and constant conditions (but would result in lower energy efficiency).

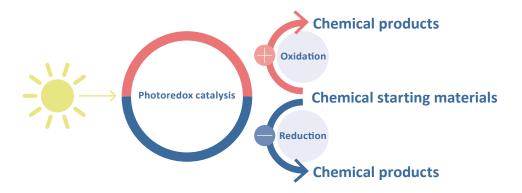


Figure 2-11: Direct use of daylight for chemical syntheses by photoredox catalysis (diagram: B. König).

reactions can be avoided and very mild reaction conditions ensured. The injected solar energy then makes it possible to carry out chemical reactions, which would otherwise have to be activated for example by heating, at temperatures as low as room temperature.

Building on work dating from the 1980s and 1990s, photoredox catalysis (figure 2-11) has developed into a very active field of research over the last 15 years. The methods which are already available make it possible to initiate chemo-, regio- and stereo-selective reactions even of complex starting molecules with visible light in the presence of suitable photocatalysts at room temperature. Initial industrial applications have been established for drug manufacture.

Despite the huge progress made in this field of research over the last decade, challenges still remain to be solved if the technology is to be put to widespread and efficient use. For instance, the stability of many photocatalysts under "production conditions" is too low and their energy efficiency also leaves something to be desired (~ 1%). The photophysical processes of light absorption and charge separation are generally very rapid, while coupled chemical reactions require more time. This leads to major energy losses and low yields in synthesis and makes the development of new photocatalysts necessary.

Since the energy of a visible photon is low in comparison with chemical bond energies, it has so far only been possible to activate relatively weak bonds photocatalytically. New concepts in which, on the model of biological photosynthesis, the energy from a number of photoexcitations is accumulated and then used for a single chemical transformation can overcome this limitation and need to be further developed. Additionally, as described above, photocatalytic water oxidation could provide reducing equivalents for chemical reactions. Combining photocatalytic water oxidation with chemical and biotechnological synthesis processes could provide access to chemical products with great value added. Finally, innovations in process engineering are also necessary, so that artificial photosynthesis can be efficiently integrated into chemical production processes.

2.4.2 Synthetic fuels from solar thermochemical conversion

In addition to the artificial photosynthesis concepts described above which, as an "initial process", all start from light-induced charge separation, valuable products such as $\rm H_2$, $\rm CH_4$ or kerosene can also be obtained from $\rm H_2O$ and $\rm CO_2$ by "solar-thermal" processes. The sunlight is here focused with the assistance of mirror arrays onto a reactor, in which the products are then formed at temperatures of 1,000 degrees Celsius and above.

As shown in figure 2-12, "synthesis gas" (a mixture of $\rm H_2$ and CO) can be produced in this way for example from $\rm H_2O$ and $\rm CO_2$ and then converted using the well-established Fischer-Tropsch process into liquid hydrocarbons which can be used as fuels.

This route has been investigated for example by the aerospace industry for the production of "solar kerosene" because there will for the foreseeable future probably be no alternative to carbon-based liquid aviation fuels. The project determined a theoretical efficiency of around 40 per cent for this solar-thermal process, 124 but the values achieved to date have remained distinctly below this maximum value. There are, however, two fundamental factors to be borne in mind in relation to this in principle highly attractive technology which has also already been demonstrated up to a kilowatt scale: the process is technically complex and can only be carried out in large plants which require high initial investment. Moreover, solar thermal energy systems need a high level of direct

sunlight and should therefore primarily be sited in regions with a hot, dry climate (thus for example in north Africa, but not in Germany).

2.5 Summary

This section has outlined the very different approaches, the huge potential, but also the numerous challenges associated with the artificial photosynthesis approach. Many of the systems presented exist at present at best as laboratory prototypes, only in part or even only on paper. It may nevertheless be stated that researchers worldwide have been able to make considerable progress in all the areas presented here, in particular over the last decade and a half, and therefore the possibility of large scale industrial production of fuels and valuable products using sunlight as the sole energy source appears much more probable today than it did at the start of the 21st century. As section 3 below will show, quite apart from the purely technical issues of feasibility, social, political and ethical consid-

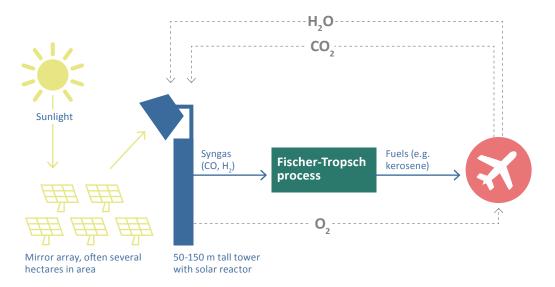


Figure 2-12: Solar-thermal process for producing aviation fuels (explanations in the text). 125

¹²⁴ http://www.solar-jet.aero.

¹²⁵ After DLR Almeria (Spain), http://www.psa.es/en/ index.php.

erations will certainly also play a part in the large scale industrial implementation because they have an impact on issues of acceptance and risk assessment as well as economic consequences. As the research currently stands, it is only possible to make limited statements about this, so, to clarify matters, table 2-2 brings the various concepts together and outlines their advantages and drawbacks.

Table 2-2: Concepts for biological, artificial and alternative photosynthesis systems.

	Advantages	Drawbacks
Biological, modi- fied and hybrid photosynthesis (section 2.1)	 Living, photosynthesising cells as starting point: evolutionarily optimised, multipliable by cell division, often very robust thanks to "self-repair" Biological/biochemical understanding of many processes now very good: many "tools" can be used to modify cell metabolism Huge diversity of possible valuable products, for example active pharmaceutical ingredients, polymers or foodstuffs 	 Energy conversion efficiency of biological photosynthesis is generally low and can be improved but is quite likely not to be usable for large-scale production of fuels such as H₂ or methanol Challenge: selective production of the desired products and isolating them from the cells Combining biological and technical systems (hybrid photosynthesis) has great potential but is still at a very early stage of development
Artificial photosynthesis (sections 2.2, 2.3)	 Completely synthetic molecules or materials as starting point; theoretically almost unlimited potential for variation and optimisation Good "candidates" are today available for industrial application for all the sub-reactions currently considered to be central (light absorption, catalysis of the formation of H₂ and O₂, and CO₂ reduction) Bringing these components together into functional artificial photosynthesis apparatuses (in particular for H₂) has already been successfully demonstrated in some pilot projects 	 Reaction rates, energy efficiency and stability of many components are currently often still too low by a factor of at least around 5 to 10 Raw materials (for example noble metals for catalysis) and manufacturing methods (for example for multi-layer artificial leaves) are still too costly for application Although more effectively usable, the routes for obtaining carboncontaining products (CH₃OH, C₂H₄, CO etc.) are currently still not energy-efficient enough and are often unselective; moreover the raw material CO₂ can at present be obtained from the air only with difficulty
Alternative approaches (section 2.4)	 Many, often already known possibilities for using photocatalysis for example to synthesise cosmetics or foodstuffs Successful use of solar furnaces for producing relatively large quantities of fuels (for example kerosene) via high-temperature processes 	 Comparatively low CO₂-saving potential of synthetic photochemistry Solar furnaces are mainly operated as large, complicated plants with high capital costs and are therefore only cost-effective in locations with high intensity sunlight

3. State of research and social context

3.1 Research activities and funding programmes

Following the pattern of section 2, a selection of research groups and funding programmes in Germany, Europe and worldwide will be presented below with the aim of providing some example insights into current activities.

3.1.1 Germany

As long ago as the 1990s, the biotechnological use of natural and genetically modified photosynthesis was the subject of a wide-ranging collaborative research project funded by the Federal Ministry of Education and Research (BMBF) entitled "Foundations for a biotechnological and biomimetic approach to hydrogen production" ("Grundlagen für einen biotechnologischen und biomimetischen Ansatz der Wasserstoffproduktion"). More recent activities investigating and developing artificial photosynthesis have been taking place in Germany in the context of numerous individual projects and also relatively small research groups which are at present supported by various funding programmes. For example, sub-processes of artificial photosynthesis (as in section 2.2 of this position paper) are being investigated at TU Darmstadt as part of German Research Foundation Priority Programme SPP 1613 "Fuels Produced Regeneratively Through Light-Driven Water Splitting" ("Regenerativ erzeugte Brennstoffe durch lichtgetriebene Wasserspaltung")¹²⁶. This programme focuses on aspects ranging from the investigation of fundamental

processes of catalytic water splitting by the light or dark reactions to science-based evaluation and the formulation of application-oriented engineering strategies. The priority programme is in its second funding phase (2015 to 2018).

The Max Planck Institute for Chemical Energy Conversion founded in Mülheim an der Ruhr in 2012 is likewise focusing on sub-processes of artificial photosynthesis. It is investigating the fundamental chemical processes of energy conversion in order to assist with the development of new, high-performance catalysts.127 The storage of energy in chemical compounds is the main topic, with the catalytic splitting of water being of central significance.

The "Renewable Energies" and "Energy Materials" divisions of the Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) are working on aspects of artificial photosynthesis, 128 in particular complex material systems (see section 2.3) for thin-film photovoltaics for producing solar fuels. The recently founded Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (HI-ERN)129 is addressing sub-aspects of the chemical storage of renewable energy.

The development of pilot and demonstration projects is a priority for the BMBF-funded "Power-to-X" Kopernikus Project, with technologies which convert electricity from renewable sources

¹²⁷ https://cec.mpg.de/home/.

¹²⁸ http://www.helmholtz-berlin.de/.

¹²⁹ http://www.hi-ern.de/hi-ern/en/home.html.

¹²⁶ http://www.solarh2.tu-darmstadt.de/solarh2/index.

into material energy stores, energy carriers and energy-intensive chemical products.130 Products are for example gaseous substances such as hydrogen or methane, liquid substances such as motor fuels for mobility or basic chemicals for the chemicals industry. Central research themes of the project are medium- and large-scale electrolysis systems for producing hydrogen from excess power from wind and solar generation and analyses for trialling various process Power-to-X routes. Overall, 18 research institutions, 27 industrial companies and three civil society organisations (such as Friends of the Earth Germany (BUND e.V.)) are involved in this initiative, which was launched in 2016 and is set to run for ten years.

The aim of the BMBF "CO₂Plus" funding initiative, which runs from 2016 to 2019, is to develop methods for producing basic chemicals from CO₂.¹³¹ There are 13 collaborative research projects with participants from universities, research institutions and industry working on the priority areas "CO₂ capture", "CO₂ as a building block for chemical primary materials" and "Electro- and photocatalytic activation of CO₂".

Eight industrial companies working together with the Max Planck Society and the Fraunhofer Society and universities are jointly developing a globally usable solution for converting blast furnace waste gases into precursors for fuels, plastics or fertilisers. The hydrogen required to do so is produced using excess electricity from renewable energy sources. Using the "Carbon2Chem" approach 20 million tonnes of Germany's annual CO discharges from the steel sector will in future be made economically usable. This corresponds to 10 per cent of annual CO

emissions from German industrial processes and manufacturing.

3.1.2 Europe

A current European Commission report on artificial photosynthesis states that, of 150 research groups worldwide, 60 per cent are active in Europe "with the largest numbers of research groups located in Germany, the Netherlands, Sweden and the UK"¹³³.

Scheduled to run for five years, the Dutch "Biosolar Cells" project included ten research institutions and 45 companies and had the aim of optimising the use of solar energy by plants, algae and bacteria (see section 2.1).¹³⁴ The intention was to enable more sustainable production of foodstuffs, energy and raw materials and the project also promoted public debate of the issues involved.

The Swedish Consortium for Artificial Photosynthesis was founded as long ago as 1993 and brings together academic partners who carry out interdisciplinary research (with a focus on molecular biology and catalysis research) into new approaches to obtaining solar fuels (primarily via the water splitting route, see section 2.2).¹³⁵

In Great Britain, SolarCAP – Consortium for Artificial photosynthesis, a consortium of academic research institutions funded by the Engineering and Physical Sciences Research Council is investigating new pathways for using solar energy to produce fuels and valuable products. The focus of research here is on catalytically coated semiconductor nanoparticles which harvest light and to which catalysts, for instance for CO₂ reduction, are attached. The

¹³⁰ http://www.kopernikus-projekte.de/projekte/power-to-x.

¹³¹ http://www.chemieundco2.de/de/.

¹³² https://www.bmbf.de/de/mit-abgas-das-klima-ret-ten-3044.html.

¹³³ Directorate-General of Research and Innovation (European Commission) 2016.

¹³⁴ http://www.biosolarcells.nl/en/home.html.

¹³⁵ http://solarfuel.se/.

¹³⁶ http://www.solarcap.org.uk/.

"UK Solar Fuels Network" is now coordinating activities in Great Britain. Most of the initiatives and consortia in Europe thus have a national focus. One pan-European project which can be mentioned is the Joint Programme "Advanced Materials and Processes for Energy Application" (AMPEA) of the European Energy Research Alliance which focuses on new materials and their modelling and characterisation.

The European Commission has launched a €5 million prize "Fuel from the Sun: Artificial Photosynthesis" to run over the period from 2017 to 2021 which is intended to stimulate the development of usable, innovative systems for producing fuels from sunlight.¹³⁹

3.1.3 Worldwide

There are major research networks outside Europe, in particular in the USA, Japan and South Korea. The US Joint Center for Artificial Photosynthesis (JCAP), which has good links with German and European research groups (see box), will be presented in somewhat more detail here.

SOFI, the Solar Fuels Institute, based at Northwestern University (Evanston, Illinois, USA) is a global network of research institutes and industrial partners whose goal is "to support the development of an efficient and cost-effective system that uses sunlight to produce a liquid fuel"¹⁴⁰. In 2012, the Japanese Ministries for the Economy and for Science set up the "Japan Technological Research Association of Artificial Photosynthetic Chemical Process" (ARPChem), a consortium of universities and companies carrying out catalysis and materials research, including investigations into the photoelectro-

The Korean Center for Artificial Photosynthesis, KCAP, is a ten year programme (launched 2009, total budget €40 million¹43). Funded by the National Research Foundation of Korea, it works in particular on materials development for photoelectrocatalysis and the development of systems for artificial photosynthesis, thus both basic research and technical development with the goal of commercial exploitation.¹44

Research is stimulated by the award of prizes. The US\$20 million NRG COSIA Carbon XPRIZE rewards the development of technologies which convert CO₂ into valuable products. ¹⁴⁵ The goal is to achieve a worldwide reduction in CO₂ emissions.

In Israel, the "Eric and Sheila Samson Prime Minister's Prize for Innovation in Alternative Fuels for Transportation" was launched in 2011, with prize money of US\$1 million. 46 Each year, one or two scientists who have made innovations or technological breakthroughs in this field receive an award.

A global artificial photosynthesis project has also been proposed,¹⁴⁷ but has not so far borne any fruit.

catalytic conversion of water and sunlight into hydrogen. ¹⁴¹ The budget for the 2012 to 2021 period is €122 million. ¹⁴²

¹³⁷ http://solarfuelsnetwork.com/.

¹³⁸ https://www.eera-set.eu/eera-joint-programmes-jps/ advanced-materials-and-processes-for-energy-application-ampea/.

¹³⁹ https://ec.europa.eu/research/eic/index.cfm?pg=prizes_sunfuel.

¹⁴⁰ https://www.solar-fuels.org/about-sofi/our-mission/.

¹⁴¹ https://www.natureindex.com/institution-outputs/ japan/japan-technological-research-association-of-artificialphotosynthetic-chemical-process-arpchem/54893416140ba083378b4567.

¹⁴² Cited from Directorate-General of Research and Innovation (European Commission) 2016, p. 63.

¹⁴³ http://www.sogang.ac.kr/newsletter/news2011_ eng_1/news12.html, cited from European Commission (ed.): Artificial Photosynthesis: Potential and Reality, 2016, p. 63.

¹⁴⁴ http://www.k-cap.or.kr/eng/info/index.html?sidx=1.

¹⁴⁵ http://carbon.xprize.org/.

¹⁴⁶ http://mfa.gov.il/MFA/InnovativeIsrael/GreenIsrael/ Pages/2015-prize-for-innovation-in-alternative-fuels-for-transportation.aspx.

¹⁴⁷ Faunce et al. 2013.

Example of coordination and visibility: Joint Centre for Artificial Photosynthesis

The Joint Centre for Artificial Photosynthesis was set up in 2010 by the US Department of Energy as an "Innovation Hub". Located at Caltech and with the Lawrence Berkeley National Laboratory as a further main location, JCAP has some 150 scientists and engineers working together.

The mission statement of funding phase I (2010 to 2015, US\$122 million) is: "To demonstrate a scalable, manufacturable solar-fuels generator using Earth-abundant elements, that, with no wires, robustly produces fuel from the sun ten times more efficiently than (current) crops." The focus at this point was on water splitting. The following advances were listed on completion of this funding phase: 150

- development of a high-throughput system for preparing and investigating light absorbers and electrocatalysts,
- · development of new mechanisms and materials for electrocatalytic water splitting and
- development of completely integrated test systems for new components of a "Solar Fuels Generator".

JCAP is considered internationally to be a good example of coordination and visibility. However, it also became clear after an initial funding phase that the assessment of the economic competitiveness of the products of artificial photosynthesis had initially been too positive and that in future still greater emphasis would have to be placed on industrial implementation.

JCAP funding was extended in 2015 (funding phase II, US\$75 million). The Mission Statement is now: "to create the scientific foundation for a scalable technology that converts carbon dioxide, water, and sunlight into renewable transportation fuels" The focus is now thus on $\rm CO_2$ reduction (effective and selective) in high energy density fuels. The main objectives for research and development are stated to be: electrocatalysis, photocatalysis and light harvesting, materials integration and modelling. The main objectives for research and development are stated to be: electrocatalysis, photocatalysis and light harvesting, materials integration and modelling.

A programme for industrial partners was set up with participants including Panasonic, Toyota, Honda, Sempra Energy Southern California Gas Company and BASF. JCAP was presented to (potential) industrial partners at an "Industry Day".

¹⁴⁸ http://science.energy.gov/bes/research/doe-energy-innovation-hubs/.

¹⁴⁹ Ager et al. 2015.

¹⁵⁰ http://science.energy.gov/~/media/bes/pdf/hubs/JCAP_Renewal_Overview.pdf.

¹⁵¹ http://solarfuelshub.org/jcap-mission/.

¹⁵² White et al. 2015.

¹⁵³ http://solarfuelshub.org/thrusts.

3.2 Challenges from the viewpoint of industry experts

In some cases, industrial partners are also participating in the work of the research groups and consortia outlined in this position paper. Although the approaches described are generally at a very early stage of commercial development, some concrete potential applications are already taking shape in relation to sub-processes of artificial photosynthesis. Experts in energy, chemistry and plant engineering were consulted for this position paper (see "Participants in the project" at the end of the position paper). Their opinions about the stated topics are summarised below and although they cannot provide a full picture of the range of opinions they do indicate the significant challenges.

Artificial photosynthesis as a concept

The term "artificial photosynthesis" is interpreted broadly by the surveyed experts (see also section 1.4) and not limited to specific processes (chemical, biological or physical) and products (fuels, sugars etc.). They, like the present position paper, understand artificial photosynthesis to be the conversion of CO₂, H₂O and solar energy into higher energy molecules or substances. Industry representatives are working on the assumption that it will be possible within ten to twenty years to convert CO₂ directly into motor fuels, chemical primary materials and electricity with the assistance of sunlight.

The respondents pointed out that the term artificial photosynthesis has no uniform and unambiguous definition in the worlds of science, business and politics and among the general public. The respondents were unanimous in thinking, however, that achieving a clear understanding is important to the ongoing debate and to coordinated research and development in this field.

The industry experts emphasised the role artificial photosynthesis can play in completing carbon cycles, for instance in the context of a strategy for storing and utilising CO₂. ¹⁵⁴

Germany's specific strengths and weaknesses in research and development

Germany has a strong tradition of catalysis research (including industrial application) and with its many major players has great potential for sustainable chemical processes. Programmes such as Horizon 2020 and some BMBF funding initiatives create a favourable environment for basic research. The respondents were unanimous that good progress had also been made in supporting technologies for artificial photosynthesis such as CO₂ storage technologies and plant engineering.

Weaknesses were considered to be a lack of coordination between artificial photosynthesis projects in Germany ("patchwork approach") and more generally in the transfer of research findings into industrial practice. In particular, there was criticism of systems integration: small and medium-sized businesses, start-ups and engineering practices were somewhat under-represented in public calls for proposals (also Kopernikus Projects) in comparison with major corporate players.

Limitations on the practical application and commercial use of approaches to artificial photosynthesis

Obstacles to successful implementation which were mentioned were shortcomings in the scalability of the approaches, specifically with regard to electrochemistry (electrolysers) and bioreactors. Such obstacles were a particular issue for scaling up to a large industrial scale. The areas required for "light harvesting" were a particular challenge for centralised solutions.

The issue of the origin of the hydrogen was considered a key factor for large scale industrial systems. Many relevant technologies (for example algal biotechnology) are already in existence but their economic viability on a large industrial scale is not yet guaranteed.

In the opinion of the industry representatives, efficient cooperation was key to bringing together the "photo" and "synthesis" components of artificial photosynthesis. Furthermore, it was important to seek out synergies (links) with existing technologies, also with a view to short-term value creation as an incentive to commit to this field. While pure photovoltaics and electrolysis systems do indeed compete with one another, integration and further development in the form of artificial photosynthesis was thought to offer potential for added value.

The experts were wondering which niches (markets, technologies) might open the "door" to artificial photosynthesis, for instance via the distributed production of high-value products. It was also pointed out that it must be borne in mind that growth in the technologies under discussion is taking place outside Europe and therefore new markets will also be outside Europe.

Potential for innovation and technical challenges over time

Despite the speculative nature of taking a longer term view of economic aspects and cost estimates, the interviewees agreed to look ahead to 2020, 2035 and 2050. The respondents expect pilot plants for initial examples of material utilisation to be in operation by 2020. They then expect electrochemical conversions relating to artificial photosynthesis to be capable of producing "valuable" products via intermediates such as ethylene in industrial plants. They estimate, however, that catalytic efficiency and systems integration of the electrochemical conversions will still not be fully mature by then.

Industry representatives predict that new materials and catalysts will have been transferred into economically viable systems by 2035. They expect that the first niches in speciality chemicals will have been filled internationally and on a relatively large scale and that electrochemical conversions will be becoming increasingly significant in the chemicals industry with the first plants for fuels and bulk chemicals.

3.3 Social aspects – ethics and communication

Technical innovations have social consequences which include an economic impact on business, government and consumers, shifts in the geographic and social distribution of opportunities and risks and changes to the living environment of citizens. This is also true of the transition from an energy supply and chemicals industry based on fossil fuels and natural resources to one based on artificial photosynthesis. While artificial photosynthesis does indeed create new areas of work, in contrast with traditional coal mining these to a great extent involve decentralised deployment of appropriately skilled staff for installing and operating the systems, in a similar way to the new jobs created in wind and solar energy use. It is uncertain whether artificial photosynthesis equipment and systems will become a major German export or whether this technology offers particular opportunities for production sites outside Europe. If current demand for fossil fuels were to be completely replaced by operating artificial photosynthesis systems within Germany, the area of land required would be considerable (some 10 per cent of national territory). The landscape would be changed or spoilt not just in isolated areas but at many locations, and aspects of nature and animal conservation would have to be weighed up, in a similar way to the corresponding issues surrounding largescale photovoltaic systems. On the other hand, operating such systems in the sunny Mediterranean countries of the European Union could be of economic benefit to those countries subject to appropriate infrastructure support, skills levels of the local labour force and the selected organisational and economic structures. Scenarios for the distributed use of artificial photosynthesis can be achieved by integration into existing or new building complexes in conjunction with an appropriate reorientation of construction, safety and architectural practices.

The impacts outlined here will give rise to processes of social adaptation. Research and innovation policy and shaping technology and adaptation processes in a socially acceptable way are tasks which will demand cooperation between politics, business, science, civil society and the public.

3.3.1 Ethical issues around technology assessment and technological futures

In addition to fundamental political and economic policy decisions, there are also ethical issues, for instance about duties to do or desist from doing something. Some of these issues relate to possible answers for which there are no clear normative grounds and where conflict is instead inevitable. It is a question here of how individuals or groups would like to live now and in future. The struggle around such positions is primarily a matter for civil society and must ultimately be negotiated politically. The first part of ethical reflection and discourse explores the parties' respective understanding of justice, duty, necessity and generally applicable factors in a particular situation, while the second part explores concepts of a good life, personal or communitarian aims and attitudes to life. Ethics clearly functions neither as a simple way of gaining acceptance nor as a radical strengthening of protest. Both come about by attaching moral value to ethical and political conflict. Using the outlined criteria and issues, ethics attempts in virtually any situation of conflict initially to step back from attaching moral values and where necessary to offer normative guidance only once this process of reflection is complete.

Environmental ethics, which is the correct forum for artificial photosynthesis, reflects principles, aims, consequences and responsibilities for human relations with non-human nature and issues of resource management. The opportunities and risks of the particular technological strategy for implementing artificial photosynthesis over its entire life cycle from development via implementation on an industrial scale to maintenance of the respective infrastructure and its environmentally and socially responsible disposal must be considered in their objective, temporal and social dimensions. Environmental ethics must take account not only of the ethical criteria sustainability, biodiversity, connectedness (interrelatedness) and resilience of ecosystems, but also of participants (above all humans) and recognises that all these criteria are in themselves highly contentious.155

It rapidly becomes apparent that a full examination of these risks will firstly entail asking ethical questions of a fair-minded person, for instance as to whether investigation of specific or indeed all kinds of artificial photosynthesis using taxpayers' money can be justified from the standpoint of a fair-minded person. Public money is inevitably limited, even in the protected field of basic research which is correctly greatly appreciated in Germany. In the event of competition for scarce funds, a research project must demonstrate why it is capable, as basic research, of adding significantly to knowledge or, as translational or applied research, of creating "added value". At the level of a fair-minded person, those research projects which are capable of demonstrat-

¹⁵⁵ Ott et al. 2016.

Artificial photosynthesis, global climate change and the costs of reducing CO, emissions

Ethical considerations can be used as the basis for evaluating the investigation and development of artificial photosynthesis in connection with the urgent issues of global climate change. By sustainably producing non-fossil fuels and valuable products, artificial photosynthesis can assist in minimising CO₂ emissions which, in conjunction with other factors, are leading to global climate change. From the standpoint of sustainability, it would appear to be obvious that such an expectation should take on an ethically justifiable political significance.

It must, however, be borne in mind that new technological developments for the timely and ultimately complete avoidance of CO₂ emissions entail an additional burden in the form of costs. This applies in particular to the storage of renewable energy sources, including the option(s) of artificial photosynthesis, which are indispensable in this connection. The development of a "miracle" technology for producing non-fossil fuels which might by itself be capable of outcompeting fossil energy carriers thanks to low production and distribution costs is not to be expected. Reducing CO₂ emissions in timely fashion will therefore continue to be associated also in future with a significant (financial) burden. The fact that, from a long-term global perspective, reducing (mitigating) climate gas emissions is also macro-economically an inexpensive solution does not solve the problem. Mitigation measures are financed and carried out at a local or national level but the corresponding returns cannot be expected to occur at the same level. This reveals the core problem of environmental or climate ethics and justice: how to distribute the burden of achieving a sufficient and timely (local) reduction in climate gas emissions in order to minimise global climate change while holding in tension the complex and conflicting demands of justice (between regions/nations, population groups and generations) and of pragmatically (technologically, politically and economically) appropriate implementation.

It would be extremely difficult to adequately justify funding and implementing appropriate measures at the national level and beyond without taking account of the "moral imperative" of global climate issues. At present, a particularly important role and a very high level of responsibility have fallen to Germany. This is because the expansion of wind and solar energy in Germany is a development which has drawn much attention internationally and is considered to demonstrate that a prosperous economy need not be inconsistent with a responsible energy policy. If the Federal Republic of Germany, with its current great economic and technological strengths, were unable to get further steps for avoiding any net CO₂ emissions in the second half of this century under way in good time, this could have extremely negative consequences for the general implementation of the Paris Agreement (see section 1). Because it serves as a model, the international significance of Germany's energy and environmental policy is much greater than might be expected on the basis of its percentage contribution to global CO₂ emissions.

It must, however, be borne in mind that the global ethical responsibility for the environment and climate relates in general to a reduction in ${\rm CO_2}$ emissions in Germany, but not to a specific technology. It still remains to be proven that artificial photosynthesis can make a substantial or even indispensable contribution in this connection. Such proof must be provided on the basis of a comparative assessment of the alternative technical solutions.

ing that they are in line with the opinion accepted among scientists and many politicians that CO₂ emissions should be reduced and a substantial alternative to non-renewable energy sources be provided would appear prima facie to be justified as ethical or even classed as requiring funding.

The demand for such research to be funded becomes all the more urgent, the sooner a concept or "technological future" 156 would appear to be implementable under discernibly realistic conditions. This is not in any way intended to provide an ethical basis for denying funding to those visions which cannot achieve this. In the light of the world's urgent environmental problems, however, those which do meet the stated criteria do have an ethical claim to priority.

3.3.2 Communication and participation

The way in which people interpret and lead their lives provides the motivation and resources for keeping a society vibrant. In the long term, it will ultimately not be possible to establish certain technical developments without taking the affected population with you. One approach, over and above different forms of participation, to countering legal and ethical or political inconsistencies in an ethically responsible manner has proven expedient: those institutions and organisations which are able to rely on established institutional credibility when developing a possibly critical research and innovation strategy tend to be more trusted than those which only attempt to create the impression that it had always been their intention to take such steps once a scandal has occurred. If institutional trust has been established in advance, it can even be strengthened by successful crisis management, providing the institution's actions are perceived externally to be plausible.

An ethical foundation for emerging technologies, in this case artificial photosynthesis, will thus have to pay careful attention to all three factors — opportunity to participate and transparency of public debate, consideration of intrinsically highly complex ethical criteria and anticipatory institutional trust — if its aim, when put into practice, is "Responsible Research and Innovation". ¹⁵⁷

Basic research into artificial photosynthesis requires government funding. Society can expect scientists to justify to politicians and the general public why this particular funding makes sense and is needed and to be entirely transparent with regard to the goals of and approaches to the research and its successes and failures. It is therefore appropriate for scientists to participate in public communication about the research into artificial photosynthesis and its industrial implementation. This participation must take account of the information needs of the political public sphere and must go beyond merely popularising the research in question. Instead, communication must present the relevance of projects and results in relation to the challenge facing society of moving away from the use of fossil energy, the implications for research funding and the implementation of technical solutions.

Public debate can be viewed as a kind of technology assessment which, while not replacing a professional analysis of technological impact, is capable of adding numerous new perspectives. If scientists are to participate in public communication about artificial photosynthesis, there is a consequent need to take on board the concerns, requirements and criticism from society, to engage in dialogue and take these factors into account in the development of the technology. Since industry will also be significantly in-

Suitable science communication

Scientific communication is facing numerous challenges which occur in different forms in various fields of new technology. For example, the metaphor underlying the term "artificial photosynthesis" is not necessarily intuitively comprehensible to laypeople. What is instead required is an explanation that the term is a metaphor for a repertoire of various technologies which mimic the function of biological photosynthesis, namely the conversion of water and CO_2 from the atmosphere by sunlight into higher chemical energy substances, but that this function proceeds quite differently from how it proceeds in plants. Details of projects measured against the goal of replacing fossil resources can be misleading if, for example, for a transitional phase, pilot plants make use of CO_2 originating from the combustion of fossil resources as a source material. This ought to be addressed and justified. Setting research in its social context is vital for assessing its significance (and how deserving it is of funding), so it must be carried out just as carefully and meeting the same requirements for correctness and accuracy as the explanation of the scientific findings and background.

Science communication must also resist attempts to put a strategic spin on communication, whether for selfish or unselfish reasons. Examples which may be mentioned are exaggerating research successes and the imminence of application ("hyping"), a one-sided focus on advantages or skating over uncertainties regarding the resolvability of scientific or technical problems or the time horizon within which industrial applications of artificial photosynthesis can be put to practical use. It is vital here to stick closely to the criteria of responsible public science communication as set out in the common recommendations by the Academies¹⁵⁸.

volved in the development and implementation of artificial photosynthesis, there is a corresponding social expectation also to participate in the public debate.

If the public is to be able to arrive at a rational opinion about artificial photosynthesis and its possible role in the production of energy carriers and chemical products, it must have access to comprehensible, relevant and correct information – this is the public's primary expectation of science. In turn, many opportunities are today open to scientists and institutions to communicate their messages and engage in public dialogue.¹⁵⁹

3.4 Summary

Many and varied activities relating to artificial photosynthesis are currently under way internationally. Germany's research activities, even when compared with the rest of Europe and of the world, are both highly varied and very visible. Industrial partners are also involved in some cases. Concrete potential applications are taking shape with regard to sub-processes of artificial photosynthesis.

Technology assessment, a debate of ethical aspects and public involvement in the development of this new technology are already important, even at this early stage of technological development, so that the challenges and opportunities of artificial photosynthesis can be clarified and debated.

¹⁵⁸ acatech et al. 2017.

¹⁵⁹ acatech et al. 2017 on the opportunities and challenges of science communication, in particular of social modia

4. Recommendations

Artificial photosynthesis is a process which draws on the basic concepts of biological photosynthesis but without endeavouring to mimic it in detail. The resulting fuels and valuable products could in future assist in replacing fossil fuels and resources. Assuming that it can be successfully implemented on a large industrial scale and realized economically viably, artificial photosynthesis could significantly improve the industrial CO₂ balance and so contribute to the energy transition and climate protection.

The last two decades in particular have seen considerable progress being made in the investigation of the scientific principles: the central processes of biological photosynthesis are today well investigated and understood. This knowledge has already been put to successful use in the development of pilot systems for artificial photosynthesis in which in particular sub-reactions of the overall process have been optimised.

This position paper focuses on artificial photosynthesis and attention is also paid to avenues of research and development which also involve the solar production of non-fossil fuels and valuable products on the basis of the above-stated key reactions. The following concepts have been addressed:

• Modified biological photosynthesis: This has the aim of directly producing fuels and valuable products by genetically engineered photosynthetic microorganisms, the particular strength of this approach being the production of complex valuable products. This technology concept differs

- fundamentally from the long-established production of biofuels or biopolymers from biomass, for example from maize and other energy crops.
- Combining biological and nonbiological components to create hybrid systems: This makes use of renewably generated electricity for the electrolytic production of hydrogen and carbon monoxide which are converted into fuels and valuable products by microorganisms in bioreactors.
- Power-to-X: This process uses renewable electricity from the power grid for the electrochemical synthesis of fuels or valuable products such as hydrogen, ethylene or, in multistage processes, methane (natural gas), alcohols or hydrocarbon-based plastics.
- Artificial photosynthesis: This
 combines the conversion of solar energy
 with catalytic processes for producing
 fuels and valuable products in completely integrated systems, such as "artificial leaves" or by directly combining
 photovoltaic and electrolysis systems.

The focus of the analysis is specifically on the non-biological production of fuels and valuable products by artificial photosynthesis and power-to-X technologies. The production of biogas, bioalcohol and biodiesel from biomass, which has long been well established, has already been addressed in depth in earlier studies¹⁶⁰ and is currently the subject of a Working Group in the Academies' Project "Energy Systems of the Future".¹⁶¹

¹⁶⁰ acatech 2012a, German National Academy of Sciences Leopoldina 2013.

¹⁶¹ https://energiesysteme-zukunft.de/projekt/arbeits-gruppen/.

On the basis of the present study, which also outlines research activities and discusses societal aspects, the Academies make the following recommendations to representatives from the worlds of politics, business, science and to society as a whole.

Future scenarios for renewable energy sources

Recommendation 1: The Academies recommend attaching a greater weight to new technologies for the sustainable production of fuels and valuable products using renewable energy sources, in particular solar energy, in future scenarios.

Meeting the goals for minimising CO, emissions set out in the Paris Agreement and in the Federal Government's Climate Action Plan 2050 will mean endeavouring to completely or at least largely stop using fossil fuels and resources by 2050. Replacing fossil resources with sustainable, non-fossil fuels and valuable products could make a major contribution. Moreover, long-term storage of large quantities of fluctuating solar energy in the form of non-fossil fuels (material energy storage) is a strategic option for substantially enhancing security of supply. The pathways to the future and guiding principles set out in the Climate Action Plan, however, take inadequate account of the solar production of fuels and valuable products from water and CO₂:

• At present, power generation by wind turbines and photovoltaics in Germany covers 4 per cent of primary energy consumption, which includes the power, heat and mobility sectors. Covering primary energy requirements climate-neutrally will primarily require a major expansion of wind power and solar energy use since other renewable energy sources such as biomass or hydroelectric power are available only in much smaller quantities. Huge generating capacity is required if Germany

wishes to completely or at least largely stop using fossil fuels and resources. Use of wind power and in particular solar energy must be multiplied by a factor of 5 to 7 over current levels.162 The marked fluctuations in wind and solar energy are a central problem, however, since a sustainable energy system of the future must also be able to guarantee security of supply over a number of windless and sunless days and despite seasonal variations. This also includes supplying electric vehicles with CO₂-neutral, renewable electricity from the power grid. Using wind and in particular solar energy to produce non-fossil fuels and valuable products is associated with the immediate storage of energy in material form and on a large scale, up to long-term stockpiling on a national level, can accordingly make a substantial contribution to the solution.

- Furthermore, the extent to which electromobility will be capable of generally replacing fossil fuels (transport or motor fuels) in the transport sector (air transport, international shipping) cannot as yet be predicted. The production of non-fossil liquid or gaseous fuels from renewable energy sources could play a major part here.
- The use of fossil energy carriers to produce valuable chemicals (for example plastics production based on oil or fertiliser manufacture from atmospheric nitrogen) is associated with considerable CO₂ emissions. Manufacturing such products from air (CO₂, nitrogen) and water using renewable energy sources can here make a distinct contribution to sustainability.

The Climate Action Plan 2050's guiding principles also include, at least looking forward, electricity-based fuel production and further applications of power-to-X technologies (under the heading of combining sectors, combining the electricity

sector with the transport or heating sector). However, the corresponding goals and implementation scenarios are not described at all or only extremely cautiously and vaguely. In order to plug major gaps in the desired CO₂-neutral energy supply of the future, the Academies recommend that policy makers at a national and international level attach greater weight to the sustainable production of fuels and valuable products in the guiding principles and scenarios of future energy supply.

Technology-neutral basic research

Recommendation 2: The Academies welcome the wide-ranging basic research into the sustainable production of fuels and valuable substances and recommend that this be continued.

Research into the sustainable production of fuels and valuable products is taking place at various locations in Germany in numerous individual projects and research groups including many different scientific disciplines. Various challenges, all of which are important to the field, are being researched, these challenges including the investigation of new light absorbers, catalyst development, synthetic biology, the use of CO₂ to produce plastics, the construction and control of pilot plants or indeed the economic modelling of sustainable materials cycles. This wide variety makes sense and could enable "game-changing" scientific and technical innovations.

Coordination of research and development work into solar fuels and valuable products

Recommendation 3: The Academies recommend stronger coordination of basic research and suitable general conditions for strengthening industrial research in this field.

Given the size and complexity of the challenges, fragmented research into sub-pro-

cesses is reaching its limits. Greater coordination and focusing of research and development in Germany and additionally in a European context can accelerate progress. It is recommended that existing structures, institutions and support schemes (for example Federal Ministry collaborative research, excellence clusters, existing Federal and State research centres) assume greater responsibility for coordination and interdisciplinary pooling, for instance on the model of the Kopernikus Projects.

It is clear that, in the medium and long term, industrial research will become of central significance. Since the technological options are still unclear and the social and legislative context for the largescale implementation of sustainable production of fuels and valuable substances is yet to be clarified (and hence earnings potential cannot be estimated), there is unfortunately currently only little ongoing industrial research in this field. Greater involvement of industrial research in the stated networks is advisable. In the short term, it is vital to boost industrial research by creating suitable conditions which provide clear economic prospects for the production of non-fossil fuels.

Integrated artificial photosynthesis systems

Recommendation 4: The Academies recommend a focus on systems integration and evaluation of the cost benefits of highly integrated artificial photosynthesis systems.

Artificial photosynthesis and power-to-X are related technologies for the non-biological production of fuels and valuable products from water and air components (CO₂ and nitrogen) using renewable energy sources. The many and varied sub-processes for obtaining the desired products are largely the same. By decoding underlying fundamental processes, research

and development work here creates a common foundation for new technological developments. In addition to the common features, however, there are clear differences with regard to involvement in national and international energy transport systems and the time horizon for technological implementation (short term for power-to-X and long term for artificial photosynthesis).

Power-to-X technologies use electricity from the power grid as an energy source and are more advanced in terms of technological implementation than artificial photosynthesis. For some important power-to-X products, scenarios for large-scale integration into future energy systems could already be developed and compared, in particular for electrolytic hydrogen production or the production of methane (replacing natural gas) from hydrogen and CO₂.

Artificial photosynthesis technologies integrate solar energy conversion with the production of fuels and valuable products in one device or system. Avoiding the "detour" via the power grid and new technological concepts for seamlessly integrating solar collectors and fuel production in one device or a compact facility have potential efficiency and cost benefits. Many individual components for artificial photosynthesis, some of which already perform very well, are now known and have been thoroughly investigated on a laboratory scale. Nevertheless, research and development is currently still at a comparatively early stage, in particular with regard to combining and integrating the various key processes in an industrial system. It is therefore firstly important to investigate new methods for combining solar energy conversion and product synthesis. Secondly, if it is to be possible to assess the actual potential of artificial photosynthesis for industrial applications, pilot plants must be constructed. This is the only way that central, currently

as yet largely unresolved, issues, for example relating to scalability, efficiency or long-term stability of the components in actual plant operation, can be addressed and, not least, can a better estimate be made of the cost benefits of producing fuels and valuable products by means of artificial photosynthesis.

For power-to-X technologies, the Academies recommend that further development efforts ranging from fundamental research via scalable pilot plants to large-scale industrial implementation be continued and intensified.

For artificial photosynthesis, the Academies recommend that around a decade of intensive research and development work be carried out which, in addition to creating integrated laboratory systems, will also include pilot plants. Once this evaluation phase is complete, it will be possible to make a well-founded assessment as to how tasks might advantageously be divided between power-to-X and artificial photosynthesis.

Technological and economic evaluation

Recommendation 5: The Academies recommend an evaluation of the technological and economic options for the sustainable production of fuels and valuable substances.

Remodelling the energy and natural resource system is a multidisciplinary task which demands solutions not only to scientific and technical problems, but also to economic, ethical and social issues. There is at present hardly any coordinated scientific debate between the scientific disciplines involved but such debate would be extremely useful for evaluating the feasibility of new concepts for the sustainable production of fuels and valuable substances. This therefore demands overarching collaboration in particular be-

tween representatives of the sciences, engineering, economics and social sciences as well as industrial research. In this way, it will be possible to subject the theoretically huge potential of the solar production of fuels and valuable substances to a reality test on issues such as scalability, energy efficiency, process engineering and plant costs. Artificial photosynthesis is an attractive but by no means the only way to cut the CO₂ emissions of Germany's or Europe's energy and natural resource systems. Such a debate should therefore demonstrate clear advantages over other approaches before artificial photosynthesis processes are further developed for large-scale industrial application. In the light of the high level of international competition and the very high bar which has been set for the goals, the assessment must however be carried out prudently and with an appropriate willingness to take risks, so that highly promising avenues of research and development are not brought to a premature end.

Dialogue with society

Recommendation 6: The Academies recommend carrying out a wide-ranging social dialogue about artificial photosynthesis in the context of the energy transition.

Society should be made aware of the major challenge involved in producing renewable fuels and valuable products and thus of the contribution artificial photosynthesis and similar technology concepts might make. Since the methods for producing solar fuels and valuable products are still at an early stage, it is important to have an objective, unprejudiced discussion of opportunities and risks which also includes aspects such as security of supply, availability of natural resources and social acceptance of these new technologies.

In so doing, it is necessary not only to communicate the scientific principles and current research results relating to artificial photosynthesis, but also to clarify the opportunities and challenges involved in this field of research and in individual projects in terms of a sustainable supply of energy carriers and valuable products.

Information and dialogue are central to communicating science. Information provided through the media can make the public aware of the topic and clarify the social significance of artificial photosynthesis. It is therefore essential for scientists and institutions not only to establish contact with journalists and carry out conventional public relations work (including social media), but also to make contact with civil society organisations.

Involving the public in technical developments from an early stage requires a social dialogue which includes the positions and evaluations of individual stakeholders, including those outside science and business, in order to identify critical issues and conditions determining acceptability at an early stage. The Academies can provide significant assistance with this social dialogue by organising relevant forums for discussion.

5. References

- Abdi et al.: Efficient solar water splitting by enhanced charge separation in a bismuth vanadate-silicon tandem photoelectrode. In: *Nature Communications*, 4, 2013, DOI: 10.1038/ncomms3195.
- acatech (ed.): Biotechnologische Energieumwandlung in Deutschland. Stand, Kontext, Perspektiven (acatech POSITION PAPER). Munich 2012a.
- acatech (ed.): Technikzukünfte. Vorausdenken –
 Erstellen Bewerten (acatech IMPULSE). Wiesbaden:
 Springer Vieweg 2012b.
- acatech (ed.): Technik gemeinsam gestalten. Frühzeitige Einbindung der Öffentlichkeit am Beispiel der Künstlichen Fotosynthese (acatech IMPULSE), Munich 2016.
- acatech Deutsche Akademie der Technikwissenschaften/ Nationale Akademie der Wissenschaften Leopoldina/ Union der deutschen Akademien der Wissenschaften (ed.): Sektorkopplung – Optionen für die nächste Phase der Energieuende. 2017.
- acatech Deutsche Akademie der Technikwissenschaften/
 Nationale Akademie der Wissenschaften Leopoldina/
 Union der deutschen Akademien der Wissenschaften
 (ed.): Social Media und digitale Wissenschaftskommunikation. Analyse und Empfehlungen zum
 Umgang mit Chancen und Risiken in der Demokratie,
 Munich 2017.
- Ager, J./Shaner, M./Walczak, K./Sharpae, I./Ardof. S.: Experimental demonstrations of spontaneous, solar-driven photoelectrochemical water splitting. In: *Energy & Environmental Science*, 8, 2015, p. 2811-2824.
- Antonietti, M./Savateev, A.: Splitting Water by electrochemistry and artificial photosynthesis: Excellent science but a nightmare of translation? In: *The Chemical Record*, 2018. URL: https://doi.org/10.1002/ tcr.201700062 [as at: 22.08.2017].
- Antonovsky, N./Gleizer, S./Noor, E. et al: Sugar Synthesis from ${\rm CO}_2$ in Escherichia coli. In: Cell, 166: 1, 2016, p. 115–125.
- Banerjee, C./Dubey, K./Shukla, P.: Metabolic Engineering of Microalgal Based Biofuel Production: Prospects and Challenges. In: Frontiers in Microbiology, 7, 2016, doi: 10.3389/fmicb.2016.00432.
- Bar-Even, A./Noor, E./Lewis, N./Milo, R.: Design and analysis of synthetic carbon fixation pathways. In: Proceedings of the National Academy of Sciences of the United States of America, 107: 19, 2010, p. 8889–8894.
- Berg, I.: Ecological aspects of the distribution of different autotrophic CO₂ fixation pathways. In: *Applied and Environmental Microbiology*, 77: 6, 2011, p. 1925–1936.
- Bernat, G./Waschewski, N./Rögner, M.: Towards efficient hydrogen production: the impact of antenna size and external factors on electron transport dynamics in Synechocystis PCC 6803. In: *Photosynthesis Research*, 99, 2009, p. 205–216.

- Bertau, M./Müller, A./Fröhlich, P./Katzberg, M.: Industrielle Anorganische Chemie, Weinheim, Wiley-VCH, 2013.
- Blankenship, R.: Molecular Mechanisms of Photosynthesis, Wiley, 2nd edition, 2014.
- Blankenship, R./Tiede, D./Barber, J. et al: Comparing photosynthetic and photovoltaic efficiencies and recognizing the potential for improvement. In: *Science*, 332, 2011, p. 805–809.
- Bora, S./Jung, G./Sa, Y. et al.: Monolayer-Precision Synthesis of Molybdenum Sulfide Nanoparticles and Their Nanoscale Size Effects in the Hydrogen Evolution Reaction. In: ACS Nano, 9: 4, 2015, p. 3728–3739.
- BP: Statistical Review of World Energy, 2017. URL: http://www.bp.com/content/dam/bp/en/corporate/ pdf/energy-economics/statistical-review-2017/bp- statistical-review-of-world-energy-2017-full-report.pdf [as at: 22.08.2017].
- Bundesanstalt für Geowissenschaften und Rohstoffe (BGR)
 (ed.): Energiestudie 2016. Reserven, Ressourcen und
 Verfügbarkeiten von Energierohstoffen. URL: https://
 www.bgr.bund.de/DE/Themen/Energie/Downloads/
 Energiestudie_2016.pdf?__blob=publicationFile&v=3
 [as at: 22.08.2017].
- Bundesministerium für Umwelt, Naturschutz, Bau und Reaktorsicherheit (BMUB) (ed.): Klimaschutzplan 2050. Klimaschutzpolitische Grundsätze und Ziele der Bundesregierung, 2016. URL: http://www.bmub.bund.de/fileadmin/Daten_BMU/Download_PDF/Klimaschutz/klimaschutzplan_2050_bf.pdf [as at: 22.08.2017].
- Bundesministerium für Wirtschaft und Energie: Primärenergieverbrauch in Deutschland 2016, 2017. URL: https://www.bmwi.de/Redaktion/DE/Infografiken/ Energie/Energiedaten/Energiegewinnung-und-Energieverbrauch/energiedaten-energiegewinnung-verbrauch-03.html) [as at: 22.08.2017].
- Chong, L./Brendan C./Ziesack, M./Silver, P./Nocera, D.: Water splitting-biosynthetic system with ${\rm CO_2}$ reduction efficiencies exceeding photosynthesis. In: *Science*, 352: 6290, 2016, p. 1210–1213.
- Comotti, M./Frigo, S.: Hydrogen generation system for ammonia-hydrogen fuelled internal combustion engines.
 In: International Journal of Hydrogen Energy. Volume 40, Issue 33, 7 September 2015, p. 10673–10686.
- Ciamician, G.: The Photochemistry of the Future, In: *Science* 36, 1912, p. 385–394.
- Coutard, N./Kaeffer, N./Artero, V.: Molecular engineered nanomaterials for catalytic hydrogen evolution and oxidation. In: Chemical Communications. 52, 2016, p. 13728–13748.

- Dau, H./Limberg, C./Reier, T./Risch, M./Roggan, S./ Strasser, P.: The mechanism of water oxidation: from electrolysis via homogeneous to biological catalysis, In: ChemCatChem 2, 2010, p. 724–761.
- Dau, H./Zaharieva, I.: Principles, efficiency, and blueprint character of solar-energy conversion in photosynthetic water oxidation, In: Accounts of Chemical Research 42, 2009, p. 1861–1870.
- Dimroth, F. et al.: Four-Junction Wafer-Bonded Concentrator Solar Cells. In: *IEEE Journal of Photovoltaics* 6, 2016, p. 343-349.
- Erb, T.: Carboxylases in Natural and Synthetic Microbial Pathways. In: Applied and Environmental Microbiologu, 77, 2011, p. 8466–8477.
- Erb, T./Zarzycki, J.: Biochemical and synthetic biology approaches to improve photosynthetic CO₂ fixation. In: Current opinion in chemical biology, 34, 2016, p. 72–79.
- European Commission: Paris Agreement, 2017. URL: https://ec.europa.eu/clima/policies/international/negotiations/paris_de [as at: 22.08.2017].
- European Association of Chemical and Molecular Sciences (EuCheMS): Solar-Driven Chemistry. A vision for sustainable chemistry production, 2016. URL: http://www.euchems.eu/wp-content/up-loads/2016/10/161012-Solar-Driven-Chemistry.pdf [as at: 22.08.2017].
- Extavour, M./Bunje, P.: CCUS: Utilizing CO₂ to Reduce Emissions, 2016. URL: https://www.cosia.ca/uploads/files/news/CEP-Magazine-June2016-CCUS-Utilizing-CO₂-to-Reduce-Emissions.pdf [as at: 22.08.2017].
- Faunce, T./Styring, S./Wasielewski, M. R. et al: Artificial photosynthesis as a frontier technology for energy sustainability, In: *Energy & Environmental Science*, 6, 2013, p. 1074–1076.
- Fischedick, M./Görner, K./Thomeczek, M. (eds.): CO₂:

 Abtrennung, Speicherung, Nutzung Ganzheitliche
 Bewertung im Bereich von Energiewirtschaft und
 Industrie, Heidelberg: Springer 2015.
- Fuchs, G.: Alternative Pathways of Carbon Dioxide Fixation: Insights into the Early Evolution of Life? In: Annual Review of Microbiology, 65, 2011, p. 631–658.
- Generaldirektion Forschung und Innovation (Europäische Kommission): *Artificial photosynthesis: Potential and reality*, 2016. URL: https://publications.europa. eu/de/publication-detail/-/publication/96af5cc3-2bd6-11 e7-9412-01aa75ed71a1 [as at: 22.08.2017].
- Giddey, S./Badwal, S. P. S./Kulkarni, A.: Review of electrochemical ammonia production technologies and materials. In: *International Journal of Hydrogen Energy* 38, 2013, p. 14576–14594.
- Glunz, S.W.: Crystalline Silicon Solar Cells with High Efficiency. In: *Advanced Concepts in Photovoltaics*, A.J. Nozik, G. Conibeer, M.C. Beard (eds.), Royal Society of Chemistry, Cambridge, 2014, p. 1-29.
- Greene, D./Whitney, S./Matsumura, I.: Artificially evolved Synechococcus PCC6301 Rubisco variants exhibit improvements in folding and catalytic efficiency. In: *The Biochemical Journal*, 404, 2007, p. 517–524.
- Haas, T./Krause, R./Weber, R./Demler, M./Schmid, G.: Technical photosynthesis involving ${\rm CO_2}$ electrolysis and fermentation. In: *Nature Catalysis*, Vol. 1, 2018, p. 32–39.

- Hatsukade, T./Kuhl, K./Cave, E./Abram, D./Jaramillo, T.: Insights into the electrocatalytic reduction of CO₂ on metallic silver surfaces. In: *Physical Chemistry Chemi*cal Physics, 16, 2014, p. 13814–13819.
- Hu, P./Chakraborty, S./Kumar, A./Woolston, B./Liu, H./ Emerson, D./Stephanopulos, G.: Integrated bioprocess for conversion of gaseous substrates to liquids. In: Proceedings of the National Academy of Sciences of the United States of America, 113, 2016, p. 3773-3778.
- Hu, S./Lewis, N./Ager, J./Yang, J./McKone, J./Strandwitz, N.: Thin-Film Materials for the Protection of Semiconducting Photoelectrodes in Solar-Fuel Generators. In: *The Journal of Physical Chemistry*, 119, 2015, p. 24201–24228.
- Intergovernmental Panel on Climate Change (IPCC): Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T. F. et al. (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2013.
- Intergovernmental Panel on Climate Change (IPCC): Climate Change 2014. Synthesis Report. IPCC, Geneva, Switzerland, 2014. URL: http://www.ipcc.ch/pdf/assessment-report/ar5/syr/SYR_AR5_FINAL_full_wcover.pdf [as at: 22.08.0217].
- International Energy Agency: CO₂ emissions from fuel combustion, 2016. URL: http://www.iea.org/publications/freepublications/publication/CO2Emissions-fromFuel-Combustion_Highlights_2016.pdf [as at: 22.08.2017].
- International Energy Agency: Key World Energy Statistics, 2009. URL: http://large.stanford.edu/courses/2009/ ph204/landau1/docs/key_stats_2009.pdf [as at: 22.08.2017].
- International Energy Agency: Key World Energy Statistics, 2016. URL: https://www.iea.org/publications/free-publications/publication/KeyWorld2016.pdf [as at: 22.08.2017].
- Jia, J./Seitz, L./Benck, J. et al: Solar water splitting by photovoltaic-electrolysis with a solar-to-hydrogen efficiency over 30%. In: *Nature Communications*, 7, 2016, DOI: 10.1038/ncomms13237.
- Klankermayer, J. et al.: Selektive katalytische Synthesen mit Kohlendioxid und Wasserstoff: Katalyse-Schach an der Nahtstelle zwischen Energie und Chemie. In: Angewandte Chemie, 128, 26, 2016, p. 7416-7467.
- Köninger, K. et al.: Recombinant Cyanobacteria for the Asymmetric Reduction of C=C Bonds Fueled by the Biocatalytic Oxidation of Water. In: *Angewandte Chemie International Edition*, 55, 2016, p. 5582–5585.
- Kreel, N./Tabita, F.: Serine 363 of a Hydrophobic Region of Archaeal Ribulose 1,5-Bisphosphate Carboxylase/ Oxygenase from Archaeoglobus fulgidus and Thermococcus kodakaraensis Affects CO₂/O₂ Substrate Specificity and Oxygen Sensitivity. In: PloS one, 10, e0138351, 2015.
- Kromdijk, J./Głowacka, K./Leonelli, L./Gabilly, S./Iwai, M./Niyogi, K./Long. S.: Improving photosynthesis and crop productivity by accelerating recovery from photo-protection. In: Science, 354, 2016, p. 857–861.
- Lan, R./Tao, S.: Ammonia as a suitable fuel for fuel cells. In: Frontiers in Energy Research, 2:35, 28 August 2014.

- Larkum, A./Ross, I./Kruse, O./Hankamer, B.: Selection, breeding and engineering of microalgae for bioenergy and biofuel production. In: *Trends in biotechnology*, 30, 2012, p. 198–205.
- Lin, M./Occhialini, A./Andralojc, P./Parry, M./Hanson, M.: A faster Rubisco with potential to increase photosynthesis in crops. In: *Nature*, 513, 2014, p. 547–550.
- Liu, C./Colón, B./Ziesack, M./Silver, P./Nocera, D.: Water splitting-biosynthetic system with ${\rm CO_2}$ reduction efficiencies exceeding photosynthesis. In: *Science*, 352, 2016, p. 1210–1213.
- Liu, Q./Wu, L./Fleischer, I./Jackstell, R./Beller, M.: Using carbon dioxide as a building block in organic synthesis. In: Nature Communications, 6, 2015, doi:10.1038/ ncomms6933.
- Long, S./Marshall-Colon, A./Zhu, X.: Meeting the global food demand of the future by engineering crop photosynthesis and yield potential. In: *Cell*, 161, 2015, p. 56–66.
- Lubitz, W./Ogata, H./Rüdiger, O./Reijerse, E.: *Hydrogenases, Chemical Reviews*, 114, 2014, p. 4081–4148.
- Luo, M./Yao, W./Huang, C./Wua, Q./Xu, Q.: Shape effects of Pt nanoparticles on hydrogen production via Pt/ CdS photocatalysts under visible light. In: *Journal of Materials Chemistry A* 26, 2015, p. 13884–13891.
- Lutterman, D. A./Surendranath, Y./Nocera, D. G.: A self-healing oxygen-evolving catalyst. In: *Journal of the American Chemical Society*, 131, 2009, p. 3838–3839.
- Manthiram, K./Beberwyck, B. J./Alivisatos, A. P.: Enhanced electrochemical methanation of carbon dioxide with a dispersible nanoscale copper catalyst. In:

 **Journal of the American Chemical Society, 2014, 136, p. 13319–13325.
- Marshall, J.: Springtime for the artificial leaf. In: *Nature*, 510, 2014, p. 22–24.
- National Renewable Energy Laboratory (ed.): U.S. Photovoltaic Prices and Cost Breakdowns: Q1 2015 Benchmarks for Residential, Commercial, and Utility-Scale Systems, 2015. URL: http://www.nrel.gov/docs/ fy15osti/64746.pdf [as at: 22.08.2017].
- Nationale Akademie der Wissenschaften Leopoldina: Bioenergie – Möglichkeiten und Grenzen, 2013. URL: http://www.leopoldina.org/uploads/tx_leopublication/2013_06_Stellungnahme_Bioenergie_DE.pdf [as at: 22.08.2017].
- Nellist, M. R. et al.: Semiconductor-Electrocatalyst Interfaces: Theory, Experiment, and Applications in Photoelectrochemical Water Splitting. In: Accounts of Chemical Research, 2016, 49, p. 733–740.
- Neubauer, S. S./Krause, R. K./Schmid, B./Guldi, D. M./Schmid, G.: Overpotentials and Faraday Efficiencies in CO₂ Electrocatalysis the Impact of 1-Ethyl-3-Methylimidazolium Trifluoromethanesulfonate. In: *Advanced Energy Materials*, 1502231, 2016.
- Nocera, D.: Personalized energy: the home as a solar power station and solar gas station. In: *ChemSusChem*, 2, 2009, DOI: 10.1002/cssc.200900040.
- Nowaczyk, M. M./Kourist, R.: Lichtgetriebene Ganzzellbiotransformation mit rekombinanten Cyanobakterien. In: *Biospektrum*, 22, 2016, p. 765-767.

- Occhialini, A./Lin, M./Andralojc, P./Hanson, M./Parry, M.: Transgenic tobacco plants with improved cyanobacterial Rubisco expression but no extra assembly factors grow at near wild-type rates if provided with elevated CO₂. In: *The Plant Journal*, 85, 2016, p. 148–160.
- Olfe-Kräutlein, B./Naims, H./Bruhn, T./Lorente Lafuente, A.M.: CO_a als Wertstoff: Herausforderungen und Potenziale für die Gesellschaft, Potsdam: Institute for Advanced Sustainability Studies (IASS), 2016.
- Oliver, J./Machado, I./Yoneda, I./Atsumi, H.: Combinatorial optimization of cyanobacterial 2,3-butanediol production. In: *Metabolic Engineering*, 22, 2014, p. 76–82.
- Oliver, J./Machado, I./Yondea, H./Atsumi, S.: Cyanobacterial conversion of carbon dioxide to 2,3-butanediol. In:

 Proceedings of the National Academy of Sciences of the Unites States of America, 110, 2013, p. 1249–1254.
- Orta, D./Merchantd, S./Alricf, J./Barkang, A. et al: Redesigning photosynthesis to sustainably meet global food and bioenergy demand. In: *Proceedings of the National Academy of Sciences of the United States of America*, 112, 2015, p. 8529–8536.
- Ott, K./Dierks, J./Voget-Kleschin, L. (eds.): *Handbuch Umweltethik*, Stuttgart: Springer-Verlag 2016.
- O'Regan, B. and Grätzel, M.: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO $_2$ films, In: *Nature*, 353, 1991, p. 737–740.
- Philips, S.P. and Bett, A.W.: III–V Multi-junction Solar Cells. In: *Advanced Concepts in Photovoltaics*, A.J. Nozik, G. Conibeer, M.C. Beard, Royal Society of Chemistry, Cambridge, 2014, p. 87-117.
- Porosoff, M./Yan, B./Chen, J.: Catalytic reduction of ${\rm CO}_2$ by ${\rm H}_2$ for synthesis of CO, methanol and hydrocarbons: challenges and opportunities. In: *Energy & Environmental Science*, 9, 2016, p. 62–73.
- Reece, S./Hamel, J./Sung, K./Jarvi, T./Esswein, A./Pijpers, J./Nocera, D.: Wireless solar water splitting using silicon-based semiconductors and earth-abundant catalysts. In: Science, 334, 2011, p. 645-648.
- Rögner, M. (ed.): *Biohydrogen*, Berlin: Walter de Gruyter GmbH 2015.
- Rögner, M.: Metabolic engineering of cyanobacteria for the production of hydrogen from water. In: *Biochemical Society Transactions*, 41, 2013, p. 1254–1259.
- Rumpel, S./Sibel, J./Farès, C./Duan, J./Reijerse, E./
 Happe, T./Lubitz, W./Winkler, M.: Enhancing hydrogen production of microalgae by redirecting electrons from photosystem I to hydrogenase. In: *Energy & Environmental Science*, 7, 2014, p. 3296–3301.
- Sanz-Pérez, E./Murdock, C./Didas, S./Jones, C.: Direct Capture of CO₂ from Ambient Air. In: *Chemical Reviews*, 116, 2016, p. 11840–11876.
- Schreier, M./Curvat, L./Giordano, F./Steier, L./Abate, A./Zakeeruddin, S./Luo, J./Mayer, M./Grätzel, M.: Efficient photosynthesis of carbon monoxide from CO using perovskite photovoltaics. In: *Nature Communications*, 6, 2015, DOI:10.1038/ncomms8326.
- Schwander, T./Schada von Borzyskowski, L./Burgener, S./ Cortina, N./Erb, T.: A synthetic pathway for the fixation of carbon dioxide in vitro. In: *Science*, 354, 2016, p. 900–904.

- Seitz, F.: Raw Material Change in the Chemical Industry and the Role of Biomass. In: Behrens, M./Datye, A.K. (eds.): Catalysis for the Conversion of Biomass and Its Derivatives. URL: http:// edition-open-access.de/proceedings/2/. Max Planck Institute for the History of Science 2013.
- Siemens (ed.): "Grüner" Wasserstoff bietet viele Perspektiven für eine nachhaltige Zukunft, 2015a.

 URL: http://www.siemens.com/press/pool/de/feature/2014/corporate/2014-05-energiepark-mainz/bgi2014052216d.pdf [as at: 22.08.2017].
- Siemens: *Ideen für eine nachhaltige Zukunft: Der SILYZ-ER* öffnet *Perspektiven*, 2015b. URL: http://www.industry.siemens.com/topics/global/de/pem-elektrolyseur/silyzer/Seiten/silyzer.aspx [as at: 22.08.2017].
- Siemens: Künstliche Photosynthese aus Kohlendioxid Rohstoffe gewinnen, 2014. URL: http://www. siemens.com/innovation/de/home/pictures-ofthe-future/forschung-und-management/material-forschung-und-rohstoffe-co2tovalue.html [as at: 22.08.2017].
- Siemens: Startschuss für weltgrößtes Elektrolysesystem in Mainz, 2015c. URL: http://www.siemens.com/press/de/feature/2014/corporate/2014-05-energie-park-mainz.php?content[]=CC&content[]=I [as at: 22.08.2017].
- Sivula, K./van de Krol, R.: Semiconducting materials for photoelectrochemical energy conversion. In: *Nature Reviews Materials*, 1:1510, 2016.
- The Royal Society of Chemistry: Solar Fuels and Artificial Photosynthesis: Science and innovation to change our future energy options, 2012. URL: http://www.rsc. org/globalassets/04-campaigning-outreach/policy/research-policy/global-challenges/solar-fuels-2012.pdf [as at: 10.08.2017].
- Torella, J.P. et al.: Efficient solar-to-fuels production from a hybrid microbial-water-splitting catalyst system. In: Proceedings of the National Academy of Sciences, 112, 2015, p. 2337–2342.
- Turan, B./Becker, J./Urbain, F./Finger, F./Rau, U./Haas, S.: Upscaling of integrated photoelectrochemical water-splitting devices to large areas. In: *Nature Communications*, 7: 12681, 2016.
- Umena, Y./Kawakami, K./Shen, J.R./Kamiya, N.: Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. In: *Nature*, 473, 2011, p. 55–60.
- Ursua, A. et al.: Hydrogen Production From Water Electrolysis. In: Current Status and Future Trends. *Proceedings of the IEEE* 100, 2012, p. 410–426.
- U.S. Department of Energy: *Joint Center for Artificial Photosynthesis*. URL: http://science.energy.gov/~/media/bes/pdf/hubs/JCAP_Renewal_Overview.pdf [as at: 22.08.2017].
- Van de Krol, R./Parkinson, B.A.: Perspectives on the photoelectrochemical storage of solar energy. In: MRS Energy & Sustainability, 4, 2017.
- Walker, B./van Loocke, A./Bernacchi, C./Ort, D.: Metabolite Damage and Metabolite Damage Control in Plants. In: Annual Review of Plant Biology, 67, 2016, p. 107–129.
- Wang, W./Wang, S./Ma, X./Gong, J.: Recent advances in catalytic hydrogenation of carbon dioxide. In: *Chemi*cal Society Reviews, 40, 2011, p. 3703–3727.

- Weber, E.R. et al.: Low-cost Harvesting of Solar Energy: the Future of Global Photovoltaics. In: Green Photonics and Electronics, G. Eisenstein and D. Bimberg (eds.), Springer International, Heidelberg 2018.
- White, J./Baruch, M./Pander, J. et al: Light-Driven Heterogeneous Reduction of Carbon Dioxide: Photocatalysts and Photoelectrodes. In: *Chemical Reviews*, 115, 2015, p. 12888–12935.
- Yan et al.: Solar fuels photoanode materials discovery by integrating high-throughput theory and experiment. In: Proceedings of the National Academy of Sciences, 114, 2017, p. 3040–3043.
- Yang, W.S. et al.: Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. In: Science, 356, 2017, p. 6345.
- Yoshikawa, K. et al.: Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%. In: *Nature Energy* 2, 2017, doi:10.1038/nenergy.2017.32.
- Zachäus, C. et al.: Photocurrent of ${\rm BiVO}_4$ is limited by surface recombination, not surface catalysis. In: *Chemical Science*, 8, 2017, p. 3712-3719.
- Zeeman, M. and Schropp, R.E.I. Photovoltaic Solar Energy, In: Comprehensive Renewable Energy, Sayigh, A. (ed.), Elsevier, Amsterdam, 2012.
- Zhu, X./Long, S./Ort, D.: Improving photosynthetic efficiency for greater yield. In: Annual Review of Plant Biology, 61, 2010, p. 235–261.
- Zhu, D./Liu, J./Qiao, S.: Recent Advances in Inorganic Heterogeneous Electrocatalysts for Reduction of Carbon Dioxide. In: *Advanced Materials*, 28, 2016, p. 3423–3455.

Participants in the project

Project management

VVU	rkin	וש ש	uuu
		00.	

Prof. Dr. Dr. h. c. Markus Antonietti	Max Planck Institute of Colloids and Interfaces
Prof. Dr. Peter Dabrock	Universität Erlangen-Nürnberg
Prof. Dr. Holger Dau	Freie Universität Berlin
Dr. Tobias J. Erb	Max Planck Institute for Terrestrial Microbiology
Prof. Bärbel Friedrich	Stiftung Alfried Krupp Kolleg Greifswald
Prof. Michael Grätzel	EPFL Lausanne
Prof. Dr. Robert Huber	Max Planck Institute of Biochemistry
Prof. DrIng. Rupert Klein	Freie Universität Berlin
Prof. Dr. Burkhard König	Universität Regensburg
Prof. Dr. Philipp Kurz	Albert-Ludwigs-Universität Freiburg
Prof. Dr. Dr. h. c. Wolfgang Lubitz	Max Planck Institute for Chemical Energy Conversion
Prof. Dr. habil. Bernd Müller-Röber	Universität Potsdam
Prof. Hans Peter Peters	Forschungszentrum Jülich
Prof. Dr. habil. Alfred Pühler	Universität Bielefeld
Prof. Dr. Bernhard Rieger	Technical University of Munich
Prof. Dr. Matthias Rögner	Ruhr-Universität Bochum
Prof. Dr. Dr. h. c. mult. Rudolf K. Thauer	Max Planck Institute for Terrestrial Microbiology
Prof. Dr. Roel van de Krol	Helmholtz-Zentrum Berlin für Materialien und Energie GmbH
Prof. Dr. Elizabeth von Hauff	Vrije Universiteit Amsterdam
Prof. Dr. Eicke Weber	Berkeley Education Alliance for Research Singapore

Interviews with industry experts

The following people were interviewed by telephone to discuss the challenges from the viewpoint of industry:

Dr. Lars-Eric Gärtner	Linde Group
Dr. Christoph Gürtler	Covestro AG
Prof. Dr. Maximilian Fleischer	Siemens AG
Dr. Günter Schmid	Siemens AG
Dr. Thomas Haas	Evonik Creavis GmbH
Dr. Martin Vollmer	Clariant International Ltd.
Prof. Richard W. Fischer	TUM & Clariant Produkte (Deutschland) GmbH

The interviews were evaluated anonymously.

Reviewers

Prof. Dr. Armin Grunwald	Karlsruhe Institute of Technology
Prof. Dr. Sophia Haussener	Swiss Federal Institute of Technology Lausanne (EPFL)
Prof. Dr. Wolfram Jägermann	Technische Universität Darmstadt
Dr. Rainer Janssen	WIP Renewable Energies
Prof. Dr. Erwin Reisner	University of Cambridge (UK)
Prof. Dr. Robert Schlögl	Max Planck Institute for Chemical Energy Conversion, Fritz Haber Institute of the Max Planck Society
Prof. Dr. Andreas Schmid	Helmholtz Centre for Environmental Research - UFZ
Project coordination	
PD Dr. Marc-Denis Weitze	acatech Office

Further participants

Dr. Johannes Fritsch	Leopoldina
Dr. Elke Witt	Leopoldina

Editorial group

The text of this position paper was drafted by an editorial group made up of the following Working Group members: Matthias Beller, Holger Dau, Tobias Erb, Bärbel Friedrich and Philipp Kurz, together with Roel van de Krol and project coordinator Marc-Denis Weitze.

Project duration

01/2016-03/2018

Appendix

Academies' Workshop

Administrative Headquarters of the Max Planck Society Munich

Programme

9 May 2016

Name	Institution	Topic
M. Beller	Leibniz-Institut für Katalyse e. V.	Welcome, introduction
N. Lewis [by telepho- ne]	California Institute of Technology / JCAP	Artificial Photosynthesis Approaches: Highlights and Recent Developments at JCAP
M. Grätzel	EPFL Lausanne	Mesoscopic Photosystems for the Generation of Fuels from Sunlight
A. Hagfeldt	EPFL Lausanne	The Versatility of Mesoscopic Solar Cells
E. v. Hauff	Vrije Universiteit Amsterdam	Organic Photovoltaics: State of the Art and Outlook

10 May 2016

R. Thauer	MPI Terrestrial Microbiology	Artificial photosynthesis with CO as intermediate
B. Rieger	Technical University of Munich	(Photo)catalytic CO ₂ conversion into materials and valuable products
A. Thiessen- husen	Evonik Creavis GmbH	Artificial photosynthesis in industrial, chemical application
B. Kaiser	Technische Universität Darmstadt	Silicon-based thin-film tandem and triple solar cells for photoelectrochemical water splitting
A. Sizmann	Bauhaus Luftfahrt e. V.	Synthetic fuels from solar-thermochemical conversion
K. Brinkert	Advanced Concepts Team, ESA	Photoelectrocatalysis: solar water splitting and hydrogen production in weightlessness
P. Dabrock	Friedrich-Alexander-Universität Erlangen-Nürnberg	On the fragility of public trust in science: consequences for the ethical and social debates around artificial photosynthesis
H.P. Peters	Forschungszentrum Jülich GmbH	Scientific communication and artificial photosynthesis
M. Beller		Closing words

Selected Publications in the Series on Science-Based Policy Advice

Coupling the different energy sectors – options for the next phase of the energy transition (2018)

Raw materials for the energy transition. Securing a reliable and sustainable supply (2018)

Doctorate in Transition (2018)

Social Media and Digital Science Communication (2017)

Additive Manufacturing (2017)

The relevance of population-based longitudinal studies for science and social policies (2016)

Government debt: causes, effects and limits (2016)

Consulting with energy scenarios – Requirements for scientific policy advice (2016)

Flexibility Concepts for the German Power Supply in 2050 (2016)

Healthcare for Asylum Seekers (2015)

The opportunities and limits of genome editing (2015)

Medical care for older people – what evidence do we need? (2015)

Public Health in Germany: Structures, Developments and Global Challenges (2015)

Quantum Technology: From research to application (2015)

Academies issue statement on progress in molecular breeding and on the possible national ban on cultivation of genetically modified plants (2015)

Incorporating the German Energiewende into a comprehensive European approach – New options for a common energy and climate policy (2015)

Palliative care in Germany – Perspectives for practice and research (2015)

Individualised Medicine – Prerequisites and Consequences (2014)

Academies call for consequences from the Ebola virus epidemic (2014)

Socialisation in early childhood – Biological, psychological, linguistic, sociological and economic perspectives (2014)

All publications in this series are available free of charge in PDF format on the Academies' web sites.

German National Academy of Sciences Leopoldina

acatech – National Academy of Science and Engineering

Union of the German Academies of Sciences and Humanities

Jägerberg 1 06108 Halle (Saale) Tel.: (0345) 472 39-867 Fax: (0345) 472 39-839

E-mail: politikberatung@leopoldina.org

Berlin Office:
Reinhardtstraße 14
10117 Berlin

Karolinenplatz 4 80333 München Tel.: (089) 52 03 09-0 Fax: (089) 52 03 09-900

Berlin Office:
Pariser Platz 4a

Geschwister-Scholl-Straße 2

55131 Main:

Tel.: (06131) 218528-10 Fax: (06131) 218528-11

Berlin Office:

Berlin Office:
Jägerstraße 22/23
10117 Berlin

The German National Academy of Sciences Leopoldina, acatech – National Academy of Science and Engineering, and the Union of the German Academies of Sciences and Humanities provide policymakers and society with independent, science-based advice on issues of crucial importance for our future. The Academies' members and other experts are outstanding researchers from Germany and abroad. Working in interdisciplinary working groups, they draft statements that are published in the series of papers *Schriftenreihe zur wissenschaftsbasierten Politikberatung* (Series on Science-Based Policy Advice) after being externally reviewed and subsequently approved by the Standing Committee of the German National Academy of Sciences Leopoldina.

Series on Science-Based Policy Advice

ISBN: 978-3-8047-3645-0