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DEVELOPMENT OF PROCESSES AND COMPONENTS FOR POWER-TO-GAS AND POWER-TO-PRODUCTS

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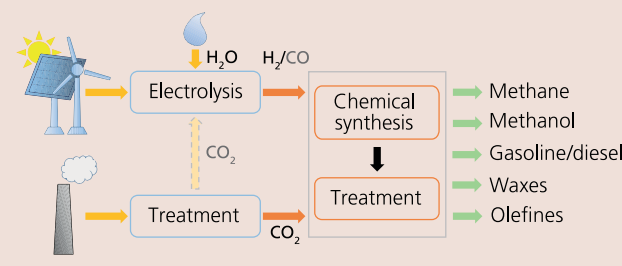
Motivation

An essential goal of the German “Energiewende” is the transition from fossil to renewable energy sources, like wind and sun. A disadvantage of these sustainable sources is their fluctuating nature. This necessitates the development of appropriate technologies for the storage of excess energy. Some concepts addressing this problem are based on the storage of energy in chemical compounds. Potential products could be conventional gaseous and liquid energy carriers as well as valuable chemical intermediates or end products. The decentralized production of renewable energy often requires decentralized process and plant concepts. The specifications of these plants differ considerably from large-scale industrial plants. The development of power-to-gas and power-to-product technologies as well as the necessary components is a focus of current research at IKTS.

Process concepts

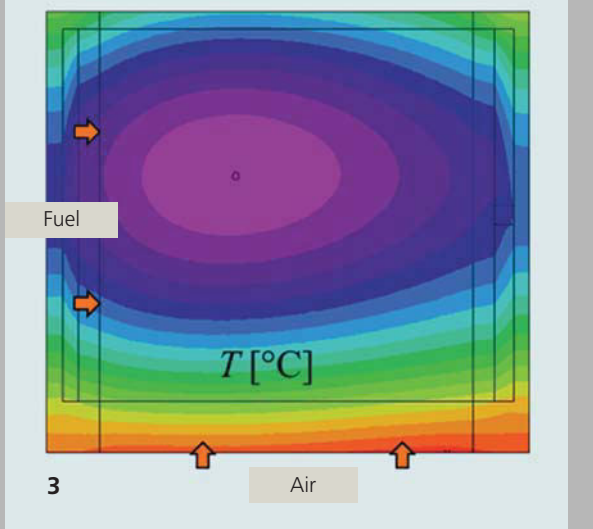
The basis of all concepts for the storage of electrical energy in chemical products is the supply of the chemical synthesis unit with hydrogen (H_2) and carbon monoxide (CO) or carbon dioxide (CO_2). Hydrogen can be produced from water in an electrolysis cell. Besides the well-established alkaline electrolysis and the PEM electrolysis (proton exchange membrane), the high-temperature electrolysis (SOEC – solid oxide electrolysis cell) is an interesting alternative. This process, currently under development, offers the potential to reach higher efficiencies. Besides that, it has another advantage with regard to the overall process concepts. For the synthesis of hydrocarbons from renewables, a carbon source is necessary, in most cases CO_2 . In contrast to other electrolysis processes, the SOEC not only allows the conversion of H_2O but also the co-electrolysis of CO_2 . Therefore, the process offers the potential to produce H_2 and CO for the subsequent chemical synthesis in one step. There are different CO_2 sources available. Besides off-gases of

Scheme displaying the utilization of renewable energy for the synthesis of chemical products



combustion processes, e.g. in power plants, also CO_2 -rich gases from several industrial processes can be utilized. Especially in the steel and cement industry, such gases are produced, which mostly need conditioning and CO_2 separation prior to CO_2 utilization. A completely renewable carbon source would be CO_2 from air but the low atmospheric concentration of CO_2 currently leads to cost-intensive and uneconomic processes. If CO_2 is not converted by co-electrolysis, it can be converted to CO in an additional process step. Some chemical syntheses can also directly utilize CO_2 as a reactant. Potential products might be methane, that can be fed into the existing natural gas grid or liquid energy carriers like gasoline or diesel. But also valuable products, like waxes or olefines, can be produced according to this approach.

Specific process concepts always depend on the desired product and the available CO_2 source. Thermal coupling of different process steps and therefore, a good heat integration are of high importance for small-scale decentralized plants, especially for achieving high efficiencies. An example is the utilization of heat from exothermic synthesis steps for the evaporation of water for the SOEC. Also the internal utilization of by-products has a huge impact on the efficiency of the respective process concept. In order to identify promising process steps, the application of process simulation tools is beneficial. In small-scale applications, dynamically operating conditions



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occur more often than in large-scale industrial plants. The development of process steps, such as electrolysis and chemical synthesis, as well as of the materials applied therein has to take place with respect to these conditions.

Electrolysis

The high-temperature electrolysis cell offers a remarkable potential for highly efficient hydrogen generation by direct and well controllable conversion of electrical into chemical energy of the produced hydrogen. The simultaneous heat production and, therefore, the compensation of endothermic water splitting allows efficiencies of up to 98 %. Operating the cells at high temperatures ($T = 700\text{ °C} - 1000\text{ °C}$) leads to decreased resistances and allows the application of Pt-free catalysts in the electrodes.

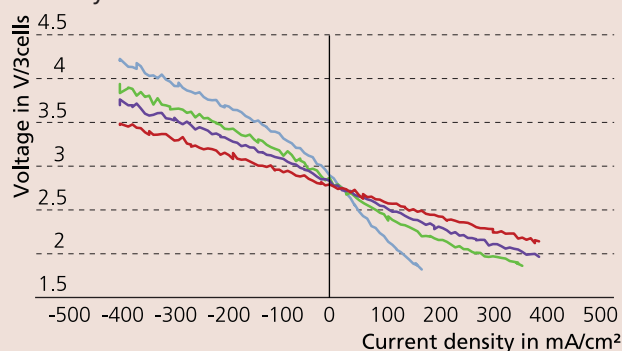
The design of an SOEC module is very similar to that of a high-temperature fuel cell (SOFC – solid oxide fuel cell). As a result, it is possible to operate the module in electrolysis as well as in fuel cell mode. Depending on the conditions, they can, therefore, store energy from the grid or feed it into the grid. Furthermore, coupling with chemical processes, e.g. the synthesis of fuels, offers the advantage of using heat from these exothermic process steps for water evaporation. This leads to an improvement of heat integration of the overall process. In contrast to the more established alkaline and PEM electrolysis, there are still development needs for high-temperature electrolysis cells regarding their long-term stability. This also distinguishes the SOEC from the high-temperature fuel cell that has already reached a commercialization-state of development.

The high operating temperatures of an SOEC allow an efficient water splitting also in presence of other gas compounds at the anode of the cell. The anode consists of highly catalytically active and, in contrast to precious metals, cheap compounds, like nickel. The local coupling of endothermic water electrolysis and exothermic power dissipation of the cell simplifies the cooling efforts in contrast to other electrolysis concepts. For example, in the case of a PEM electrolysis cell a high additional air stream is essential for cooling the cell. Additionally, the electrical energy necessary for water is splitting is lower for 800 °C than for room temperature. This can be ex-

plained by thermodynamic considerations and was confirmed by experimental results.

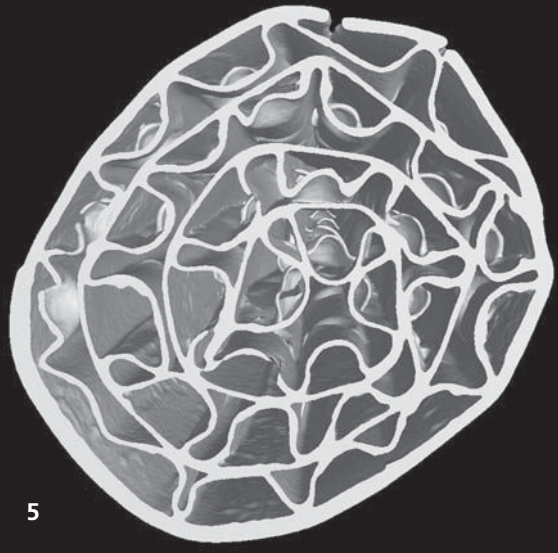
The challenge of higher degradation in comparison to the fuel cell mode is currently addressed by researchers in USA (Ceramtec) [1] and Europe (Haldor Topsoe) [2]. The degradation of all stack components under water vapor atmosphere is mostly unexplored. Since it is expected that the components of the developed SOFC module can withstand these conditions, the research efforts are focused on cell development. An important additional goal of research is the demonstration of stable operation under increased pressure. For the development of electrolysis cells, vast knowledge from the development of SOFC modules can be used. Since 1998, a planar stack (so-called CFY stack) for SOFC application has been developed at IKTS, which has reached commercial maturity at the current stage. Based on this platform, stacks suitable for SOEC mode are currently developed. They use thin ZrO_2 -based materials as electrolyte. Experimental results on long-term stability already show a very small degradation. One reason for this is a very homogeneous tem-

Current-voltage characteristic curve of a 30-cell stack in electrolysis and fuel cell mode



$H_2O/H_2=1$ — $T=700\text{ °C}$ — $T=770\text{ °C}$ — $T=800\text{ °C}$ — $T=850\text{ °C}$

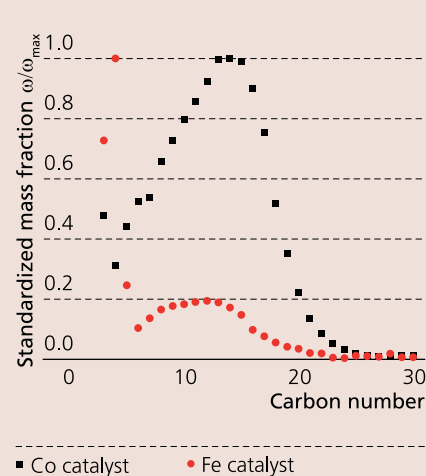
- 1 30-cell CFY stack in transport device.
- 2 Lab-scale plant for methanation and Fischer-Tropsch synthesis.
- 3 Temperature distribution in a high-temperature electrolysis cell.
- 4 MK351 interconnector with protective coating developed with Plansee SE.



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Long-term stability of a 30-cell CFY stack in electrolysis mode



perature distribution within the stack that is reached in the thermoneutral operating point. Under these conditions, the current within the stack produces the same amount of heat as necessary for the endothermic electrolysis reaction. This point can be calculated prior to the experimental tests by simulations. Therefore, simulation tools are an important element for the development of stacks and their integration within an SOEC system. It is also possible to operate stacks in a slightly exothermic operating point. The produced excess heat on a high-temperature level might be advantageous for other process steps when a highly integrated process is developed.

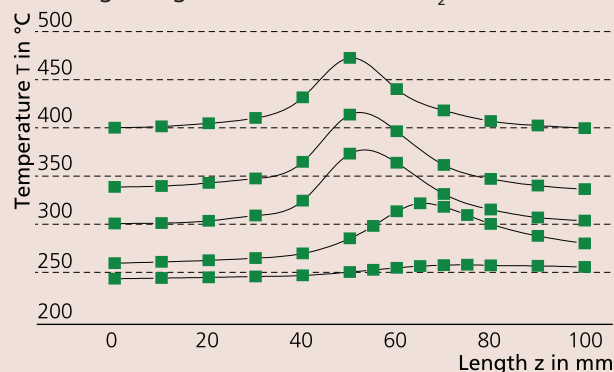
Chemical syntheses

The development activities on chemical conversion routes are focused on methanation and Fischer-Tropsch synthesis. For both reactions, novel structured ceramic catalyst supports are focused in current analyses. These supports based on ceramic tape casting technologies offer the advantage of allowing a targeted adjustment of residence time distribution and a reduction in temperature gradients and hotspot formation. The support structures are characterized by increased material and heat transfer in comparison to common honeycombs or pellet beds. Especially for multiphase reactions, like Fischer-Tropsch synthesis, heat and material transfer have a significant influence on product selectivity. The Fischer-Tropsch synthesis is characterized by producing a spectrum of hydrocarbon products. Therefore, a good adjustment of selectivity is advantageous because often only a specific fraction is the desired synthesis product.

The investigations on the application of novel support structures for Fischer-Tropsch synthesis are focused on waxes and short-chained olefins as products. Both are, in contrast to methane, gasoline or diesel, not only energy storage materials but also important intermediates or end products in chemical industry. Currently, they are produced from crude oil. In contrast to fossil source-based products, the products from renewable sources offer – besides their sustainable production – several advantages. For example, synthetic waxes are free from aromatic and polycyclic compounds and, therefore, particularly suitable for the application in the cosmetics industry [3]. This example demonstrates that power-to-product concepts also allow the production of compounds of highly economical value. For the production of waxes, Co-based catalysts are applied. In order to increase the reducibility and activity, Ru is added as a promotor. Short-chained olefins are of high importance as intermediates in chemical industry. For their synthesis, promoted Fe catalysts are used. High yields of olefins require short residence times and narrow residence time distributions. Therefore, the novel structures are highly suitable for the transition from fluidized bed reactors applied in large-scale industrial plants to fixed-bed reactors. The identification of suitable catalyst systems is also an essential part of the works on olefin synthesis.

Different Ni-based catalysts are prepared and tested regarding their activity for methanation. Focus of the research is the utilization of CO₂ from air or from off-gas streams for the synthesis of CH₄. As CO₂ can be converted to CO in an upstream electrolysis step, measurements with both CO and CO₂ are per-

Temperature profiles for different entrance temperatures regarding the methanation of H₂/CO





formed. Due to the higher exothermic reaction regarding CO methanation, this reaction is used for the evaluation of the support structures. Catalysts are used in the form of powders or applied to structured supports via washcoating processes. By means of measuring temperature profiles, the influence of support structure on the heat transfer within the reactor is evaluated.

State of development and current research

Based on past research regarding solid oxide fuel cells, a high-temperature electrolysis cell was successfully developed and tested. The current research efforts are focused on stack design, reduction of CO₂ to CO and on further improvements in long-term stability. In the field of chemical syntheses, novel ceramic catalyst supports were developed and applied to different synthesis reactions. Currently, an increase of selectivity for valuable products, like waxes and olefins, is focused. A process model based on Matlab/Simulink was developed allowing the identification of advantageous process concepts and an evaluation of the expected process efficiency. For the utilization of CO₂ from air as carbon source, additional research is necessary to reach economic feasibility. The coupling of high-temperature electrolysis and Fischer-Tropsch synthesis allows the production of alternative fuels as well as base chemicals and, therefore, offers a variety of possible concepts for the application of excess energy from renewable resources for chemical syntheses. Depending on conditions and possible application, customer-specific solutions can be developed.

Services offered

- Development of application-specific process concepts and reactors
- Process and reactor simulation
- Innovative ceramic support structures for the application in synthesis reactions
- Catalyst development and screening
- High-temperature electrolysis cells, stacks and modules
- Design and manufacturing of reactors and pilot-scale plants

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- [3] M. Bekker, N. R. Louw, V. J. Jansen van Rensburg, J. Potgieter, International Journal of Cosmetic Science, 35 (1) 99-104 (2013).

5 Computed tomographic image of a ceramic tape structure.

6 Liquid and waxeous products of Fischer-Tropsch synthesis.

7 Product distribution of Fischer-Tropsch synthesis.

8 Catalyst preparation.

9 Preparation for joining stacks.