

Chemistry for the Energy Transformation

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The transformation of energy systems into a sustainable future will be impossible without chemical energy conversion

Introduction

The 5th oil price shock[1-3] started from anticipated shortages in availability and supply of the most visible energy carrier and created intensive responses throughout the society prevailing now already since several years. Besides coping with the eco-political issues we all feel for the first time that the present energy supply system needs some fundamental changes. Both, the finite resources of fossil liquid fuels and the high awareness for the climate changes[4-8] resulting from our fossil fuel consumption have sensitized the society and hence also the scientific community. Chemistry is reacting more sensitively as in earlier „oil crises“ as it provides a critical contribution through catalysis and material science for all non-nuclear alternative energy conversion processes. This time, however, many other sciences also react[9-12] to the challenge creating an interdisciplinary wave of activities in energy research.

Energy research is a broad interdisciplinary topic. A large variety of fundamental approaches are proposed and actively pursued in order to address the different issues of sustainable and safe energy supply strategies. Several reviews[13-18] deal with the overall strategy for creating an energy mix that introduces mainly completely novel approaches of energy conversion. As it is clear that energy cannot be created we always deal with conversion processes. Many of them involve molecular or solid energy carriers and thus it is evident that chemistry is at the centre of the energy challenge. Chemical science can control the energetic “cost” of the conversion of energy carriers. After all, our present fossil energy carriers were created by biochemical processes in photosynthesis and later converted to its present high-density form by geochemical processes.

This concept paper seeks at elucidating the pivotal role of chemistry in pursuing actively the transition from the fossil energy scenarios to more sustainable energy supply systems. The likewise most relevant issues about primary electricity generation, about electricity distribution[19, 20] and about energy saving strategies are not covered here to maintain some clarity in the approach. The role of nuclear fission and fusion technologies is not discussed in depth. The paper intends at clarifying some underlying lines of thought and thus refrains from discussing individual examples for its theses. Examples can be found in the literature quoted that is selected to illustrate points made in the text and not to cover the issue in any exhaustive way.

Energy and Climate

It is now recognized by everybody that global warming is a large-scale experiment[7] that mankind started without knowing the boundary conditions and the complexity[5, 21] of the interactions in the climate system. The cause of the climate change is the chemical conversion of carbonaceous materials into thermal and derived forms of energy. Not only direct combustion but also excessive and inadequate land use practices[22-24] contribute

substantially to the greenhouse gas emission. The most important lesson to learn from the evolving situation is not to create alternative or “renewable” energy systems[25] without exactly understanding their involvement in the complex regulatory systems of our planet. That means that all concepts of future energy conversion must be designed and verified in the light of their impact on the various biological and physico-chemical regulatory systems on earth. The often used word “sustainability” has not only a term describing the balance between input of energy carriers and output of waste but contains also a kinetic term[4, 26-29] describing the time constant of equilibration between input and output. The neglect of this kinetic term caused the climate change problem to arise. Great care is needed when energy scenarios are classified as “renewable” and “regenerable” as much less obvious[26, 28] unwanted consequences than the emission of carbon dioxide may occur from large-scale chemical conversions of energy carriers. Typical examples are the consequences of energy farming for biodiversity, the residence time of emitted carbon dioxide in the atmosphere[4, 27-29] over various ecosystems or the consequences of large-scale deposition of carbon dioxide in deep seawater or in aquifers[30, 31] underground.

It is most relevant to consider energy conversion scenarios as hierarchical systems of process chains encompassing the generation of energy carriers, the conversion of energy carriers, the management of the waste products and effects of the usage of the energy liberated. A typical example of the complexity of interactions was the recent price explosion for foodstuff caused by the still small-scale energy farming[32]. This example highlights that not only scientific but also sociological-political factors[33] are of decisive influence on the evolution of the energy challenge. These implications are not discussed in the present work although some base assumptions influence the construction of plausible energy scenarios described below.

Even for purely chemical considerations the systemic approach demands not only considerations about efficiency, security and sustainability of the processes but also about the availability of critical materials for the intended scale of use. In this respect the application of noble metals or their compounds exemplified with the use of Pt, Ir and Ru is a critical issue. For all grid-scale sustainable applications chemistry has to provide solutions circumventing the use of such elements or minimizing their application to the absolute essential level. The extent to which this is possible is not yet clear, as despite phenomenological approaches such as high-throughput screening[34] only limited systematic approaches[35, 36] were applied. A promising development[37, 38] is the facile creation of a complex molecular electrocatalyst based on Co-phosphate species. The highly dynamical character of the system[39] capable of oxygen evolution is reminiscent on the dynamics of phosphate catalysts[40, 41] used for the inverse process of catalytic selective oxidation. The deliberate exploitation of structural dynamics for a catalytic system is considered as a guiding principle for finding novel material solutions that can be used under the constraints of the sustainable energy conversion.

The big picture

The already significant modification of the climate by CO₂ emission calls for a most rapid reduction of further emissions. Chemistry can contribute to this task in multiple ways as discussed below but few of these contributions will be large on the scale of present emissions within short timescales of below one decade. The fastest method is saving emissions by saving energy through existing technologies and behavioral adaptations. Large emission savings can further be realized by using immediately the already existing solutions for a better efficiency of thermal energy conversion even if this requires the rapid replacement of fossil power stations. This measure must be supported by an intelligent management of distribution grids[13, 20] allowing the utilization of renewable primary electricity. These measures can buy time to allow chemistry to develop and implement the measures described below. It is unrealistic to promise large-scale novel solutions from chemistry for a sustainable energy

system to be effective within the next decade. The more it is essential not to lose out on the momentum of the “Energiewende” initiated in 2011 and to work towards the necessary innovations. This seems hampered by the complex interplay of stakeholders in the energy system that is only to a limited extent a technological system.

Although many speak about the “energy system” it is poorly defined what are the key components and who are their stakeholders. Some insight into the complex relations between technical and non-technical aspects are essential to estimate the chances that sufficient attention is dedicated to the necessary technical breakthroughs and their scientific basis that alone enable the desired energy sustainability. The timescales of the energy transformation request that this attention is being paid over several legislative periods, a task requiring practical action of the scientific community in information and communication. The Max-Planck-Institute for chemical energy conversion (MPI CEC) contributes to this task in several ways but in particular through its webpage www.solarify.de.

The by far predominant part of our energy systems is based on actual or historic sunlight. The actual form of the German energy system including realizations and concepts of transformation pathways into sustainability is represented in Figure 1. This Figure does not imply any quantitative description and omits all layers of non-technical system components. The energy that is stored in structural and functional materials is also not shown in this diagram. Such a system would be fully functional if we did not over-utilize the fossil part with consequences for our climate and with issues for geopolitical stability with decreasing abundance of fossil resources.

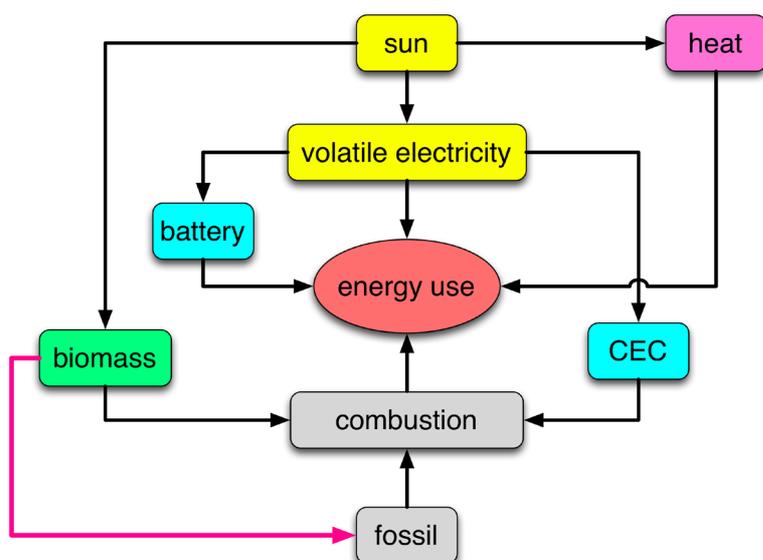


Figure 1: A simple view on the energy system. “CEC” stands for chemical energy conversion. The red arrow indicates the chemical transformation of biomass in geological timescales into fossil energy carriers. The two elements in blue boxes indicate critical contributions of actual chemistry to the transformation of the system into a low-fossil state. Their poor functioning today will limit the progress in system transformation for economical reasons soon and for technical reasons in possibly a decade from now.

We may ask why we cannot stabilize such a simple system that requires already two technological components that are not yet developed to an extent to be useful on world-scale dimensions. Both are systems storing electricity in chemical bonds that can either be recuperated as electricity (battery) for the price of low storage capacities or require another conversion step with significant losses but exhibiting storage capacities three orders of

magnitude larger than batteries: solar fuels through chemical energy conversion. To answer our question we need considering a more complete array of key influence factors on the energy system. These and some components constituting the energy system are displayed in Figure 2.

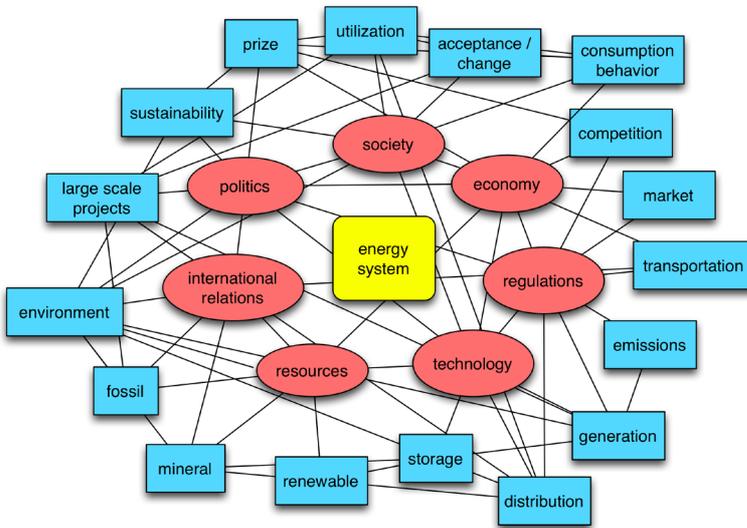


Figure 2: (red) some key factors controlling the energy system through (blue) elements describing the properties of the system. Only selected interrelations are indicated. The contributions of science and technologies are absolutely critical but must be seen in the concert of many factors outside of the technology arena.

It becomes clear that a large number of factors and elements are non-technical in nature. Hence it would be naïve to treat the problem of stabilizing the energy system between the use of fossil and renewable resources as a purely technical challenge. Could we implement the technologically feasible renewable energy generation now and on a global scale we would have still a long time to go until we can no longer compensate the volatility of solar energy by fossil energy carriers. Such a solution is presently made complicated by influences from the economic and political arenas controlling the energy system.

Energy is made available for users consuming it individually and collectively in organizations called “companies” and “societies”. These collective bodies organize their representation in different ways but are presently dominated by considerations of economy and finance to such an extent that it seems impossible to optimize the energy system against the sole descriptor “prize”. As scientists we have to recognize this fact as all our efforts and our necessary requests for funding will be interrogated for maintaining this descriptor low. “Uneconomical” solutions or their fundamental science will be without much chance, as long as not additional descriptors for the energy systems such as “sustainability” will be imposed on the existing energy system and its control structure indicated in Figure 3.

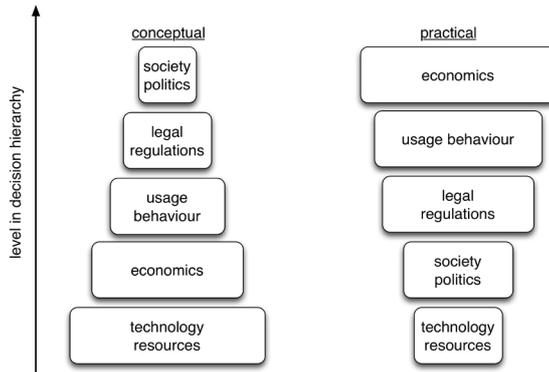


Figure 3: Conceptual and practical hierarchy of key stakeholders deciding over the evolution of the energy system. The width of the boxes indicates the number of options available in each category of decisions. The need is obvious for science and technology to broaden the base of options for the evolution of the energy system.

The hierarchy of decisions indicated in Figure 3 as “conceptual” is not given by deep scientific insight but should be understood as one suggestion allowing rational implementations of sustainable energy systems. The desired conceptual structure requires a broad societal dialogue and a decision process directed by politics. It is not the intention of the author to deepen this discussion. It seems however adequate to raise this point in order to qualify the mission that science has for the energy transformation. The elements of the energy system dealing with the technological options and their scientific basis are to be understood as offers of viable options. On the basis of a responsible assessment of the consequences of their implementation for the anthroposphere[42] the choice and implementation needs decisions from outside the scientific community. It is, however, important to understand that efforts in prioritizing and pushing scientific activities to overcome the technical hurdles of the energy transformation are impeded as long as no directions of the energy transformation are agreed between the stakeholders. Such agreement can be promoted by constant request coming from science towards society to unlock the solution potential of technology. The impact of scientific discoveries on energy technology will come only with substantial temporal delay of decades, as the dimensions of the energy systems are so large. The evolution of novel approaches in energy conversion into proven world-scale technologies and the necessary investments make rapid contributions on the time scale of periods of legislative bodies unlikely.

Dimensions and dynamics

The global primary energy consumption (by 2010) is about 18 billion tons coal equivalents (SKE) per year. This very large number contains the net used energy plus the large contribution for the losses of energy conversion. The US consume 3.2 billion tons, Germany takes 0.47 billion tons. From these 470 Mt the amount of 316 Mt are consumed as end energies the rest of 154 Mt are conversion losses. This compares for example with 83 Mt equivalents of all gas imports of Germany. These numbers tell that any effort to reduce losses from converting energy carriers is of great relevance now and also in future energy scenarios.

Chemistry as the underlying science of energy conversion can play a substantial role in bringing down these losses. This refers to processes of combustion and chemical synthesis of materials as well as to designing materials enabling more energy-efficient processes and end uses. Solid-state lighting and materials for insulating buildings are prominent examples for everybody with significant impact on their energy bills. Figure 4 gives an impression of the cross-sectional function of chemistry in the energy challenge.

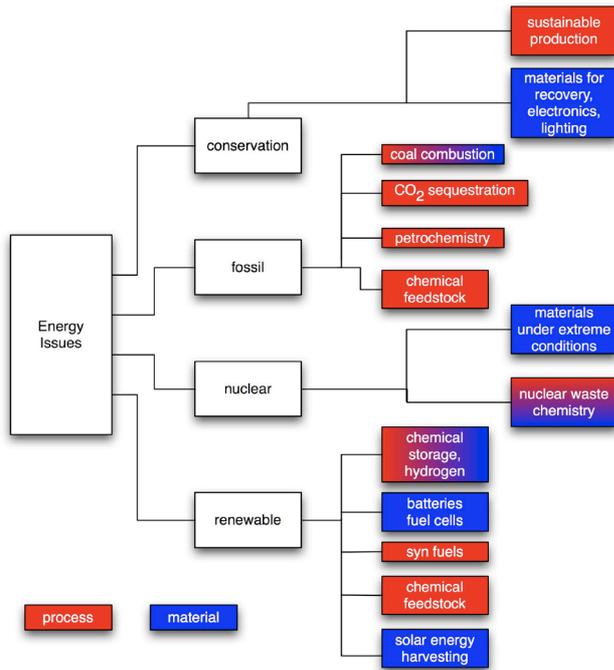


Figure 4: Chemistry plays a strategic role in transforming the energy system. It is not confined to the energy storage issue with renewable energy but also greatly affects existing streams of technology enabling better energy efficiency. Note the role of chemical process design achieved mainly by catalysis and the contribution of material science.

Catalysis plays the pivotal role in the efforts for improving processes in energy efficiency. This science deals with the control of energy barriers and thus allows designing reactions with high selectivity and rapid performance. Heterogeneous[43] and electro-catalysis[44] will be the workhorses of the initial generations of renewable energy conversion systems. Molecular catalysis in artificial[39] or biological systems may, however, increasingly contribute not only to effective transformations of energy storage systems, but in later generations of energy systems maybe also to direct solar light conversion through photocatalytic[37, 45-50] systems. Bio-catalytic processes will be of relevance for the safe sequestration of CO₂, as they convert under direct solar energy utilization gaseous diluted CO₂ into carbon-dense precursor materials for safe and useful deposition.

With respect to the still large losses in our present fossil-based energy conversion, chemistry could make a very substantial saving contribution[51] now and also in a sustainable system with solar storage fuels if we could convert fuels[52] into electricity without flames and the losses of Carnot machines. PEM cells for alcohols or solid oxide fuel cells for solid carbon ex coal [53-56] or carbon-based primary elements are examples of such concepts. An alternative use for solid fuels like coal would be their gasification for electricity generation and the upgrade of the generated synthesis gas with hydrogen from renewable sources generating fuels[42] or chemicals.

The scale of chemical conversions for energy is roughly 10 times larger than the scale of the global chemical industry. When we create new processes it is thus not only important to be as effective as possible but also to consider the scalability of a process from its material requirement as well as from its unit operations. The design strategy of chemical plants has brought about an excellent toolbox[57] for estimating such aspects of a new process already in early stages of development. This practice should also be implemented in the search for energy solutions.

This paper does not aim at describing all the many approaches towards energy conversion[33, 58-60] that chemists have described over the years and recently after the general awareness about the energy challenge. It rather focuses on the contributions expected from chemistry to initiate technologically the re-structuring of our present energy scenario. Many of the novel approaches such as those intending to design the “artificial leaf” [61] are still far from becoming relevant to “grid-scale” technologies and many of these approaches will face problems with fulfilling the sustainability[33, 62] criteria when considered as technological systems. Some of them will circumvent all these obstacles and will contribute as advanced generations of energy conversion technologies to future energy scenarios. It is thus detrimental to the total effort to pre-select the topics at which energy research should concentrate on. Chemical energy research should enable the identification and verification of ingenious concepts of chemical conversion and of materials that create new technologies.

It is, on the other hand, necessary to focus to a certain extent onto those issues[58, 59, 63, 64] that are critical for the near or foreseeable future. Many of them have to deal with conversion of solar energy into a storable energy carrier[65-70]. Storage of primary energy can occur both in energy carrier chemicals and in battery electrodes[71, 72] having the advantage of allowing for facile recovery of the electrical energy. It appears to be most critical to enable the transition from purely fossil energy systems to a mixed situation with an increasing contribution of renewable energy that allows phasing out fossil fuel technologies (such as saving on heating for buildings or rebuilding inefficient thermal power stations). It is the purpose of this paper to draw the attention towards selecting some of these focal challenges for chemistry. The approach rests upon assuming generalized energy supply scenarios and analyzing the resulting systems network in terms of bottlenecks. Fundamental research challenges result from this analysis for circumventing the bottlenecks in large dimensions while observing the boundary conditions of sustainability and climate compatibility outlined above. Attempts in this direction and towards sustainability are by no means new but have inspired generations of chemists since the ages of the Industrial Revolution. The fact that we have still no satisfying toolbox of fundamental insights and resulting technological options indicates that the underlying science problems are tough and need large concerted efforts for their solution.

The temporal dynamics of the energy system demands different types of measures for the integration of renewable energies with the fossil infrastructure and with our demand structure. This integration is the corner stone in all policies driving the energy transformation. The co-existence of fossil and renewable energy systems will prevail for many decades and shortcomings in their integration will strongly hinder the whole transformation process. The example of the German energy system shall illustrate some scales at which actions are necessary. The author suggests that a network of measures linking different technologies such as chemical energy conversion, pumped hydro storage or thermal energy storage will deliver stable solutions and that consequently pre-selection of the related fundamental science is adverse to the target as long as each science-based alternative fulfills the above mentioned boundary conditions. This holds the more if we consider that energy systems are different in the regions of the world and likely will need different packages of measures for their transformation.

In Figure 5 some data are given on the temporal evolution of the German energy system and of the US system for comparison.

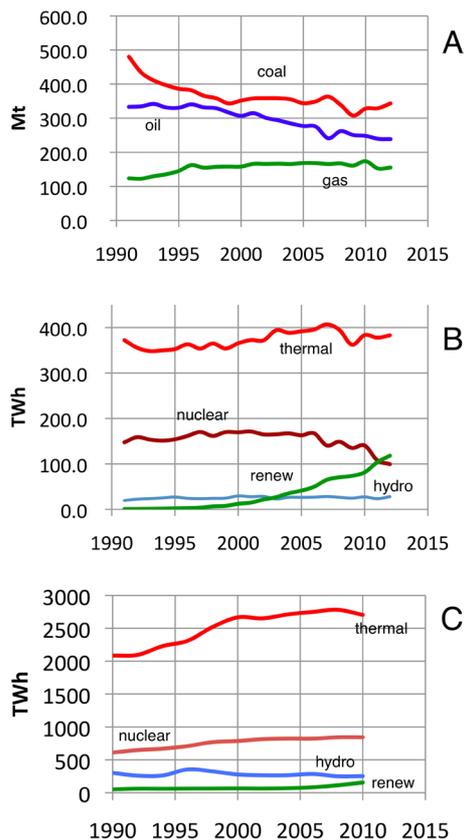


Figure 5: Selected data on the temporal evolution of the German (A,B) and the US (C) energy systems. (A) presents the CO₂ emissions from several energy carriers in Germany after the unification of the country. (B) presents the contributions of different energy sources for electricity generation in Germany over the same time span as Figure (A). (C) reports the same data as Figure (B) for the US energy system.

The CO₂ emissions of Germany show besides some short-term wiggles caused by seasonal and economic events a general trend of stability after the de-industrialization of East Germany and after the still ongoing replacement of oil by gas for heat generation. The electricity generation in Germany is still dominated by thermal processes based on coal and lignite followed by nuclear energy. This contribution is gradually replaced by renewable generation initiated by the increasing age of the nuclear installations and the lacking acceptance of this technology. Renewable energy plants grew rapidly by capital-driven investments into revenue streams secured through national legislation (EEG). In the United States not only the dimensions of electricity generation are differing from that of Germany but also the stability of contributions from the various energy carriers. In particular, renewable sources play a subordinate relative (not on the absolute scale) role and no trend in reducing nuclear power can be seen.

The impressive contribution of renewable electricity in Germany lies on a steep trend towards becoming a major source of electrical energy in this country. At the timescale of annual integration no issues of integration can be seen as renewable outperforms the unwanted nuclear and thermal energy is adapting to the new market situation. The challenge becomes more apparent when we increase the temporal resolution to single days in the year of 2013. This is shown in Figure 6.

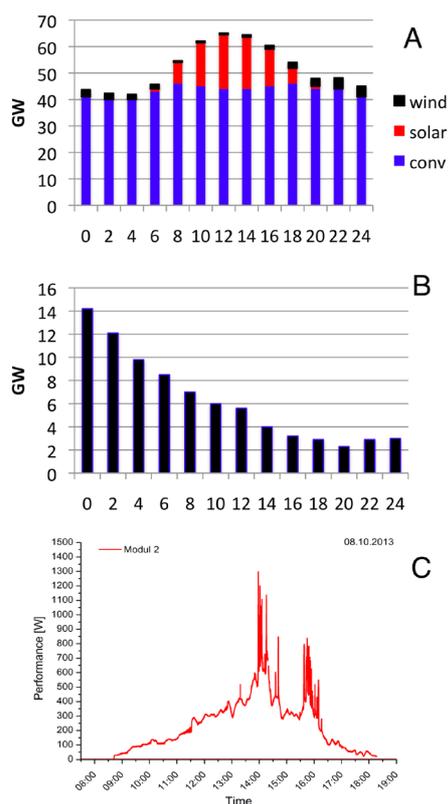


Figure 6: Time resolved generation of renewable electricity. (A) The solar peak in the German national grid during a summer day in 2013 fits well to the daily demand maximum. (B) a winter storm in January 2013 is out of phase with the daily load profile of the German national grid. (C) a single solar generator on an autumn day exhibits massive spikes in its generation profile lasting for some seconds arising from cloud shadowing.

The integration of renewable electricity generation with the demand structure can be without problems as indicated in Figure 6(A), but can easily create substantial challenges both for the dispatch of the grid and for local elements of the grid with rapid current changes at timescales where thermal power stations have problems to accommodate.

Regardless which grid structure and what load management will be introduced it is obvious that some sort of cascade storage system with differing response times and capacities would greatly support the operation of the grid now and will be indispensable at substantially larger fractions of volatile electricity (see also Figure 1). This storage function can be executed to a limited extent by thermo-mechanical storage[15, 17, 73-76] (pumped hydro, compressed air storage, heat storage media) or by biomass[32, 77-81]. Both options are in use today and from there we can conclude that response times and energy densities are inadequate for the storage requirements estimated to arise from a large fraction of volatile primary energy as basis of sustainable energy systems.

We consider thus the contributions of chemical energy conversion in the form of batteries and storage molecules. They represent two classes of storage systems. Whereas batteries[71, 72, 82] have limited impact on grid operations in the short-term operation but are relevant for e-mobility[83, 84] and for decentralized energy systems[13], the use of chemical bonds in synthetic energy carrier molecules generates a long-term load of substantial capacity during overproduction. The storage products can be used either in the electrical or in other parts of the energy system to reduce fossil energy carrier consumption. The immediate back-conversion of products from “power-to-chemicals” (p2c) is only necessary in the more distant future when fossil carriers will be scarce.

For the design and construction of such storage systems it is clear that large dimensions are needed for a detectable impact on the national grid representing only a tiny fraction of the global electrical system. The volatility of the electricity input creates for chemical storage the challenge of intermittent operation and substantial dead times during the year. Both generate constraints on operational stability and on the economics, which in turn limit process conditions (variable temperatures and material loads) and the economic value of materials in use. The author dares to state that none of the chemical energy storage systems that we conceptually have in the laboratory[12, 38, 85-88] would fulfill these boundary conditions at the required scale. It must be stressed that much effort was already spent during earlier phases of augmented energy research to address these challenges with clearly limited success.

These observations allow for two conclusions. One is that the underlying fundamental science is not adequately developed to rationally design energy storage processes. This will be discussed in more detail below. Here it should be stated that the Max-Planck-Society with its exclusive dedication to fundamental science has reacted to this need and founded in 2012 a new MPI for chemical energy conversion (MPI CEC) in Mülheim/Ruhr. This institute addresses the basic chemical energy science with an integrated approach towards understanding and designing catalytic processes for converting small molecules like water, nitrogen and CO₂ into energy carriers. It tackles this challenge by cross-linking theory with experiment and in an orthogonal vector molecular with interfacial catalysis. Chemo- electro- and photo-catalysis are studied with the aim of generating solar fuels on the basis of understanding the potentials and limitations of these approaches. The photosynthesis reaction suite that evolved in nature is used as inspiration and benchmark for the evolution of knowledge. The special dedication of the MPI calls for a technology transfer unit implemented as company joint with the State of Northrhine-Westfalia and the Fraunhofer Society, as the MPG by itself is ill-equipped to develop scalable energy technologies within its profile of activities.

The other consequence is that we do not sufficiently know about the multitude of options. We need substantial efforts in “blue-skies” research creating novel options and unconventional views on the energy conversion challenge. This need is only apparently in contrast to the clear dedication of energy science. The German National Academy has expressed this critical desire in its white paper on research needs for the energy transformation ([http://www.leopoldina.org/de/publikationen/detailansicht/?publication\[publication\]=295](http://www.leopoldina.org/de/publikationen/detailansicht/?publication[publication]=295)).

A technical energy scenario

In the literature applications of energy scenarios[13-17, 89] are discussed that describe economic or climatic consequences of regional developments. These scenarios assume different types of forcing from markets and politics and predict the consequences in macroscopic variables. The approaches document the necessity to discuss energy chemistry in systemic contexts. Non-technical factors are emphasized with a strong weight controlling the implementation and the use of energy technologies. The technologies themselves occur just as parameters in these scenarios.

In the present work a different type of scenario is used. It is based upon networks of technologies (represented as individual “black boxes”) required to convert and store energy. Without economic or political forcing the interaction is described of critical unit operations for providing energy to various non-related and non-coordinated applications (transportation, communication, production, domestic, retailing). The networks concentrate on chemical aspects and omit all physics-based components. They assume the existence of grid systems for exchange of electrical energy, for information exchange and for bulk material transport.

It is suggested to use the instrument of energy scenarios to identify research efforts leading through de-bottlenecking of the network to a large impact of sustainable energy generation on the present fossil energy mix. Essential ingredients into future energy scenarios are besides sustainability[90] the continuity in usage of existing technologies wherever possible. Further, the scenarios rely on primary solar energy and aim at minimizing the usage of fossil energy carriers. The contribution of biomass is indispensable for closing the carbon cycle[4, 91] as long as we use carbon-based energy storage systems and structural materials. The use of biomass is restricted in these scenarios to a minimum on account for a possible interference with food production[32, 92] and for the unknown risks for biodiversity and ecology associated with excessive energy farming.

It is imperative to minimize the greenhouse gas emission as fast as possible in order to keep the already unavoidable consequences of climate change[4, 7, 93] to their minimum. For the scientific justification of this postulate see the reports[89] of IPCC. For this motivation the utilization of CO₂ as a “raw material” is considered[94] as integral part of the solar energy storage portfolio. The use of this energetically “unreasonable” raw material in energy storage creates an additional sink for the most relevant greenhouse gas for the prize of significant expenditures on renewable chemical energy likely in the form of hydrogen.

Realistic energy scenarios take into account that the ownership of fossil and non-fossil energy carriers is not identical and thus a competition will result with a strong retarding momentum for the out-phasing of fossil energy carriers. The time scales and severity of this competitive situation will be largely determined by socio-political factors and by the awareness of the general public as indicated above.

In Figure 7 we present a technical scenario describing major components of an energy system in transition from fossil to renewable primary energy supply. The scenario links the world of energy carrier materials with the world of electricity. The sun delivers all primary energy but its collection and conversion technologies vary broadly from biomass to artificial leaves. The energy system displayed can well convert chemical energy into electricity mostly by combustion, conceptually also by flameless oxidation. It cannot, however, back-convert electricity into material energy storage with the notable exception of “batteries” designating accumulators. The storage of volatile photo-electrical energy in molecules through the artificial leaf device or through coupling electricity generation with electrolysis[95-99] are no existing technologies as judged by their readiness for world-scale deployment. The lack of reliable cheap and stable conversion technologies for electricity represents the most critical bottleneck in transforming the present fossil-only energy systems into a sustainable operation. Bulk amounts of primary electricity cannot be matched in their temporal availability to the temporal evolution of demand, even not with the most advanced regulatory tools of the smart grid[19, 20]. With the long-term reduction of base-load fossil power stations the as-requested supply of electricity will become more difficult as exemplified with Figure 6 and the grid system may become unreliable. To operate in stable modes energy systems based on primary electricity will need a chemical bulk storage solution as replacement or addition to fossil fuels. This justifies placing the energy storage issue at the top of the priority list for future energy scenarios.

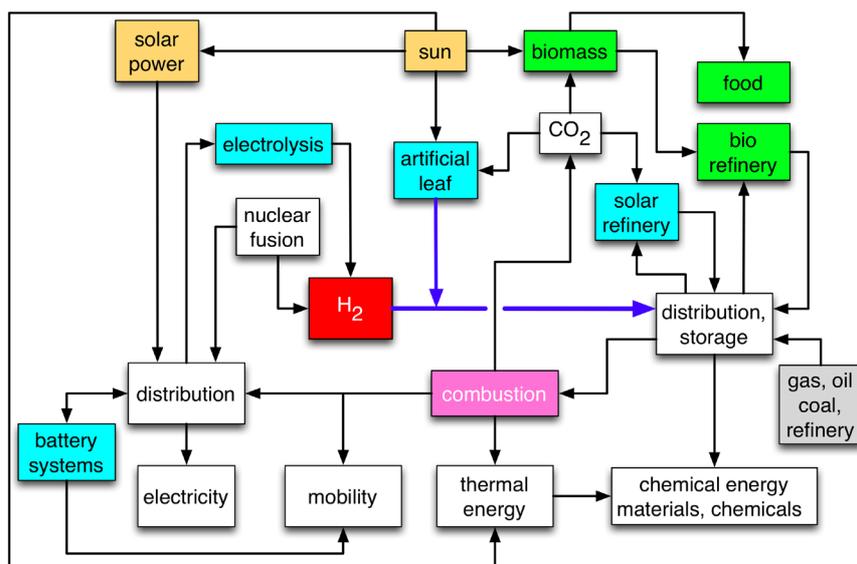


Figure 7: A “chemical” view on an energy system allowing for the transition from fossil-based to renewable energy-based. The blue boxes denote sub-systems where chemistry has still to contribute novel solutions for their useful implementation. The blue arrows designate the critical processes where electrical energy needs conversion into chemical energy. The central combustion process is well developed as flame-based process family but could still be massively improved if flameless oxidation reactions would be possible.

Without effective and fast storage plus recovery systems there is only limited control over the temporal distribution of energy. The capacity of the electrical energy grid is even with intelligent management strategies limited to about 15 – 20% of the load in regulating temporal differences between supply and demand. Larger fluctuations need to be dispatched by reducing the efficiency of combustion power stations that lead to enhanced CO₂ emission despite extensive utilization of renewable energy. Such a negative feedback situation is recorded since 2012 in the German electricity system that increases CO₂ emission with increasing renewable energy use.

A large number of future energy consumers has no access to an electricity grid infrastructure. It may be debated[100] if the construction of grid infrastructures will be the most suitable solution; if not, then decentralized chemical energy storage of primary electricity will be required. Suitable technologies may be not the most effective storage systems but they must operate in rough environments without much supervision and without being able to rely on economy-of-scale advantages. This may require completely different chemical storage solutions than obtained from scale-down strategies of systems indicated in the present scenario. The development of such strategies has a high priority to be able to compete in time with the tendency to build a grid in the developing parts of the world. It is remarkable that in this debate[100] mostly socio-economic arguments and not technological possibilities play a decisive role.

The direct chemical utilization[45, 46, 49] of sunlight in artificial leaf systems leading to energy storage molecules (photosplitting of water or other photochemistry) represents a huge challenge for the chemist[101, 102]. This is based upon the notion that it is very hard to optimize simultaneously a network of photon-driven charge separation systems and devices allowing the use of the energy from the charge separation immediately for conversion into chemical energy[60, 65, 66, 73] within a single material combination. This is due to conflicting property requirements for the sub-systems and multiple material interfaces the design of which we still have to learn. The fascination of the idea to combine the solar energy

conversion with chemical energy storage into a single step process is not disregarded[46, 50] but from the present status to a sustainable and scalable process there is still a long way to go.

A large fraction of the primary electricity from solar sources (Figure 7) can be used directly; a smaller fraction may be stored in batteries[13, 71, 72] partly operating in mobile applications such as cars and partly smoothening in the grid the steep flanks of volatile power contributions (see Figure 6). Decentralized electricity supply solutions will most likely need batteries. A long-term form of electrochemical energy storage systems represent redox-flow batteries[103] in which the energy is stored in electrolyte fluids; such systems are fast and can store large amounts of energy but are of low energy density and thus only suitable for stationary applications.

Current research into batteries is largely phenomenological[13, 71, 72, 82, 104-107] resulting in a multiplicity of “design” philosophies and still incremental improvements in performance. The necessary breakthrough to increase specific storage capacities will have to rely on an in-depth understanding of the complex interface processes involving the charge-carrying[108, 109] chemical species (Li) during discharge and charge[110] of the battery. Only few studies work systemically with a battery constituting the co-operation of electrodes, electrolyte and membrane. The general practice of studying single electrode reactions obscures the view on the systemic function of single cells and even of cell stacks relevant for applications. The most studied process of Li metal storage is much better understood than the other equally necessary unit operations of the battery. A bottleneck in the advancement of batteries is the cathode having to store Li ions and electrical charge carriers simultaneously. Here a new conceptual solution is required. The much praised solution of a [111, 112]metal-air battery is in its practical rechargeable realization also plagued by issues of solid state kinetics and irreversibility of phase change processes. Many aspects of material transport through membranes, adsorption or intercalation into electrode solids and charge-exchange processes are not yet understood on the necessary atomic level. In particular, the solid-solid reaction processes occurring during charging and discharging in batteries[71, 106, 113] represent an area of fundamental research[9-12] concentrating on issues of defect dynamics, grain boundary chemistry and reversibility of internal nanostructuring.

Design and control of these properties in functional storage materials require robust synthetic concepts[114-116] and in-situ analytical tools rarely used[108, 117, 118] so far. The augmented use of solid state NMR gave clear insight into the complexity[108, 109] of the system Li-ion battery under operation. New in-situ tools are needed which provide experimental access to solid-fluid interfaces at ambient conditions. Synchrotron-based electron spectroscopy at tunable high energy and high resolution[119] can offer such information[118, 120-122]. Scalable synthetic concepts based upon composite materials such as nanostructured carbon systems[11, 123, 124] will be carried further and extended to other functions aiming at replacing expensive or in bulk amounts unavailable electrode materials such as Ru oxide[125, 126]. Progress in this area depends on the capacity to handle the complexity of solid-liquid and solid-solid interfaces without present-day simplifications that prevent facile transfer of existing fundamental knowledge into functional systems.

Combining solid-state chemistry with electrochemistry[127] is critical for the whole energy issue and has far-reaching implications beyond batteries into many aspects of the energy challenge such as fuel cells and water electrolysis. The operation of solid-state storage systems for thermal energy[128, 129] or hydrogen[18, 130, 131] depends crucially on defect engineering and on nanostructuring in order to allow reversible diffusion processes to occur with constant kinetics. Electrochemistry could serve as diagnostic tool in these systems. The interdisciplinary nature of such research is realized[132] but rarely approached[9-12], as substantial disciplinary boundaries exist between experimentalists in both fields and theorists.

A chemical intermediate energy carrier is hydrogen[18, 46, 66, 99, 133, 134] that may be used in energy conversion plants either as storage molecule by itself or as precursor for other chemical systems intended for bulk transportation, storage and for end users. In the scenario of Figure 7 hydrogen is the central chemical storage form. In contrast to the common perception of “hydrogen economy”[34, 133, 135] it is here assumed that hydrogen will not become an energy carrier for the end user but rather be applied in processes dealing with energy storage in the background of the electricity grid.

Hydrogen generation from water electrolysis[37, 38, 96, 134] is a fundamental challenge to electrochemistry and material science. Neither the present efficiency nor the applied electrode materials render present technologies scalable to grid dimensions with realistic life times and economic performances. As this challenge has been tackled for quite some time it is expected that massive progress in understanding the underlying interfacial processes[136, 137] as well as tailoring surface electronic structures[138] of electrode materials of non-noble metals[139, 140] will be needed for any scenario utilizing solar primary energy. Substantial help for designing and understanding[98, 141] the relevant experiments comes from theory. Reaction mechanisms and derived descriptors for the prediction of the most relevant surface properties of electrode materials are being developed allowing to conclude that new compositions besides the conventional noble metals focusing on Ru and Pt can be found[97] for water splitting applications. The discovery of the Co-phosphate system[37] is a promising step in this direction.

Like in the battery case where one single process (the storage of Li ions) is strongly limiting also in the electro-catalytic reaction sequence of water splitting one step namely the evolution of oxygen (OER) is the difficult[142, 143] reaction. This conceptually unnecessary reaction is absolutely vital to the whole energy storage function as the discharge of the O^{2-} ions provides the electrons needed to generate molecular hydrogen. It is thus not adequate to circumvent the OER by using “sacrificial donors” for electrons as in a systemic view there no room for large-scale electron sources besides oxygen anions.

The reason for this difficulty lies in the material transformation of the metallic (metal or conducting oxide) electrode during oxygen evolution. The active form of the system is metal-oxide hydrate[144] in non-crystalline form forming an over-layer on the metal or oxide bulk conductor. The thickness of this over-layer determines the resistance of the electron transfer and thus part of the “overpotential”[145] being lost activating energy and creates structural and dimensional instability. The hydrous oxide slowly condenses into a poorly crystalline metal oxide being insulating and forming a deactivating crust on the working electrode. This happens both on e.g metallic noble Pt[146] and on conducting Ru-or Ir oxides[147] becoming non-stoichiometric and unstable during operation[148, 149] and dissolve in the electrolyte. This material dynamics explains also why supported noble metal systems on carbon are unstable. Their interface is chemically modified during operation and in addition, carbon itself is only kinetically stable against electro-oxidation at potentials of the OER reaction.

These observations tie in with the described instability of the Co-phosphate system[37, 38] and also the Mn-oxide system[150] suffers from chemical instability. A conceptual breakthrough is required[44, 151] here optimizing the opposing trends of required chemical dynamics with likewise necessary dimensional stability of the active phase in OER. Knowing all this it becomes better understandable why in nature[61, 152, 153] a small inorganic Ca-Mn₃O₄ cluster is embedded in a large and complex protein scaffold and why this cluster changes its structure[154, 155] during the water splitting reaction sequence reversibly.

The combination of water electrolysis and primary electricity generation from PV[96] or from wind[156] has been studied quantitatively and reveals clearly that a combination of

electrolysis with storage of hydrogen is a technologically and scalable option exceeding other forms of electricity storage by far in efficiency and in storage capacity. The study using a PV array[96] further demonstrated that such technologies can well operate in a stand-alone mode and would not require backing-up by a grid system.

Hydrogen is unsafe for energy transfer over long distances. The transformation of hydrogen into a safe transport form is thus desirable for bulk energy transport. Ammonia[157-161] is a transport form of hydrogen[88, 162] that does not contribute to the carbon footprint of energy supply. It can be manufactured practically without any energy loss and a transport infrastructure for grid-relevant dimensions of ammonia already exists to supply the fertilizer demands in the world. The ammonia splitting reaction is less-well developed and requires for fundamental reasons[163] a different catalyst than used for the forward synthesis[164] reaction. Multiple efforts in this direction show promising results so that an ammonia exchange energy chain[88, 158, 165] is quite feasible. The frequent concerns expressed with the possible use of ammonia as energy storage system address the toxicity and the smell as well as the potent greenhouse effect of ammonia causing severe constraints for leakage. Most of these concerns arise from a biased comparison of energy carrier systems: would the existing petrochemical energy carrier systems be evaluated for the same criteria of handling safety, odor and toxicity and would the decades of development towards optimized handling systems be considered, then little difference in risk potentials would occur. The concerns are all valid to a certain extent but many measures can be taken to minimize the risks. This is evidently shown by the existing worldwide trading system of ammonia that operates at large scale without any major accident. The poor attention that ammonia is receiving as potent energy storage system (not for end-use applications but as medium-to long term trading and storage form) is caused by a strong influx of non-scientific arguments leading to a premature exclusion of a potential solution with low barriers towards large-scale application.

Alternative forms for hydrogen transport are methane or methanol[86, 166] (could be generated in dry sunny areas from CO₂ and solar hydrogen in a bi-directional gas transport operation yielding the valuable by-product water). Here substantial efforts in catalyst development and process design are still necessary[94, 167] to reach grid-scale molecular conversions with acceptable (as we face in the present energy supply system) energy losses. CO₂ may be considered as raw material for a variety of uses as shown in Figure 8.

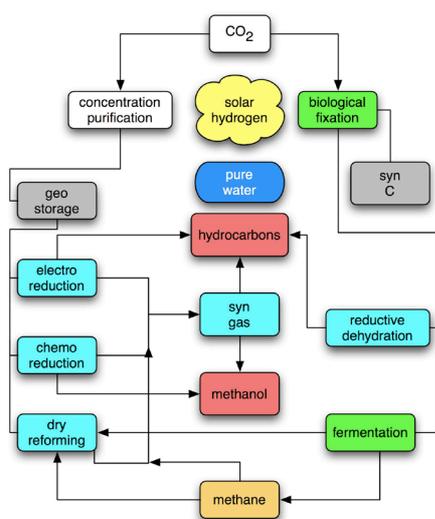


Figure 8: Uses of CO₂ as raw material. Solar hydrogen (cloud) is required in all conversion processes, including the biological fixation. The boxes in turquoise denote catalytic processes,

the green boxes stand for biological transformations. Methane is an intermediate and energy carrier, the red boxes denote products for the chemical industry.

There are multiple uses of the greenhouse gas as long as abundant solar hydrogen allows chemical transformation of CO_2 , or biological processes can harvest CO_2 and the resulting biomass can be fermented or chemically refined. All these uses are, however, energetically uphill and require excessive solar energy to compensate for that. Figure 9 presents some thermodynamic data. CO_2 is a stable molecule and its activation through reductive transformations requires substantial energy generated mainly by the formation of water or of a larger oxidized hydrocarbon. It is interesting to see that coordination of water or of an additional oxygen atom lowers the energy still significantly disproving the argument that CO_2 is the “most stable molecule” and should not be used for further chemistry. These data also form the basis to understand that aqueous solutions of CO_2 are still reactive with respect to corrosion or mineralization, a fact that is most relevant for underground dumping in the CCS technology. CO_2 is a useful raw material at large scale when the unavoidable high-energy byproduct water is of additional value. It should be added that the collection and purification of the CO_2 presents a significant and energy-consuming “detail”, often ignored in the energy discussion. Otherwise the sequestration of CO_2 alone may be more effectively achieved by biological collection and chemical transformation into solid carbon as described in Figure 7.

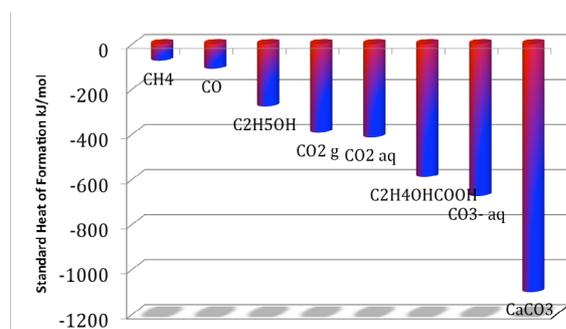


Figure 9: Heat of formation data for some species related to CO_2 . The data were taken from ref.[94]

The key purpose of CO_2 chemistry is the removal of the greenhouse gas in large quantities. This must be done without creating immediate or long-term dangers from a high-density storage of this in concentrated form deadly toxic gas. In Figures 7 and 8 its use is indicated in a cycle of converting solar hydrogen to synthetic fuel. This cycle may be seen as a chemical alternative to photosynthesis leading to hydrocarbons in contrast to oxygenated molecules such as carbohydrates resulting from the biological process. The energy density of the resulting products from such a chemical process chain is high. The efficiency per photon of solar energy may be low but will be substantially higher as if one would use existing biological systems to generate synthetic fuel (e.g. through growing corn and fermentation to alcohols followed by acid-base chemistry to arrive at hydrocarbons). If one combines solar hydrogen with solar thermal process energy[129] then quite substantial efficiencies can be expected.

The necessary catalytic technologies[168-174] to reduce CO_2 are in a state that large-scale processes can be operated. There is a good understanding[175] of the basic chemistry of the molecule and its activation by coordination to metal active sites. A beneficial boundary condition of such a process should be its stand-alone technology, i.e. its operation without having to connect the process to other chemical synthesis processes. This design is a prerequisite for scalability in decentralized units that are attached to the points of CO_2 creation avoiding further losses by transportation of this already energetically undesired process.

The use of methanol as primary energy storage molecule in the solar refinery indicated in Figure 7 bears the advantage that many downstream applications can benefit from chemical energy taken from electricity to be used in other applications of the energy system. This has been advocated strongly[86, 94, 166, 176] and is practiced already now where GTL (gas-to-liquid) processes[177-179] are being installed at world scale. The very demanding direct hydrogenation of CO₂ to methanol may be substituted with dry reforming of methane stemming from biological or photo-electrochemical reduction of CO₂ to methane[178, 180, 181] being however, also a process requiring substantial development. Whatever solution will be preferred or to what extent such scenarios will co-exist in different parts of the world is impossible to predict. It becomes clear, however, that the constituting processes need to be developed to large-scale maturity and then they may be combined as a “toolbox” to satisfy the demand for synthetic fuels and help reduce[17, 81] the CO₂ emission.

The hydrogenation of CO₂ to larger oxygenated molecules such as DME (dimethyl ether) and the OME (oxomethylene ether) family[182] gives access to families of designer fuels for mobile applications with existing motor technologies. Such synthetic fuels carry in contrast to the alternative of Fischer-Tropsch-based molecular mixtures the unique option of perfect combustion without the formation of undesired particulate matter and allow omitting exhaust gas treatment systems from the power train.

The reverse conversion process of hydrogen generation is the oxidation of hydrogen to water leading to electrical energy. This can be done rather conventional by combustion in motors or turbines or by fuel cell[183-186] technologies. The resulting clean water is an additional valuable product in areas of the world where energy is used to generate drinking or irrigation water. The underlying chemical issues of catalytic oxidation of hydrogen are being studied since long[137, 187, 188] and have brought about many technologically viable solutions. One of the greatest problems is the need to use noble metals representing the same problem as for water electrolysis. It can be expected that the material issues will be solved together for both processes. There are additional challenges about high-temperature combustion requiring catalysts for avoiding nitrogen oxidation and materials for mobile parts of turbines in the high-temperature zones. The general advancement of combustion science[189] allows stating that these issues do not represent a critical bottleneck as compared to the storage of primary electricity in chemical bonds.

A Master plan

Considering these many details from only the contribution of chemistry we may ask how one coordinates such efforts into concerted action transforming the whole energy system. This can be achieved by a “master plan” describing the pathways of migration of each element in the energy system towards a target state that can be deduced from the overall target of the energy system. The complexity of the system and its multi-layered factors of influence discussed with Figures 2 and 3 plus the constantly changing situation of the whole anthropocene render it impossible to imagine a fixed and even quantitative target description of national energy system. The master plan as necessary as it is will thus be a moving target. This calls for a minimum of planning elements in it and for a maximum of flexibility utilized by the elements of the energy system to adapt to the main targets.

The present regulatory situation is the sheer opposite of such a simple and reliable master plan that would create trust of the stakeholders in their scientific, technological and economical investments. This trust is a core pre-requisite for a successful transformation. We see many even conflicting regulations, punctual subsidies, politically motivated preference of technologies and a fragmented landscape of energy science.

The most important step for science and the whole transformation process is thus the construction of a “flexible” master plan with clear boundary regulations and a maximum of scientific, technological and economic freedom for realization of opportunities. In Europe little is done to define or orchestrate such a process at the time of writing this article.

Science may motivate the relevant discussion with conceptual suggestions how to direct the already started transformation tearing apart the formerly compact energy system into many parts with un-coordinated actions. From the viewpoint of chemistry and summarizing the analysis given above it is helpful to start with a target definition of the electricity system. Reasons for that are the excessive losses during fossil electricity generation with their large contribution of greenhouse gas emission (see Figure 5) and the substantial deployment of windmills or PV systems producing electricity as primary renewable energy source.

In Figure 10 an schematic outline of a transformation path of the German national electricity system is suggested using the representation of an annual load curve for electricity. Such a diagram is no master plan but can induce discussion about it. This representation ignores all aspects of temporal dynamics and regional specificity. It assumes the existence of a smart distribution grid capable of transporting energy bidirectional between users and generators who may switch their roles several times during a day.

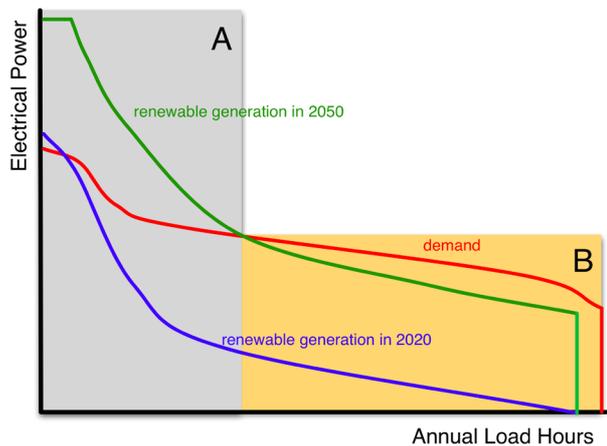


Figure 10: Schematic representation of the German national electric grid load over a year (red). This is compared to the renewable electricity generation by wind onshore and offshore plus PV for the near future (blue) and for a possible foreseeable planning period (green). The slopes of the generation curves depend on the relative contributions of wind and PV and vary with geographic location and possibly with to be expected historic evolution (efficiency improvements, redistribution of generation technologies, addition of novel sources such as energy farming). For the longterm situation in region (A) a surplus of renewable electricity needs to be converted, in region (B) residual fossil sources are required to meet the demand.

The Figure illustrates in the possibly simplest form the challenge of integration between demand and volatile generation. The areas between the red curve in Figure 10 and the other curves represent the power required or to be stored with respect to a stable demand structure.

One may conclude the following items for a master plan.

- (1) It may not be most useful to define the grid and storage options such as to harvest the complete generation capacity of renewable sources: the steepness of the generation curve suggests to omit the top 5-10 % of the power generation for its exceedingly uneconomical use of the necessary capacities in transportation and storage.
- (2) This top surplus may either be discarded or may be used locally for either incentivizing new uses (imagine to give away excess electricity for free on plug-in hybrid vehicles being plugged in) or for very cheap storage such as local heating systems. Here a large field for marketing activities opens if one is prepared to give away some of the cheapest electricity locally for unloading the burden on the national energy system.
- (3) There will be always a gap in supply that is best filled with dynamical fossil sources as long as fuel is economically available, Otherwise energy storage and re-generation of electricity is necessary which can solve the problem but is uneconomical as long as fossil sources are operational.
- (4) The surplus of electricity with acceptable temporal availability should be used for storage. A mixture of solutions is probably required to optimize the economic as well as the grid stability. Thermo-mechanical systems for regeneration of electricity or for heating/cooling applications may co-exist with chemical energy conversion in all its variants discussed above.
- (5) The re-generation of electricity from chemical energy storage is a quite wasteful overall process and should be avoided as long as the supply gaps can be filled with fossil sources. The use of the chemicals form CEC in other parts of the energy system such as for production of fuels for mobility or as raw material basis for the chemical industry or to utilize CO₂ emissions from large non-energetic sources (blast furnaces, cement ovens) through hydrogenation with H₂ from electrolysis are all viable options with better economics as judged today.
- (6) The implementation of energy storage and in particular of chemical energy storage is a long-term target if we consider the maturity of world-scale technologies and the economic aspects. It is, however the prerequisite for mastering the energy challenge in times where little or no fossil resources are left.
- (7) The lever of such advanced combined electricity-other energetic use concepts in other parts of the world with different energy systems must not be underestimated; simply this effect may contribute to stabilizing the global energy systems much more than saving resources and emissions only in the German national system (see section on dimensions and dynamics).
- (8) The prerequisite for a systemic approach towards integrated renewable energy is the existence of the bidirectional grid and its information sub-system. Constructing this system after considering the option of discarding peak loads from renewable energy generation is the first action ranging in higher priority than installing additional regenerative energy generation devices with high growth rates. This should be no excuse to go ahead in other parts of the energy system faster where technologies are further advanced such as in reducing energy use for heating/cooling or in the mobility sector. Their links to the electricity sector can be defined and managed through the master plan in such a way that no blockage between the segments should occur (e.g. double utilization of harvested energy or over-usage of scarce resources).

- (9) The sciences required for these technologies need to be advanced with high priority in the coming decade. This holds as well for new systems and their operation using existing technologies (distribution, smart grid, thermo-mechanical storage, batteries) as for the still much less advanced chemical energy conversion systems where we still lack substantial fractions of fundamental knowledge. Thus a national sub-master plan for advancement of science and technology is needed taking also into account the international advances and possibilities of co-operation.
- (10) Design and operation of a system as sketched in Figure 10 is at conflict with the present regulatory system in many points. A reconsideration of the national and at least European regulatory system for the evolution of regional energy systems is vital for this transformation pathway or for alternatives. The concept of a systemic approach with dynamical boundary conditions is adverse to the present set of strict and punctual regulatory subsystems with multiple contradictions in their effects due to their lack of coherent design and function.

Conclusions

The transformation of the energy system into a sustainable operation that offers reliable supply to everybody and for all purposes is a massive challenge as the present fossil system is already highly complicated. It represents a convolution of technical, economic, regulatory and societal factors. Any attempt to transform energy generation without taking this system character into account is doomed for failure. We thus need a broad discussion about targets and boundary conditions of the energy system that should be cast into guidelines by politics. These guiding lines must have medium-term stability but should be flexible to respond on fundamental external changes of the conditions in which the energy system is defined.

Science at large and chemistry in particular will have to deliver a set of novel energy conversion technologies with high standards in stability, scalability and sustainability. Whereas in some areas the necessary fundamental knowledge is already developed and advanced technological optimizations can be carried out it is still hard to design chemical energy conversion processes based on a quantitative understanding of underlying elementary reactions. This deficit should be removed with substantial effort even if no immediate practical solution will emerge from it. We further need continuous blue skies research in energy conversion in order to widen our library of options from which technology can choose. A prominent example of this is the nuclear fusion technology where we should arrive at proven demonstration plants before we decide over the fate of this approach. It is a general observation that in many new technologies statements on performance and potential risks are given without solid and experimental verification. Sufficient demonstration experiments at grid level dimensions are needed to bring back the discussion on technologies on reliable grounds.

There is no fundamental reason to believe that the energy challenge cannot be met. The sun provides enough energy and we have a set of technologies that convert this primary energy into free energy useful for our societal activities. The missing technologies for the complete systemic operation will occur over time. The most critical factors are outside the science and technology arena. Lack of information and poor management of expectations together with limited insight into temporal and economic dimensions present the main challenges for moving forward with the energy transformation. An observation of the author in this respect is that our society exhibits a complex behavior on judging about risks and ethics of technologies such as the energy system. A more open and information-based discussion may replace the partly ideological debate that creates many adverse influences on the evolution of science and technologies at a pre-mature stage.

References

- [1] K. Doroodian, R. Boyd, The linkage between oil price shocks and economic growth with inflation in the presence of technological advances: a CGE model, *Energy Policy*, 31 (2003) 989-1006.
- [2] A.M. Herrera, E. Pesavento, OIL PRICE SHOCKS, SYSTEMATIC MONETARY POLICY, AND THE "GREAT MODERATION", *Macroeconomic Dynamics*, 13 (2009) 107-137.
- [3] L. Kilian, The Economic Effects of Energy Price Shocks, *Journal of Economic Literature*, 46 (2008) 871-909.
- [4] D. Archer, V. Brovkin, The millennial atmospheric lifetime of anthropogenic CO₂, *Climatic Change*, 90 (2008) 283-297.
- [5] A. Egan, A MORAL CLIMATE: THE ETHICS OF GLOBAL WARMING, *Theological Studies*, 70 (2009) 491-493.
- [6] J.I.L. Morison, D.W. Lawlor, Interactions between increasing CO₂ concentration and temperature on plant growth, *Plant Cell and Environment*, 22 (1999) 659-682.
- [7] C. Parmesan, Ecological and evolutionary responses to recent climate change, *Annual Review of Ecology Evolution and Systematics*, 37 (2006) 637-669.
- [8] J. Zachos, M. Pagani, L. Sloan, E. Thomas, K. Billups, Trends, rhythms, and aberrations in global climate 65 Ma to present, *Science*, 292 (2001) 686-693.
- [9] A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon, W. Van Schalkwijk, Nanostructured materials for advanced energy conversion and storage devices, *Nature Materials*, 4 (2005) 366-377.
- [10] P. Balaya, Size effects and nanostructured materials for energy applications, *Energy & Environmental Science*, 1 (2008) 645-654.
- [11] Y.-S. Hu, X. Liu, J.-O. Müller, R. Schlögl, J. Maier, D.S. Su, Synthesis and Electrode Performance of Nanostructured V₂O₅ by Using a Carbon Tube-in-Tube as a Nanoreactor and an Efficient Mixed-Conducting Network, *Angew. Chem. Int. Ed.*, 48 (2009) 210-214.
- [12] A. Manthiram, A.V. Murugan, A. Sarkar, T. Muraliganth, Nanostructured electrode materials for electrochemical energy storage and conversion, *Energy & Environmental Science*, 1 (2008) 621-638.
- [13] S.M. Shaahid, I. El-Amin, Techno-economic evaluation of off-grid hybrid photovoltaic-diesel-battery power systems for rural electrification in Saudi Arabia-A way forward for sustainable development, *Renewable & Sustainable Energy Reviews*, 13 (2009) 625-633.
- [14] C. Cosmi, S. Di Leo, S. Loperte, M. Macchiato, F. Pietrapertosa, M. Salvia, V. Cuomo, A model for representing the Italian energy system: The NEEDS-TIMES experience, *Renewable & Sustainable Energy Reviews*, 13 (2009) 763-776.
- [15] N.F. da Silva, L.P. Rosa, M.R. Araujo, The utilization of wind energy in the Brazilian electric sector's expansion, *Renewable & Sustainable Energy Reviews*, 9 (2005) 289-309.
- [16] R. Ghanadan, J.G. Koomey, Using energy scenarios to explore alternative energy pathways in California, *Energy Policy*, 33 (2005) 1117-1142.
- [17] M. Islam, A. Fartaj, D.S.K. Ting, Current utilization and future prospects of emerging renewable energy applications in Canada, *Renewable & Sustainable Energy Reviews*, 8 (2004) 493-519.
- [18] K. Nath, D. Das, Production and storage of hydrogen: Present scenario and future perspective, *Journal of Scientific & Industrial Research*, 66 (2007) 701-709.

- [19] M. Beccali, M. Cellura, V. Lo Brano, A. Marvuglia, Forecasting daily urban electric load profiles using artificial neural networks, *Energy Conversion and Management*, 45 (2004) 2879-2900.
- [20] D. Charles, ENERGY Renewables Test IQ of the Grid, *Science*, 324 (2009) 172-+.
- [21] J.F.B. Mitchell, THE GREENHOUSE-EFFECT AND CLIMATE CHANGE, *Reviews of Geophysics*, 27 (1989) 115-139.
- [22] R. Lal, Soil carbon sequestration to mitigate climate change, *Geoderma*, 123 (2004) 1-22.
- [23] C.H. Cheng, J. Lehmann, J.E. Thies, S.D. Burton, M.H. Engelhard, Oxidation of black carbon by biotic and abiotic processes, *Organic Geochemistry*, 37 (2006) 1477-1488.
- [24] K. Paustian, J. Six, E.T. Elliott, H.W. Hunt, Management options for reducing CO₂ emissions from agricultural soils, *Biogeochemistry*, 48 (2000) 147-163.
- [25] E.M.W. Smeets, A.P.C. Faaij, I.M. Lewandowski, W.C. Turkenburg, A bottom-up assessment and review of global bio-energy potentials to 2050, *Progress in Energy and Combustion Science*, 33 (2007) 56-106.
- [26] T. Berntsen, J. Fuglestvedt, G. Myhre, F. Stordal, T.F. Berglen, Abatement of greenhouse gases: Does location matter?, *Climatic Change*, 74 (2006) 377-411.
- [27] D.J. Hofmann, J.H. Butler, P.P. Tans, A new look at atmospheric carbon dioxide, *Atmospheric Environment*, 43 (2009) 2084-2086.
- [28] A. Montenegro, V. Brovkin, M. Eby, D. Archer, A.J. Weaver, Long term fate of anthropogenic carbon, *Geophysical Research Letters*, 34 (2007).
- [29] J.R. Van Hise, CO₂ removal rate in earth's atmosphere, *Research Journal of Chemistry and Environment*, 12 (2008) 14-16.
- [30] J.M. Ketzer, R. Iglesias, S. Einloft, J. Dullius, R. Ligabue, V. de Lima, Water-rock-CO₂ interactions in saline aquifers aimed for carbon dioxide storage: Experimental and numerical modeling studies of the Rio Bonito Formation (Permian), southern Brazil, *Applied Geochemistry*, 24 (2009) 760-767.
- [31] M. de Best-Waldhober, D. Daamen, A. Faaij, Informed and uninformed public opinions on CO₂ capture and storage technologies in the Netherlands, *International Journal of Greenhouse Gas Control*, 3 (2009) 322-332.
- [32] A. Muller, Sustainable agriculture and the production of biomass for energy use, *Climatic Change*, 94 (2009) 319-331.
- [33] K. Voorspools, Sustainability of the future; rethinking the fundamentals of energy research, *Renewable & Sustainable Energy Reviews*, 8 (2004) 599-608.
- [34] M. Woodhouse, B.A. Parkinson, Combinatorial approaches for the identification and optimization of oxide semiconductors for efficient solar photoelectrolysis, *Chemical Society Reviews*, 38 (2009) 197-210.
- [35] J. Greeley, T.F. Jaramillo, J. Bonde, I.B. Chorkendorff, J.K. Nørskov, Computational high-throughput screening of electrocatalytic materials for hydrogen evolution, *Nature Materials*, 5 (2006) 909-913.
- [36] J. Greeley, J.K. Nørskov, Large-scale, density functional theory-based screening of alloys for hydrogen evolution, *Surface Science*, 601 (2007) 1590-1598.
- [37] M.W. Kanan, D.G. Nocera, In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co²⁺, *Science*, 321 (2008) 1072-1075.
- [38] M.W. Kanan, Y. Surendranath, D.G. Nocera, Cobalt-phosphate oxygen-evolving compound, *Chemical Society Reviews*, 38 (2009) 109-114.

- [39] H. Dau, C. Limberg, T. Reier, M. Risch, S. Roggan, P. Strasser, The Mechanism of Water Oxidation: From Electrolysis via Homogeneous to Biological Catalysis, *Chemcatchem*, 2 (2010) 724-761.
- [40] M. Conte, G. Budroni, J.K. Bartley, S.H. Taylor, A.F. Carley, A. Schmidt, D.M. Murphy, F. Girgsdies, T. Ressler, R. Schloegl, G.J. Hutchings, Chemically induced fast solid-state transitions of omega-VOPO₄ in vanadium phosphate catalysts, *Science*, 313 (2006) 1270-1273.
- [41] M. Havecker, R.W. Mayer, A. Knop-Gericke, H. Bluhm, E. Kleimenov, A. Liskowski, D. Su, R. Follath, F.G. Requejo, D.F. Ogletree, M. Salmeron, J.A. Lopez-Sanchez, J.K. Bartley, G.J. Hutchings, R. Schlogl, In situ investigation of the nature of the active surface of a vanadyl pyrophosphate catalyst during n-butane oxidation to maleic anhydride, *Journal of Physical Chemistry B*, 107 (2003) 4587-4596.
- [42] W. Liao, R. Heijungs, G. Huppes, Natural resource demand of global biofuels in the Anthropocene: A review, *Renewable & Sustainable Energy Reviews*, 16 (2012) 996-1003.
- [43] H.-J. Freund, G. Meijer, M. Scheffler, R. Schlögl, M. Wolf, CO Oxidation as a Prototypical Reaction for Heterogeneous Processes, *Angew. Chem. Int. Ed.*, 50 (2011) 10064-10094.
- [44] C. Galeano, J.C. Meier, V. Peinecke, H. Bongard, I. Katsounaros, A.A. Topalov, A. Lu, K.J.J. Mayrhofer, F. Schueth, Toward Highly Stable Electrocatalysts via Nanoparticle Pore Confinement, *Journal of the American Chemical Society*, 134 (2012) 20457-20465.
- [45] J.H. Alstrum-Acevedo, M.K. Brennaman, T.J. Meyer, Chemical approaches to artificial photosynthesis. 2, *Inorganic Chemistry*, 44 (2005) 6802-6827.
- [46] J. Barber, Photosynthetic energy conversion: natural and artificial, *Chemical Society Reviews*, 38 (2009) 185-196.
- [47] M. Gratzel, ARTIFICIAL PHOTOSYNTHESIS - WATER CLEAVAGE INTO HYDROGEN AND OXYGEN BY VISIBLE-LIGHT, *Accounts of Chemical Research*, 14 (1981) 376-384.
- [48] T.J. Meyer, CHEMICAL APPROACHES TO ARTIFICIAL PHOTOSYNTHESIS, *Accounts of Chemical Research*, 22 (1989) 163-170.
- [49] D.J. Milliron, S.M. Hughes, Y. Cui, L. Manna, J.B. Li, L.W. Wang, A.P. Alivisatos, Colloidal nanocrystal heterostructures with linear and branched topology, *Nature*, 430 (2004) 190-195.
- [50] M. Yagi, A. Syouji, S. Yamada, M. Komi, H. Yamazaki, S. Tajima, Molecular catalysts for water oxidation toward artificial photosynthesis, *Photochemical & Photobiological Sciences*, 8 (2009) 139-147.
- [51] T.M. Guer, Critical Review of Carbon Conversion in "Carbon Fuel Cells", *Chemical Reviews*, 113 (2013) 6179-6206.
- [52] A.C. Rady, S. Giddey, S.P.S. Badwal, B.P. Ladewig, S. Bhattacharya, Review of Fuels for Direct Carbon Fuel Cells, *Energy & Fuels*, 26 (2012) 1471-1488.
- [53] F. Terzi, C. Zanardi, S. Daolio, M. Fabrizio, R. Seeber, Au/Pt nanoparticle systems in methanol and carbon monoxide electrooxidation, *Electrochimica Acta*, 56 (2011) 3673-3678.
- [54] M.S. Hamdan, N. Nordin, S.F.M. Amir, Riyanto, M.R. Othman, Electrochemical Behaviour of Ni and Ni-PVC Electrodes for the Electrooxidation of Ethanol, *Sains Malaysiana*, 40 (2011) 1421-1427.
- [55] C.C. Jara, D. Fino, Cost optimization of the current density for electrooxidation wastewater processes, *Chemical Engineering Journal*, 160 (2010) 497-502.
- [56] A.L. Dicks, The role of carbon in fuel cells, *Journal of Power Sources*, 156 (2006) 128-141.
- [57] S.A. van den Heever, I.E. Grossmann, Disjunctive multiperiod optimization methods for design and planning of chemical process systems, *Computers & Chemical Engineering*, 23 (1999) 1075-1095.

- [58] M.K. Deshmukh, S.S. Deshmukh, Modeling of hybrid renewable energy systems, *Renewable & Sustainable Energy Reviews*, 12 (2008) 235-249.
- [59] N. Khan, Z. Saleem, A. Wahid, Review of natural energy sources and global power needs, *Renewable & Sustainable Energy Reviews*, 12 (2008) 1959-1973.
- [60] M. Ni, M.K.H. Leung, D.Y.C. Leung, K. Sumathy, A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production, *Renewable & Sustainable Energy Reviews*, 11 (2007) 401-425.
- [61] W. Lubitz, E.J. Reijerse, J. Messinger, Solar water-splitting into H₂ and O₂: design principles of photosystem II and hydrogenases, *Energy & Environmental Science*, 1 (2008) 15-31.
- [62] K. Alanne, A. Saari, Distributed energy generation and sustainable development, *Renewable & Sustainable Energy Reviews*, 10 (2006) 539-558.
- [63] G.M.J. Herbert, S. Iniyar, E. Sreevalsan, S. Rajapandian, A review of wind energy technologies, *Renewable & Sustainable Energy Reviews*, 11 (2007) 1117-1145.
- [64] T.V. Ramachandra, RIEP: Regional integrated energy plan, *Renewable & Sustainable Energy Reviews*, 13 (2009) 285-317.
- [65] V.M. Aroutiounian, V.M. Arakelyan, G.E. Shahnazaryan, Metal oxide photoelectrodes for hydrogen generation using solar radiation-driven water splitting, *Solar Energy*, 78 (2005) 581-592.
- [66] T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects, *International Journal of Hydrogen Energy*, 27 (2002) 991-1022.
- [67] J.R. Bolton, D.O. Hall, PHOTO-CHEMICAL CONVERSION AND STORAGE OF SOLAR-ENERGY, *Annual Review of Energy*, 4 (1979) 353-401.
- [68] D.O. Hall, SOLAR-ENERGY CONVERSION THROUGH BIOLOGY - COULD IT BE A PRACTICAL ENERGY-SOURCE, *Fuel*, 57 (1978) 322-333.
- [69] T. Kodama, High-temperature solar chemistry for converting solar heat to chemical fuels, *Progress in Energy and Combustion Science*, 29 (2003) 567-597.
- [70] T. Umeyama, H. Imahori, Carbon nanotube-modified electrodes for solar energy conversion, *Energy & Environmental Science*, 1 (2008) 120-133.
- [71] J.M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature*, 414 (2001) 359-367.
- [72] M. Wakihara, Recent developments in lithium ion batteries, *Materials Science & Engineering R-Reports*, 33 (2001) 109-134.
- [73] A. Sharma, V.V. Tyagi, C.R. Chen, D. Buddhi, Review on thermal energy storage with phase change materials and applications, *Renewable & Sustainable Energy Reviews*, 13 (2009) 318-345.
- [74] M.M. Farid, A.M. Khudhair, S.A.K. Razack, S. Al-Hallaj, A review on phase change energy storage: materials and applications, *Energy Conversion and Management*, 45 (2004) 1597-1615.
- [75] B. Zalba, J.M. Marin, L.F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, *Applied Thermal Engineering*, 23 (2003) 251-283.
- [76] M.I. Hoffert, K. Caldeira, G. Benford, D.R. Criswell, C. Green, H. Herzog, A.K. Jain, H.S. Kheshgi, K.S. Lackner, J.S. Lewis, H.D. Lightfoot, W. Manheimer, J.C. Mankins, M.E. Mauel, L.J. Perkins, M.E. Schlesinger, T. Volk, T.M.L. Wigley, Advanced technology paths to global climate stability: Energy for a greenhouse planet, *Science*, 298 (2002) 981-987.

- [77] R.E.H. Sims, W. Mabee, J.N. Saddler, M. Taylor, An overview of second generation biofuel technologies, *Bioresource Technology*, 101 (2010) 1570-1580.
- [78] A. Demirbas, Biofuels sources, biofuel policy, biofuel economy and global biofuel projections, *Energy Conversion and Management*, 49 (2008) 2106-2116.
- [79] P. Claus, Vogel, H., The Roll of Chemocatalysis in the Establishment of the Technology Platform "Renewable Resources", *Chemical Engineering & Technology*, 31 (2008) 678-699.
- [80] P. McKendry, Energy production from biomass (part 2): conversion technologies, *Bioresource Technology*, 83 (2002) 47-54.
- [81] P. McKendry, Energy production from biomass (part 1): overview of biomass, *Bioresource Technology*, 83 (2002) 37-46.
- [82] B. Scrosati, J. Garche, Lithium batteries: Status, prospects and future, *Journal of Power Sources*, 195 (2010) 2419-2430.
- [83] K. Clement-Nyns, E. Haesen, J. Driesen, The Impact of Charging Plug-In Hybrid Electric Vehicles on a Residential Distribution Grid, *Ieee Transactions on Power Systems*, 25 (2010) 371-380.
- [84] H.L. MacLean, L.B. Lave, Evaluating automobile fuel/propulsion system technologies, *Progress in Energy and Combustion Science*, 29 (2003) 1-69.
- [85] M. Peters, B. Koehler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T.E. Mueller, Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain, *Chemsuschem*, 4 (2011) 1216-1240.
- [86] G.A. Olah, A. Goepfert, G.K.S. Prakash, Chemical Recycling off Carbon Dioxide to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons, *Journal of Organic Chemistry*, 74 (2009) 487-498.
- [87] G. Centi, S. Perathoner, Opportunities and prospects in the chemical recycling of carbon dioxide to fuels, *Catalysis Today*, 148 (2009) 191-205.
- [88] A. Klerke, C.H. Christensen, J.K. Norskov, T. Vegge, Ammonia for hydrogen storage: challenges and opportunities, *Journal of Materials Chemistry*, 18 (2008) 2304-2310.
- [89] S. Solomon, D., M. Quin, Z. Manning, M. Chen, K.B. Marquis, IPCC 2007 Climate Change The Physical Science Base, Cambridge University Press, 2007.
- [90] M. Asif, T. Muneer, Energy supply, its demand and security issues for developed and emerging economies, *Renewable & Sustainable Energy Reviews*, 11 (2007) 1388-1413.
- [91] W. Steffen, I. Noble, J. Canadell, M. Apps, E.D. Schulze, P.G. Jarvis, D. Baldocchi, P. Ciais, W. Cramer, J. Ehleringer, G. Farquhar, C.B. Field, A. Ghazi, R. Gifford, M. Heimann, R. Houghton, P. Kabat, C. Korner, E. Lambin, S. Linder, H.A. Mooney, D. Murdiyarso, W.M. Post, I.C. Prentice, M.R. Raupach, D.S. Schimel, A. Shvidenko, R. Valentini, G. Terrestrial Carbon Working, The terrestrial carbon cycle: Implications for the Kyoto Protocol, *Science*, 280 (1998) 1393-1394.
- [92] P. Mader, A. Fliessbach, D. Dubois, L. Gunst, P. Fried, U. Niggli, Soil fertility and biodiversity in organic farming, *Science*, 296 (2002) 1694-1697.
- [93] C. Parmesan, G. Yohe, A globally coherent fingerprint of climate change impacts across natural systems, *Nature*, 421 (2003) 37-42.
- [94] M. Aresta, A. Dibenedetto, Utilisation of CO₂ as a chemical feedstock: opportunities and challenges, *Dalton Transactions*, (2007) 2975-2992.

- [95] P. Millet, N. Mbemba, S.A. Grigoriev, V.N. Fateev, A. Aukauloo, C. Etievant, Electrochemical performances of PEM water electrolysis cells and perspectives, *International Journal of Hydrogen Energy*, 36 (2011) 4134-4142.
- [96] R.E. Clarke, S. Giddey, F.T. Ciacchi, S.P.S. Badwal, B. Paul, J. Andrews, Direct coupling of an electrolyser to a solar PV system for generating hydrogen, *International Journal of Hydrogen Energy*, 34 (2009) 2531-2542.
- [97] J. Rossmeisl, Z.W. Qu, H. Zhu, G.J. Kroes, J.K. Norskov, Electrolysis of water on oxide surfaces, *Journal of Electroanalytical Chemistry*, 607 (2007) 83-89.
- [98] J. Rossmeisl, K. Dimitrievski, P. Siegbahn, J.K. Norskov, Comparing electrochemical and biological water splitting, *Journal of Physical Chemistry C*, 111 (2007) 18821-18823.
- [99] M. Fischer, REVIEW OF HYDROGEN-PRODUCTION WITH PHOTOVOLTAIC ELECTROLYSIS SYSTEMS, *International Journal of Hydrogen Energy*, 11 (1986) 495-501.
- [100] D.P. Kaundinya, P. Balachandra, N.H. Ravindranath, Grid-connected versus stand-alone energy systems for decentralized power-A review of literature, *Renewable & Sustainable Energy Reviews*, 13 (2009) 2041-2050.
- [101] M.D. Archer, J.R. Bolton, REQUIREMENTS FOR IDEAL PERFORMANCE OF PHOTOCHEMICAL AND PHOTOVOLTAIC SOLAR-ENERGY CONVERTERS, *Journal of Physical Chemistry*, 94 (1990) 8028-8036.
- [102] F.E. Osterloh, Inorganic materials as catalysts for photochemical splitting of water, *Chemistry of Materials*, 20 (2008) 35-54.
- [103] C.P. de Leon, A. Frias-Ferrer, J. Gonzalez-Garcia, D.A. Szanto, F.C. Walsh, Redox flow cells for energy conversion, *Journal of Power Sources*, 160 (2006) 716-732.
- [104] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nanocomposite polymer electrolytes for lithium batteries, *Nature*, 394 (1998) 456-458.
- [105] Y. Gao, J.R. Dahn, Synthesis and characterization of $\text{Li}_{1+x}\text{Mn}_2-x\text{O}_4$ for Li-ion battery applications, *Journal of the Electrochemical Society*, 143 (1996) 100-114.
- [106] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, Phospho-olivines as positive-electrode materials for rechargeable lithium batteries, *Journal of the Electrochemical Society*, 144 (1997) 1188-1194.
- [107] J.R. Dahn, U. Vonsacken, M.W. Juzkow, H. Aljanaby, RECHARGEABLE LiNiO_2 CARBON CELLS, *Journal of the Electrochemical Society*, 138 (1991) 2207-2211.
- [108] J. Breger, K. Kang, J. Cabana, G. Ceder, C.P. Grey, NMR, PDF and RMC study of the positive electrode material $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ synthesized by ion-exchange methods, *Journal of Materials Chemistry*, 17 (2007) 3167-3174.
- [109] J. Wontcheu, W. Bensch, M. Wilkening, P. Heitjans, S. Indris, P. Sideris, C.P. Grey, S. Mankovsky, H. Ebert, Tuning the structural and physical properties of $\text{Cr}_2\text{Ti}_3\text{Se}_8$ by lithium intercalation: A study of the magnetic properties, investigation of ion mobility with NMR Spectroscopy and electronic band structure calculations, *Journal of the American Chemical Society*, 130 (2008) 288-299.
- [110] M.E. Schuster, D. Teschner, J. Popovic, N. Ohmer, F. Girgsdies, J. Tornow, M.G. Willinger, D. Samuelis, M.-M. Titirici, J. Maier, R. Schloegl, Charging and Discharging Behavior of Solvothermal LiFePO_4 Cathode Material Investigated by Combined EELS/NEXAFS Study, *Chemistry of Materials*, 26 (2014) 1040-1047.
- [111] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.M. Tarascon, Li-O-2 and Li-S batteries with high energy storage, *Nature Materials*, 11 (2012) 19-29.
- [112] G. Girishkumar, B. McCloskey, A.C. Luntz, S. Swanson, W. Wilcke, Lithium - Air Battery: Promise and Challenges, *Journal of Physical Chemistry Letters*, 1 (2010) 2193-2203.

- [113] D. Pasero, N. Reeves, V. Pralong, A.R. West, Oxygen nonstoichiometry and phase transitions in $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_{4-\delta}$, *Journal of the Electrochemical Society*, 155 (2008) A282-A291.
- [114] P. Tae-Hwan, Y. Jae-Seong, J. Sang-Min, J. Miyawaki, I. Mochida, Y. Seong-Ho, Synthesis of silicon monoxide-pyrolytic carbon-carbon nanofiber composites and their hybridization with natural graphite as a means of improving the anodic performance of lithium-ion batteries, *Nanotechnology*, 23 (2012) 355601 (355607 pp.).
- [115] D.S. Su, R. Schlögl, Nanostructured Carbon Materials for Electrochemical Energy Storage Applications *ChemSusChem*, 3 (2010) 136-168.
- [116] S.H. Yoon, C.W. Park, H.J. Yang, Y. Korai, I. Mochida, R.T.K. Baker, N.M. Rodriguez, Novel carbon nanofibers of high graphitization as anodic materials for lithium ion secondary batteries, *Carbon*, 42 (2004) 21-32.
- [117] R.C. Agrawal, A. Chandra, A. Bhatt, Y.K. Mahipal, Investigations on ion transport properties of and battery discharge characteristic studies on hot-pressed Ag^+ -ion-conducting nano-composite polymer electrolytes: $(1-x) [90\text{PEO} : 10\text{AgNO}_3] : x\text{SiO}_2$, *New Journal of Physics*, (2008) 043023 (043010 pp.).
- [118] J. McBreen, The application of synchrotron techniques to the study of lithium-ion batteries, *Journal of Solid State Electrochemistry*, 13 (2009) 1051-1061.
- [119] M. Salmeron, R. Schlogl, Ambient pressure photoelectron spectroscopy: A new tool for surface science and nanotechnology, *Surface Science Reports*, 63 (2008) 169-199.
- [120] C. Hong-Wei, D. Jenq-Gong, S. Hwo-Shuenn, In situ Synchrotron X-ray diffraction investigations of $\text{LiCu}_x/\text{Mn}_{2-x}\text{O}_4$ surface coated LiMn_2O_4 spinel cathode material during charge with various rates, *Journal of the Electrochemical Society*, 153 (2006) A1533-1538.
- [121] A. Knop-Gericke, E. Kleimenov, M. Hävecker, R. Blume, D. Teschner, S. Zafeirotos, R. Schlögl, V.I. Bukhtiyarov, V.V. Kaichev, I.P. Prosvirin, A.I. Nizovskii, H. Bluhm, A. Barinov, P. Dudin, M. Kiskinova, Chapter 4 X-Ray Photoelectron Spectroscopy for Investigation of Heterogeneous Catalytic Processes, *Advances in Catalysis*, 52 (2009) 213-272.
- [122] D. Mori, H. Kobayashi, M. Shikano, H. Nitani, H. Kageyama, S. Koike, H. Sakaebe, K. Tatsumi, Bulk and surface structure investigation for the positive electrodes of degraded lithium-ion cell after storage test using X-ray absorption near-edge structure measurement, *Journal of Power Sources*, 189 (2009) 676-680.
- [123] Y.-S. Hu, R. Demir-Cakan, M.-M. Titirici, J.-O. Müller, R. Schlögl, M. Antonietti, J. Maier, Superior Storage Performance of a $\text{Si}@\text{SiO}_x/\text{C}$ Nanocomposite as Anode Material for Lithium-Ion Batteries, *Angew. Chem. Int. Ed.*, 47 (2008) 1645-1649.
- [124] J. Zhang, Y. Hu, J.-P. Tessonier, G. Weinberg, J. Maier, R. Schlögl, D.S. Su, CNFs@CNTs: Superior Carbon for Electrochemical Energy Storage, *Adv.Mater.*, 20 (2008) 1450-1455.
- [125] M. Armand, F. Dalard, D. Deroo, C. Mouliom, MODELING THE VOLTAMMETRIC STUDY OF INTERCALATION IN A HOST STRUCTURE - APPLICATION TO LITHIUM INTERCALATION IN RuO_2 , *Solid State Ionics*, 15 (1985) 205-210.
- [126] S. Music, S. Popovic, M. Maljkovic, K. Furic, A. Gajovic, Influence of synthesis procedure on the formation of RuO_2 , *Materials Letters*, 56 (2002) 806-811.
- [127] J. Jamnik, J. Maier, Nanocrystallinity effects in lithium battery materials - Aspects of nano-ionics. Part IV, *Physical Chemistry Chemical Physics*, 5 (2003) 5215-5220.
- [128] S.A. Kalogirou, Solar thermal collectors and applications, *Progress in Energy and Combustion Science*, 30 (2004) 231-295.

- [129] A. Steinfeld, Solar thermochemical production of hydrogen - a review, *Solar Energy*, 78 (2005) 603-615.
- [130] L. Schlapbach, A. Züttel, Hydrogen-storage materials for mobile applications, *Nature*, 414 (2001) 353-358.
- [131] L.F. Wang, R.T. Yang, New sorbents for hydrogen storage by hydrogen spillover - a review, *Energy & Environmental Science*, 1 (2008) 268-279.
- [132] D.J. Gooch, Materials issues in renewable energy power generation, *International Materials Reviews*, 45 (2000) 1-14.
- [133] N.Z. Muradov, T.N. Veziroglu, "Green" path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies, *International Journal of Hydrogen Energy*, 33 (2008) 6804-6839.
- [134] H. Tributsch, Photovoltaic hydrogen generation, *International Journal of Hydrogen Energy*, 33 (2008) 5911-5930.
- [135] L. Barreto, A. Makihiro, K. Riahi, The hydrogen economy in the 21st century: a sustainable development scenario, *International Journal of Hydrogen Energy*, 28 (2003) 267-284.
- [136] J.O. Bockris, E.C. Potter, THE MECHANISM OF HYDROGEN EVOLUTION AT NICKEL CATHODES IN AQUEOUS SOLUTIONS, *Journal of Chemical Physics*, 20 (1952) 614-628.
- [137] B.E. Conway, J.O. Bockris, ELECTROLYTIC HYDROGEN EVOLUTION KINETICS AND ITS RELATION TO THE ELECTRONIC AND ADSORPTIVE PROPERTIES OF THE METAL, *Journal of Chemical Physics*, 26 (1957) 532-541.
- [138] A. Heller, CONVERSION OF SUNLIGHT INTO ELECTRICAL-POWER AND PHOTOASSISTED ELECTROLYSIS OF WATER IN PHOTOELECTROCHEMICAL CELLS, *Accounts of Chemical Research*, 14 (1981) 154-162.
- [139] H.B. Martin, A. Argoitia, U. Landau, A.B. Anderson, J.C. Angus, Hydrogen and oxygen evolution on boron-doped diamond electrodes, *Journal of the Electrochemical Society*, 143 (1996) L133-L136.
- [140] T.F. Jaramillo, K.P. Jorgensen, J. Bonde, J.H. Nielsen, S. Horch, I. Chorkendorff, Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts, *Science*, 317 (2007) 100-102.
- [141] R.R. Salem, Theory of the electrolysis of water, *Protection of Metals*, 44 (2008) 120-125.
- [142] T. Reier, M. Oezaslan, P. Strasser, Electrocatalytic Oxygen Evolution Reaction (OER) on Ru, Ir, and Pt Catalysts: A Comparative Study of Nanoparticles and Bulk Materials, *Acs Catalysis*, 2 (2012) 1765-1772.
- [143] I.C. Man, H.-Y. Su, F. Calle-Vallejo, H.A. Hansen, J.I. Martinez, N.G. Inoglu, J. Kitchin, T.F. Jaramillo, J.K. Norskov, J. Rossmeisl, Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces, *Chemcatchem*, 3 (2011) 1159-1165.
- [144] B.E. Conway, ELECTROCHEMICAL OXIDE FILM FORMATION AT NOBLE-METALS AS A SURFACE-CHEMICAL PROCESS, *Progress in Surface Science*, 49 (1995) 331-452.
- [145] J.O. Bockris, A. Huq, THE MECHANISM OF THE ELECTROLYTIC EVOLUTION OF OXYGEN ON PLATINUM, *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences*, 237 (1956) 277-296.
- [146] R. Arrigo, M. Hävecker, M.E. Schuster, C. Ranjan, E. Stotz, A. Knop-Gericke, R. Schlögl, In Situ Study of the Gas-Phase Electrolysis of Water on Platinum by NAP-XPS, *Angew. Chem. Int. Ed.*, 52 (2013) 11660-11664.

- [147] B. Johnson, F. Girgsdies, G. Weinberg, D. Rosenthal, A. Knop-Gericke, R. Schloegl, T. Reier, P. Strasser, Suitability of Simplified (Ir,Ti)O_x Films for Characterization during Electrocatalytic Oxygen Evolution Reaction, *Journal of Physical Chemistry C*, 117 (2013) 25443-25450.
- [148] A.A. Topalov, I. Katsounaros, M. Auinger, S. Cherevko, J.C. Meier, S.O. Klemm, K.J.J. Mayrhofer, Dissolution of Platinum: Limits for the Deployment of Electrochemical Energy Conversion?, *Angewandte Chemie-International Edition*, 51 (2012) 12613-12615.
- [149] K. Schlogl, K.J.J. Mayrhofer, M. Hanzlik, M. Arenz, Identical-location TEM investigations of Pt/C electrocatalyst degradation at elevated temperatures, *Journal of Electroanalytical Chemistry*, 662 (2011) 355-360.
- [150] K. Mette, A. Bergmann, J.-P. Tessonnier, M. Hävecker, L. Yao, T. Ressler, R. Schlögl, P. Strasser, M. Behrens, Nanostructured Manganese Oxide Supported on Carbon Nanotubes for Electrocatalytic Water Splitting, *ChemCatChem*, 4 (2012) 851-862.
- [151] Q. Yin, J.M. Tan, C. Besson, Y.V. Geletii, D.G. Musaev, A.E. Kuznetsov, Z. Luo, K.I. Hardcastle, C.L. Hill, A Fast Soluble Carbon-Free Molecular Water Oxidation Catalyst Based on Abundant Metals, *Science*, 328 (2010) 342-345.
- [152] L. Rapatskiy, N. Cox, A. Savitsky, W.M. Ames, J. Sander, M.M. Nowaczyk, M. Roegner, A. Boussac, F. Neese, J. Messinger, W. Lubitz, Detection of the Water-Binding Sites of the Oxygen-Evolving Complex of Photosystem II Using W-Band O-17 Electron-Electron Double Resonance-Detected NMR Spectroscopy, *Journal of the American Chemical Society*, 134 (2012) 16619-16634.
- [153] R.J. Debus, THE MANGANESE AND CALCIUM-IONS OF PHOTOSYNTHETIC OXYGEN EVOLUTION, *Biochimica Et Biophysica Acta*, 1102 (1992) 269-352.
- [154] V. Krewald, F. Neese, D.A. Pantazis, On the Magnetic and Spectroscopic Properties of High-Valent Mn₃CaO₄ Cubanes as Structural Units of Natural and Artificial Water-Oxidizing Catalysts, *Journal of the American Chemical Society*, 135 (2013) 5726-5739.
- [155] N. Cox, D.A. Pantazis, F. Neese, W. Lubitz, Biological Water Oxidation, *Accounts of Chemical Research*, 46 (2013) 1588-1596.
- [156] F. Crotogino, R. Hamelmann.
- [157] R. Schlögl, Catalytic synthesis of ammonia - A "never-ending story"? [Review], *Angew.Chem.Int.Ed.*, 42 (2003) 2004-2008.
- [158] K.M. Lovegrove, High pressure ammonia dissociation experiments for solar energy transport and storage, *International Journal of Energy Research*, 20 (1996) 965-978.
- [159] C.H. Christensen, T. Johannessen, R.Z. Sorensen, J.K. Norskov, Towards an ammonia-mediated hydrogen economy?, *Catalysis Today*, 111 (2006) 140-144.
- [160] C.H. Christensen, R.Z. Sorensen, T. Johannessen, U.J. Quaade, K. Honkala, T.D. Elmoe, R. Kohler, J.K. Norskov, Metal ammine complexes for hydrogen storage, *Journal of Materials Chemistry*, 15 (2005) 4106-4108.
- [161] R.Z. Sorensen, L.J.E. Nielsen, S. Jensen, O. Hansen, T. Johannessen, U. Quaade, C.H. Christensen, Catalytic ammonia decomposition: miniaturized production of CO_x-free hydrogen for fuel cells, *Catalysis Communications*, 6 (2005) 229-232.
- [162] R. Kothari, D. Buddhi, R.L. Sawhney, Comparison of environmental and economic aspects of various hydrogen production methods, *Renewable & Sustainable Energy Reviews*, 12 (2008) 553-563.
- [163] A. Hellman, E.J. Baerends, M. Biczysko, T. Bligaard, C.H. Christensen, D.C. Clary, S. Dahl, R. van Harrevelt, K. Honkala, H. Jonsson, G.J. Kroes, M. Luppi, U. Manthe, J.K. Norskov, R.A. Olsen, J. Rossmeisl, E.

Skulason, C.S. Tautermann, A.J.C. Varandas, J.K. Vincent, Predicting catalysis: Understanding ammonia synthesis from first-principles calculations, *Journal of Physical Chemistry B*, 110 (2006) 17719-17735.

[164] G. Ertl, H.J. Freund, *Catalysis and Surface Science, Physics Today*, 52 (1999) 32-38.

[165] R. Schlögl, Catalytic synthesis of ammonia - A "never-ending story"? [Review], *Angew.Chem.Int.Ed.*, 42 (2003) 2004-2008.

[166] G.A. Olah, Beyond oil and gas: The methanol economy, *Angewandte Chemie-International Edition*, 44 (2005) 2636-2639.

[167] X.D. Xu, J.A. Moulijn, Mitigation of CO₂ by chemical conversion: Plausible chemical reactions and promising products, *Energy & Fuels*, 10 (1996) 305-325.

[168] Y. Liu, Y. Zhang, T.J. Wang, N. Tsubaki, Efficient conversion of carbon dioxide to methanol using copper catalyst by a new low-temperature hydrogenation process, *Chemistry Letters*, 36 (2007) 1182-1183.

[169] J. Nakamura, Y. Choi, T. Fujitani, On the issue of the active site and the role of ZnO in Cu/ZnO methanol synthesis catalysts, *Topics in Catalysis*, 22 (2003) 277-285.

[170] R. Raudaskoski, E. Turpeinen, R. Lenkkeri, E. Pongracz, R.L. Keiski, Catalytic activation of CO₂: Use of secondary CO₂ for the production of synthesis gas and for methanol synthesis over copper-based zirconia-containing catalysts, *Catalysis Today*, 144 (2009) 318-323.

[171] J. Sloczynski, R. Grabowski, A. Kozłowska, P. Olszewski, J. Stoch, J. Skrzypek, M. Lachowska, Catalytic activity of the M/(3ZnO center dot ZrO₂) system (M = Cu, Ag, Au) in the hydrogenation of CO₂ to methanol, *Applied Catalysis a-General*, 278 (2004) 11-23.

[172] Q.L. Tang, Q.J. Hong, Z.P. Liu, CO₂ fixation into methanol at Cu/ZrO₂ interface from first principles kinetic Monte Carlo, *Journal of Catalysis*, 263 (2009) 114-122.

[173] S. Yang, E. Iglesia, A.T. Bell, Nature, Density, and Catalytic Role of Exposed Species on Dispersed VO_x/CrO_x/Al₂O₃ Catalysts, *J. Phys. Chem. B FIELD Full Journal Title:Journal of Physical Chemistry B*, 110 (2006) 2732-2739.

[174] M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R.W. Fischer, J.K. Nørskov, R. Schlögl, The Active Site of Methanol Synthesis over Cu/ZnO/Al₂O₃ Industrial Catalysts, *Science*, 336 (2012) 893-897.

[175] W. Leitner, The coordination chemistry of carbon dioxide and its relevance for catalysis: A critical survey, *Coordination Chemistry Reviews*, 153 (1996) 257-284.

[176] N.S. Lewis, D.G. Nocera, Powering the planet: Chemical challenges in solar energy utilization, *Proceedings of the National Academy of Sciences of the United States of America*, 103 (2006) 15729-15735.

[177] X. Hao, M.E. Djatmiko, Y.Y. Xu, Y.N. Wang, J. Chang, Y.W. Li, Simulation analysis of a GTL process using ASPEN plus, *Chemical Engineering & Technology*, 31 (2008) 188-196.

[178] H.S. Roh, K.Y. Koo, U.D. Joshi, W.L. Yoon, Combined H₂O and CO₂ reforming of methane over Ni-Ce-ZrO₂ catalysts for gas to liquids (GTL), *Catalysis Letters*, 125 (2008) 283-288.

[179] R.W.R. Zwart, H. Boerrigter, High efficiency co-production of synthetic natural gas (SNG) and Fischer-Tropsch (FT) transportation fuels from biomass, *Energy & Fuels*, 19 (2005) 591-597.

[180] S. Han, R.J. Piccolini, New catalytic chemistry for industrial needs, *Book of Abstracts, 219th ACS National Meeting, San Francisco, CA, March 26-30, 2000*, (2000) CATL-012.

- [181] A.J. Brungs, A.P.E. York, M.L.H. Green, Comparison of the group V and VI transition metal carbides for methane dry reforming and thermodynamic prediction of their relative stabilities, *Catalysis Letters*, 57 (1999) 65-69.
- [182] J. Burger, E. Strofer, H. Hasse, Production process for diesel fuel components poly(oxymethylene) dimethyl ethers from methane-based products by hierarchical optimization with varying model depth, *Chemical Engineering Research & Design*, 91 (2013) 2648-2662.
- [183] S.M. Haile, Fuel cell materials and components, *Acta Materialia*, 51 (2003) 5981-6000.
- [184] N.Q. Minh, CERAMIC FUEL-CELLS, *Journal of the American Ceramic Society*, 76 (1993) 563-588.
- [185] S.C. Singhal, Advances in solid oxide fuel cell technology, *Solid State Ionics*, 135 (2000) 305-313.
- [186] B.C.H. Steele, A. Heinzl, Materials for fuel-cell technologies, *Nature*, 414 (2001) 345-352.
- [187] G.B. Fisher, J.L. Gland, S.J. Schmieg, THE SPECTROSCOPIC OBSERVATION OF WATER FORMATION, *Journal of Vacuum Science & Technology*, 20 (1982) 518-521.
- [188] S. Volkening, K. Bedürftig, K. Jacobi, J. Wintterlin, G. Ertl, Dual-path mechanism for catalytic oxidation of hydrogen on platinum surfaces, *Physical Review Letters*, 83 (1999) 2672-2675.
- [189] C.K. Law, O.C. Kwon, Effects of hydrocarbon substitution on atmospheric hydrogen-air flame propagation, *International Journal of Hydrogen Energy*, 29 (2004) 867-879.