
IASS WORKING PAPER

Institute for Advanced Sustainability Studies (IASS)

Potsdam, February 2014

Workshop Report

Sustainable Fuels from Renewable Energies



Synthetic Methanol

Surplus Energy Storage

Synthesis of Liquid Fuels

Green House Gas
Emissions

Power-to-Liquids

Highly Efficient
Technologies

Renewable Energy

Depleting
Fossil Reserves

Climate Change

Electrolysis

Carbon Neutral

Solar

Carbon Negative

Thermochemical

Methanol
Economy

Splitting

Introduction

* IASS Workshop, 19–20 November 2013

The combustion of fossil hydrocarbons currently forms the basis of our energy systems, and petroleum-derived chemical compounds are the source of a wide range of essential products. The exhaustible nature of fossil reserves as well as climate change concerns require a switch to alternative, renewable energy provision. Concepts such as the ‘hydrogen economy’ or the extensive use of electric vehicles in the transport sector are hindered by significant drawbacks, from low energy density to technological hurdles and prohibitive costs. On the contrary, the synthesis of liquid fuels represents a promising avenue for the production of petroleum substitutes that would help achieve the Green House Gas emissions mitigation targets while also satisfying energy demand in a practical way.

Synthetic methanol in particular holds great potential for meeting our future chemical and fuel needs – a concept defined as “The Methanol Economy” in the 1990’s by Nobel Laureate George Olah and elaborated further by Olah, G. K. Surya Prakash and Alain Goepfert during the last decade. Indeed, methanol can be directly integrated into existing fuel delivery and use infrastructure without excessive investment costs, is an excellent fuel for internal combustion engines, and represents a practical and safer alternative to hydrogen and liquid natural gas. It can also easily be transformed into higher (octane or cetane) fuels and precursors for the chemical industry (e.g. olefins for polymer production).

Combining the synthesis process with energy from renewable sources like wind or solar opens the way to truly sustainable fuels that also help offsetting the intermittency of renewable sources by storing peak energy production in the more convenient form of a liquid (i.e. the power-to-liquids concept). It is not a surprise therefore that the synthesis of sustainable fuels is attracting more and more interest from sci-

entists and businesses alike, with experimental and industrial applications in many countries and particularly Germany.

Within this context, the IASS research project focuses on the chemical recycling of carbon dioxide into methanol (and DME), with the assumption that CO₂-capture (e.g. from large point sources, biomass and ultimately from the air) will become increasingly efficient and available. In this regard, the effects of photosynthesis can be artificially reproduced, transforming carbon from waste product to energy carrier; and if the synthesis is performed using highly efficient technologies coupled with renewable energy sources, the whole cycle is potentially “Carbon Neutral” or even “Carbon Negative”.

Different aspects of this and other approaches were discussed during this workshop, with the purpose of addressing core questions such as: How should the required hydrogen be produced (e.g. via water electrolysis)? What are the most suitable synthesis pathways (e.g. based on CO₂ directly or on CO/H₂ mixtures)? How do we derive the electrical/thermal energy needed in the process?

The production of the required hydrogen is at the core of many such processes, and methods using the high temperature co-electrolysis of CO₂ and H₂O to produce syngas (CO₂/CO/H₂ mixtures) are of particular interest. High temperature electrolysis in SOECs makes very efficient use of electricity and heat (near-100% electricity-to-syngas efficiency), provides high reaction rates, and the syngas produced can be catalytically converted to hydrocarbons in well-known fuel synthesis reactors (e.g. Fischer-Tropsch). Other H₂ production and CO₂ conversion methods (e.g. solar thermochemical, (photo)electrochemical, etc.) were also discussed.



The methanol synthesis reaction is an example of a structure sensitive catalytic reaction. There is an increasing interest in methanol synthesis via syn-gas conversion and the direct hydrogenation of carbon dioxide. A vast volume of literature exists on the process and catalysts; however, the roles of the active site, the effects of the support and promoter, and the reaction mechanism are still being fully elucidated. The characterization and description of new and commercial catalysts for such processes were discussed, as were the latest developments regarding the catalytic recovery of H_2 from the liquid methanol store.

A number of commercial projects are now coming online as market conditions for sustainable fuels become increasingly friendlier. However, important obstacles still remain which require further research efforts in different disciplines. This workshop provided an opportunity for the leading scientists and industrialists in this field of green fuel production to present their most recent results, discuss growing commercial perspectives, and identify the challenges ahead.

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Prof. Carlo Rubbia, Scientific Director IASS
Nobel Laureate 1984

1. Workshop Agenda

November 19th, Morning session, Theme Setting

Welcome and introduction

Prof. Carlo Rubbia,
Nobel Laureate, Scientific Director IASS

Developments Towards the Methanol Economy

Prof. G. K. Surya Prakash, Loker Hydrocarbon
Research Institute, USC, USA

A greenhouse gas-neutral Germany in 2050

Dr. Harry Lehmann, Federal Environment Agency,
Germany

Solar Thermochemical Splitting of H₂O and CO₂ using Metal Oxide Based Redox Cycles

Dr. Jonathan Scheffe, ETH Zurich, Switzerland

Carbon dioxide – a suitable material for hydrogen storage

Dr. Henrik Junge, Leibniz Institute for Catalysis,
University of Rostock (LIKAT), Germany

November 19th, Afternoon session, Chemical Catalysis Research

Catalysis for CO₂ conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries

Dr. Alessandra Quadrelli, CPE Lyon and CNRS,
France

Electrocatalytic Conversion of CO₂ to Higher Alcohols

Prof. Matthew Kanan, Stanford University, USA

Catalysis of Methanol Synthesis from CO₂

Dr. Malte Behrens, Fritz-Haber-Institute of the
Max Planck Society, Germany

Artificial photosynthesis with molecular catalysts integrated in nanostructured materials

Dr. Erwin Reisner, University of Cambridge, UK

20th, Morning session, Electrolysis and Fuel Cells

SOEC: A key enabling technology for sustainable energy scenarios

Dr. John B. Hansen, Haldor Topsoe AS,
Topsoe Fuel Cells, Denmark

Electrolysis for conversion of H₂O and CO₂ into green fuels

Prof. Mogens B. Mogensen, Technical University of Denmark, Denmark

Using the High Temperature Electrolysis for Producing Synthetic Fuels

Dr. Annabelle Brisse, EIFER, Karlsruhe, Germany

Reversible fuel cells instead of electrolyzers and batteries for large-scale renewable energy storage

Dr. Christopher Graves, Technical University of Denmark, Denmark

November 20th, Afternoon session, Commercial Perspectives

Surplus of Electric Solar and Wind Power – Where to Go?

Prof. Roland Meyer-Pittroff, Technical University Munich, Germany – Silicon Fire, Switzerland

Demonstration of Technology Options for Storage of Renewable Energy

Dr. S. Elango Elangovan, Ceramatec®, USA

Business Model for Power to Gas/Liquids – Potentials, Challenges and Uncertainties

Mr. Wolfgang Verdegaal, SunFire GmbH, Germany

Bio-Methanol from Forest Product Industry Byproducts

Prof. Rikard Gebart, Lulea University, Sweden

DME – Renewable fuel for heavy vehicles

Mr. Henrik Landälv, Volvo Power Train Corp., Sweden

Round-Table Discussion

Summary and Conclusions

2. Participants

Dr. Malte Behrens, Fritz-Haber-Institute of the Max Planck Society, Germany
Dr. Annabelle Brisse, EIFER, Karlsruhe, Germany
Dr. S. Elango Elangovan, Ceramatec, USA Mr. Per Fagerlund, ScandiNAOS AB, Sweden
Mr. Per Fagerlund, ScandiNAOS AB, Sweden
Dr. Qingxi Fu, EIFER, Karlsruhe, Germany Prof. Rikard Gebart, Lulea University, Sweden
Prof. Rikard Gebart, Lulea University, Sweden
Dr. Christopher Graves, Technical University of Denmark, Denmark
Dr. John B. Hansen, Haldor Topsoe AS, Topsoe Fuel Cells, Denmark
Dr. Henrik Junge, Leibniz Institute for Catalysis, University of Rostock (LIKAT), Germany
Prof. Matthew Kanan, Stanford University, USA
Mr. Kai Kuhnhen, Federal Environment Agency, Germany
Mr. Henrik Landälv, Volvo Power Train Corp., Sweden
Dr. Harry Lehmann, Federal Environment Agency, Germany
Prof. Roland Meyer-Pittroff, Technical University Munich, Germany –
Silicon Fire, Switzerland
Prof. Mogens B. Mogens, Technical University of Denmark, Denmark
Prof. Siglinda Perathoner, Laboratory of Catalysis for Sustainable Production and Energy,
University of Messina, Italy
Prof. G. K. Surya Prakash, Loker Hydrocarbon Research Institute, USC, USA
Dr. Alessandra Quadrelli, CPE Lyon and CNRS, France
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Mr. Wolfgang Verdegaal, SunFire GmbH, Germany
Dr. Horst Wenninger, European Organization for Nuclear Research CERN, Switzerland
Dr. Robin J. White, Institute for Advanced Sustainability Studies e.V., Potsdam, Germany



3. Presentations





Prof. G. K. Surya Prakash

Loker Hydrocarbon Research Institute,
USC, USA

Developments Towards the Methanol Economy

Liquid methanol is much preferable to gaseous hydrogen for energy storage and transportation. It is also an excellent fuel for heat engines and fuel cells and a convenient raw material for petroleum-based products. Chemical recycling of excess carbon dioxide formed from anthropogenic activities, natural and industrial sources, or even from the air to methanol via capture followed by reductive conversion with hydrogen is possible. Any available energy source (preferably al-

ternative energies such as solar, wind, atomic, etc.) can provide the needed energy to produce hydrogen. Direct electrochemical reduction of CO_2 is also possible. Methanol can also be produced in new ways from natural (shale) gas through newly developed *Bireforming* and *Oxidative Bireforming* processes. Our continuing work on Methanol Economy, developed in cooperation with Nobel Laureate George A. Olah, will be presented.



Dr. Harry Lehmann

Head of Division, Environmental Planning and Sustainability Strategies, Federal Environment Agency (UBA), Germany

A greenhouse gas-neutral Germany in 2050

In order to prevent serious disruption to the climate system and its uncontrollable consequences, industrial countries must reduce their GHG emissions by approximately 80–95% compared to 1990. Our study shows that a virtually greenhouse gas-neutral Germany with annual per capita emissions of around one tonne of CO_{2eq} by 2050 is technically achievable (reduction of approximately 95% compared to 1990). In our scenario analysis, we assume that Germany in 2050 is still an exporting industrial nation with an average annual growth rate of 0.7% of GDP and a population of 72 million, whose consumption and behavior patterns are similar to today's.

Our study looks at all greenhouse gas (GHG) emission sources in Germany, including the following sectors: energy (including transport), agriculture, industrial processes and land use. For sustainability reasons, it is based on the following premises:

- No use of fossil or nuclear energy carriers
- No cultivation of biomass crops for energy purposes
- No CCS (Carbon Capture and Storage)

At the heart of a completely renewable energy supply is the generation of hydrogen through the electrolysis of water, using renewable power. Through further catalytic processes, hydrogen can be converted (by power to gas, PtG, or power to liquid, PtL) into methane and other hydrocarbons, which, in turn, provide renewably produced fuel for freight transport on our roads, aviation and marine transport.



There are areas that have not been comprehensively dealt with and require further investigation. These include economic cost-benefit analysis, interrelations with resource productivity, possible relocation of emissions outside Germany (carbon leakage), emission reduction through behavioral changes, policy measures and instruments that are required to implement GHG neutrality in Germany.

Dr. Jonathan Scheffe

ETH Zurich, Switzerland

Solar Thermochemical Splitting of H_2O and CO_2 using Metal Oxide Based Redox Cycles

Conversion of abundant but intermittent solar energy to fungible liquid hydrocarbon fuels can potentially provide a seamless transition for integration of renewable fuel sources in the existing transportation infrastructure. There are numerous pathways to convert sunlight to chemical intermediates, including photochemical, electrochemical, thermochemical and their combinations. In particular, thermochemical processes using concentrated solar energy offer the potential to achieve high solar-to-fuel energy conversion efficiencies ($\eta_{\text{solar-to-fuel}}$, defined as the ratio of heating value of the fuel to the solar energy input). This is primarily related to the fact that solar thermal processes inherently operate at high temperatures and utilize the entire solar spectrum, and as such provide a thermodynamically favorable path to solar fuels production. Solar thermochemical redox cycles most commonly operate in two separate reduction/oxidation steps utilizing a metal oxide (MO) as a reactive intermediate. In the first step, the metal oxide is reduced at elevated temperatures (generally $T_{\text{high}} > 1473 \text{ K}$) driven by concentrated solar energy. In the second step, the reduced oxide is reacted with H_2O and CO_2 at temperatures $T_{\text{low}} \leq T_{\text{high}}$ to produce $H_2(g)$ and $CO(g)$. The resulting synthesis gas mixture can be catalytically converted to fungible liquid hydrocarbon fuels (gasoline, diesel, kerosene, etc.) through industrially proven technologies such as Fischer-Tropsch synthesis.

This talk will focus on fundamental material aspects of these cycles from a thermodynamic and kinetic perspective, and relate these properties to the practical aspects of implementing and testing prototype



solar reactors. Thermochemical and physical characterization of state of the art materials will be emphasized, including ceria, doped ceria and perovskites. Two reactor concepts based on ceria will be introduced, a batch reactor utilizing a novel reticulated porous structure capable of volumetrically absorbing the concentrated solar radiation and a continuous aerosol drop-tube reactor designed for driving the endothermic reduction.

Dr. Henrik Junge

Leibniz Institute for Catalysis at the
University of Rostock (LIKAT), Germany

Carbon dioxide – a suitable material for hydrogen storage

Advancements in hydrogen technology such as the generation of hydrogen, its storage and its conversion to electrical energy are the prerequisite for the application of hydrogen as power source. Recently, the use of carbon dioxide or bicarbonate as suitable storage materials for hydrogen has received considerable attention. A cycle comprising of the storage of hydrogen in liquid CO₂-hydrogenation products and the release from it by dehydrogenation can be envisioned. As a significant advantage this cycle is reversible and sustainable. Two stable compounds with good to

high hydrogen contents are in focus as hydrogen storage materials in this presentation: Formic acid (4.4% H₂ by mass) and methanol (12.6% H₂ by mass).

We have recently demonstrated that the selective hydrogenation of carbon dioxide to formic acid or formates and the release of hydrogen can be coupled leading to a closed carbon cycle for hydrogen storage applying a ruthenium-based catalyst system for both reactions.¹ For the latter reaction in a continuous flow setup turnover numbers and turnover frequencies are achieved, which meet already the requirements of hydrogen supply for applications in the 100 W range.

With respect to the higher hydrogen content also methanol seems to be a promising source of hydrogen. However, current state-of-the-art hydrogen production from methanol (methanol reforming) is conducted at high temperatures (>200 °C) and pressures (2550 bars), preventing potential applications. Here, we present an efficient low temperature aqueous-phase methanol dehydrogenation process employing molecular-defined ruthenium complexes. Ultimately, this technique leads to the same distribution of hydrogen and carbon dioxide (3:1) as provided by methanol reforming. Notably, hydrogen generation proceeds at 65–95 °C and ambient pressure with excellent catalyst activity. Thus, in combination with state of the art methanol synthesis hydrogen storage in this material will become possible.²

Moreover, besides the ruthenium based systems both reactions, hydrogenation and dehydrogenation, can also be catalyzed by more abundant iron catalysts.³



¹ A. Boddien, F. Gärtner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, *Angew. Chem. Int. Ed.*, 50; 6411–6414, (2011)

² M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladioli, M. Beller, *Nature*, 495, 85–89, (2013)

³ A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science*, 333, 1733–1736, (2011)

Dr. Alessandra Quadrelli

CPE Lyon and CNRS, France

Catalysis for CO₂ conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries.

Replacement of part of the fossil fuel consumption by renewable energy, in particular in the chemical industry, is a central strategy for resource and energy efficiency. This perspective will show that CO₂ is the key molecule to proceed effectively in this direction. The routes, opportunities and barriers in increasing the share of renewable energy by using CO₂ reaction and their impact on the chemical and energy value chains are discussed after introducing the general aspects of this topic evidencing the tight integration between the CO₂ use and renewable energy insertion in the value chain of process industry. The focus of this perspective article is on the catalytic aspects of the chemistries involved, with an analysis of the state-of-the-art, perspectives and targets to develop.

The reactions discussed are the production of short-chain olefins (ethylene, propylene) from CO₂, and the conversion of carbon dioxide to syngas, formic acid, methanol and dimethylether, hydrocarbons via Fisher-Tropsch and methane. The relevance of availability, cost and environmental footprint of H₂ production routes using renewable energies is addressed. The final part discusses the possible scenario for CO₂ as an intermediary for the incorporation of renewable energy in the process industry, with a concise roadmap for catalysis needs and barriers to reach this goal.¹



¹ Gabriele Centi, Elsje Alessandra Quadrelli, and Siglinda Perathoner, *Energy Environ. Sci.*, 2013, 6, 1711–1731 (DOI: 10.1039/C3EE00056G)

Prof. Matthew Kanan
Stanford University, USA

Electrocatalytic Conversion of CO₂ to Higher Alcohols

Controlling the atmospheric CO₂ concentration may ultimately require recycling CO₂ into liquid fuels using renewable energy as the power source. Arguably the greatest challenge for this vision is to develop efficient catalysts that reduce CO₂ and its derivatives to a fuel of choice. This talk will describe our development of “oxide-derived” nanocrystalline metal electrocatalysts. These materials are prepared by reducing thin-film metal oxide precursors. This process kinetically traps nanograined polycrystalline metals with unique catalytic properties. I will describe examples of these catalysts that electrochemically reduce CO₂

to CO at potentials close to the thermodynamic minimum as well as catalysts that selectively reduce CO to multi-carbon oxygenates. The catalysts operate in water at ambient temperature and pressure and are remarkably robust. The structural origins of the catalytic activity will be discussed based on diffraction and high-resolution electron microscopy. Oxide-derived nanocrystalline metals enable a two-step electrochemical conversion of CO₂ to ethanol that could make CO₂ a feedstock for synthetic liquid fuel.



Dr. Malte Behrens

Fritz-Haber-Institute of the
Max Planck Society, Germany

Catalysis of Methanol Synthesis from CO₂

Efficient chemical storage of fluctuating regenerative energy is an important cornerstone of a sustainable energy scenario. In such energy storage reaction, small low-energy molecules like CO₂ and/or H₂O are activated and converted. The electrocatalytic or photocatalytic splitting of water is a technology with great potential for this purpose. However, carbon-based synthetic fuels like methanol offer advantages over the primary product H₂. Methanol is liquid at ambient conditions, can be easily distributed and stored, and is a versatile platform molecule for the chemical

industry. Although the current industrial synthesis of methanol from fossil syngas is a mature and scalable technology, there still are many challenges and open questions regarding active sites and reaction mechanism of the hydrogenation of anthropogenic CO₂ with renewable H₂. In particular, more efficient and stable catalysts are needed to face the unfavorable thermodynamics and the inhibiting effect of water. An approach for a knowledge-based optimization of the applied Cu/ZnO catalyst will be presented.

Dr. Erwin Reisner

University of Cambridge, UK

Artificial photosynthesis with molecular catalysts integrated in nanostructured materials

Direct solar fuel generation requires the finely tuned combination of light absorption, charge separation and redox catalysis. This demanding task is highly controlled by natural photosynthesis but much less so by artificial systems. It was previously shown that ruthenium-dye sensitized TiO₂ nanoparticles can be modified with enzymes known as hydrogenases for proton reduction to H₂ during visible light irradiation.¹ The enzymes can also be replaced by inexpensive synthetic catalysts such as cobaloximes to generate H₂ on dye-sensitized TiO₂ (Figure 1A).² In these systems, electron transfer from the dye occurs through ultrafast and quantitative electron injection into TiO₂ and creation of a sufficiently long-lived TiO₂ conduction band electron for the reduction of the cobalt catalyst.³ We found that the cobalt catalyst and hydrogenases does not only operate at room temper-

ature and in pH neutral aqueous solution, but also in the presence of O₂.⁴ A second generation cobaloxime catalyst can also be immobilized on conducting metal oxide electrodes for electrochemical H₂ evolution.⁵ A fuel forming reductive process such as H₂ evolution can only operate if electrons are provided from an oxidative process such as water oxidation to O₂. Visible light driven water oxidation to O₂ can be achieved with a hybrid photoanode consisting of nature's water oxidizer photosystem II adsorbed on a mesoporous metal oxide electrode (Figure 1B).⁶ Limitations and prospects of these artificial photosynthetic hybrid materials for solar water splitting will be discussed. We thank the EPSRC, the Christian Doppler Research Association and the OMV Group for financial support.

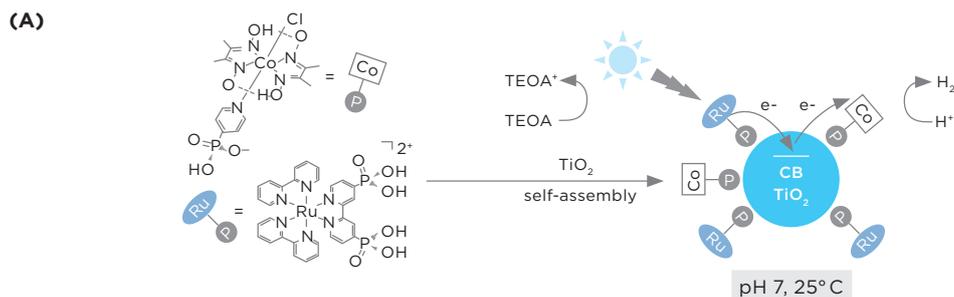
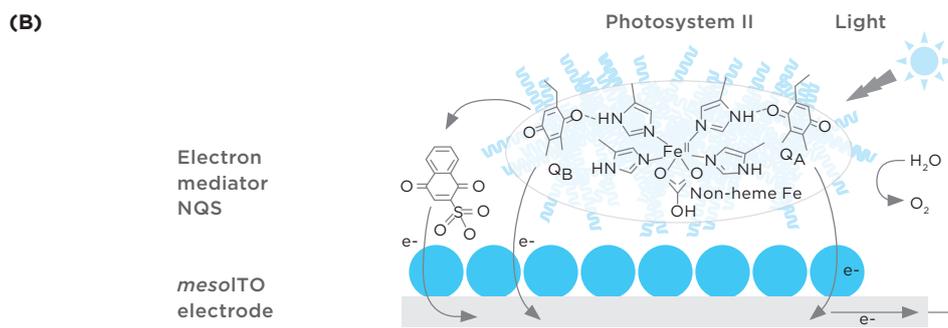


Figure 1. (A) Photo-catalytic H₂ production nanoparticles loaded with a cobalt-based proton reduction catalyst and a ruthenium-based photosensitizer.³ (B) Visible light driven water oxidation with photosystem II integrated in a mesoporous indium tin oxide.⁷



¹ Reisner, E.; Powell, D. J.; Cavazza, C.; Fontecilla-Camps, J. C.; Armstrong, F. A. J. *Am. Chem. Soc.* 2009, 131, 18457–18466.

² Lakadamyali, F.; Reisner, E. *Chem. Commun.* 2011, 47, 1695–1697.

³ Lakadamyali, F.; Reynal, A.; Kato, M.; Durrant, J.; Reisner, E. *Chem. Eur.* 2012, 18, 15464–15475.

⁴ (a) Lakadamyali, F.; Kato, M.; Muresan, N. M.; Reisner, E. *Angew. Chem. Int. Ed.*, 2012, 51, 9381–9384; (b) Sakai, T.; Mersch, D.; Reisner, E. *Angew. Chem. Int. Ed.*, 2013, in press (doi:10.1002/anie.201306214).

⁵ (a) Muresan, N. M.; Willkomm, J.; Mersch, D.; Vaynzof, Y.; Reisner, E. *Angew. Chem. Int. Ed.*, 2012, 51, 12749–12753; (b) Scherer, M.; Muresan, N. M.; Steiner, U.; Reisner, E. *Chem. Commun.*, 2013, 49, 10453–10455.

⁶ (a) Kato, M.; Cardona, T.; Rutherford, A. W.; Reisner, E. *J. Am. Chem. Soc.*, 2012, 134, 8332–8335; (b) Kato, M.; Cardona, T.; Rutherford, A. W.; Reisner, E. *J. Am. Chem. Soc.*, 2013, 135, 10610–10613.

Dr. John B. Hansen

Haldor Topsoe AS, Topsoe Fuel Cells,
Denmark

SOEC: A key enabling technology for sustainable energy scenarios

Solid oxide electrolysis (SOEC) technology can provide solutions to many of the challenges posed by future energy systems based on significant fraction of electrical power produced by intermittent sources like wind or solar power.

SOEC can not only electrolyze steam to hydrogen at very high efficiency but can also co-electrolyze carbon dioxide and steam. The produced synthesis gas can then be converted catalytically to methane, methanol, DME, gasoline or diesel. There are strong

synergies between the SOEC and the downstream chemical syntheses because the gas composition can be fine-tuned to the optimum for the product in question and the heat of reaction can be utilized to generate the steam needed for the hydrogen production in the SOEC.

The SOEC unit can be coupled to biomass conversion in the form of biogas or gasification gas and double or triple the biomass potential.



Prof. Mogens B. Mogensen

Danish Technical University, Denmark

Electrolysis for conversion of H₂O and CO₂ into green fuels

Synthetic fuels (synfuels) in the form of CO₂ neutral “green” hydrocarbon fuels seem particularly advantageous to replace fossil fuels, and electrolysis seems to be a feasible step in the production of green fuels. In particular, synthetic hydrocarbon-based fuel will be necessary for heavy transportation vehicles such as airplanes, ships, and trucks.

The cost of H₂ produced by electrolysis originates from electricity cost, more than 65% depending on the actual electricity price, and depends further on efficiency, investment cost and lifetime of electrolyzers. Investment costs are inversely proportional to the current density at a given cell voltage, to lifetime and directly proportional to materials cost.

SOEC has probably the biggest potential for a low-cost electrolysis system, but there are combined performance and lifetime issues that must be solved before it will become an affordable technology. The technical status and degradation mechanisms of the electrodes and electrolyte at high overvoltages (high current densities) will be described and measures against the degradations are discussed.

The presentation will briefly summarize the perspectives and the challenges of electrolytic production of H₂ and CO and the future possibilities for production of synfuels based on these two gases.



Dr. Annabelle Brisse

Project leader on electrolysis technologies and hydrogen pathways at the European Institute for Energy Research (EIFER), Germany

Using the High Temperature Electrolysis for P Prof. Rikard Gebart, Lulea University, Sweden producing Synthetic Fuels

Hydrogen production through water electrolysis is one of the key processes required in the conversion of electricity to fuels, which could offer a large-scale solution for both energy storage and carbon neutral fuel production. Carbon free hydrogen produced through electrolysis can be used as a fuel for hydrogen powered applications or grid injection, or as a reactant in downstream processes to produce synthetic fuels such as synthetic natural gas (SNG), diesel or methanol.

Among available technologies, high temperature electrolysis potentially offers significantly higher electrical to chemical conversion efficiencies compared to alkaline and PEM electrolyzers, with values in excess of 100% achievable if additional thermal energy is supplied to the system. It offers also the possibility to co-electrolyse water and CO₂ to produce directly syngas (CO+H₂). High temperature electrolyzers are essentially solid oxide fuel cells operated in reverse.

Hence, the development of solid oxide electrolyzers (SOE) has hugely benefited from the intensive research carried out for the development of Solid Oxide Fuel Cells (SOFCs) in the past decades. However, although industrials appear to be confident in the technology commercial readiness within the next 5 years, efforts are still required to understand, improve and demonstrate the durability of SOE systems in both laboratory and field test environments. The lifetime of high temperature electrolyser systems will indeed strongly depend on the degradation of the SOE stack.

With respect to the depicted context, EIFER is evaluating electrolysis technologies and hydrogen pathways with a special attention to high temperature



electrolyzers, which would be able to produce either hydrogen or syngas to be used for the production of synthetic fuels. Experimental tests at cells and stacks level are carried out aiming ultimately to test a high temperature electrolyser system.

Dr. Christopher Graves

Danish Technical University, Denmark

*Reversible fuel cells instead of electrolyzers and batteries
for large-scale renewable energy storage*

Reversible fuel cells (RFCs) store electrical energy as chemical fuels in electrolysis/charge mode and convert the fuel back to electricity in fuel-cell/discharge mode. A RFC is a special type of rechargeable flow battery and is a part-time electrolyser. This presentation describes major advantages of RFCs compared with conventional batteries and electrolyzers applied for large-scale intermittent renewable electricity storage, based on economics, resource use, and new experimental results.

Compared with conventional batteries, RFCs can provide lower cost energy storage for longer time scales. Whereas conventional batteries store energy in expensive metals, RFCs advantageously store energy in inexpensive hydrogen and carbon based fuels. Accordingly, RFCs are also more sustainable due to lower use of scarce resources. The round-trip efficiency of RFCs is typically perceived as too low, but this assumption is usually based on the properties of only the common $\text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{O}_2$ redox chemistry; other redox chemistries such as hydrocarbons and ammonia can have much higher efficiency. Hydrocarbons are especially interesting energy storage media because they can be used in existing infrastructure and the transport sector.

Compared with dedicated electrolyzers, RFCs can provide lower cost electrolytic fuel production. In an intermittent renewable (e.g. solar and wind powered) dominated electricity system, an electrolyser will only be operated occasionally, during periods of surplus electricity supply when the electricity cost is low. This leads to a low operating cost but a high capital cost. RFCs, on the other hand, can be operated a greater fraction of time or possibly even all of the time depending on the energy system needs. Finally, our recent experimental results with solid oxide electrolyte RFCs show that cell lifetime can be greatly extended by reversible electrolysis/fuel cell operation compared with electrolysis mode operation, giving new insights into their use for highly efficient and robust storage of intermittent energy supplies.

Prof. i.R. Dr.-Ing. Roland Meyer-Pittroff

Technical University Munich, Germany
Silicon Fire, Switzerland

Surplus of Electric Solar and Wind Power – Where to Go? Power-to-Liquid

The capacities of solar and wind power in Germany have reached more than 30 GW each, which, at present, sum up to 66 GW compared to the maximum demand of 80 GW, and the installation of further new plants is unbroken because of the will of society and politics. Already now during approx. 1000 hours per year wind plants must be shut down and electric energy must be exported at very low or even negative prices to avoid the breakdown of the electric grid, where at any given moment and at any place, the equilibrium must be held between supply and consumption. Therefore a great demand for electric storage devices arises additionally to the existing 6,5 GW electric power of the pumped storage power plants (PSPP) in Germany. The potential for new PSPP in Germany is very limited.

The only real alternative for electric storage above the capacities of PSPP is the chemical storage: the production of synthetic fuels by means of the surplus of renewable electric energy. The basic technology for it is the electrolysis of water, its decomposition into hydrogen and oxygen. The Swiss Silicon Fire AG together with the Technical University Munich developed and tested successfully a technology to synthesize the liquid fuel methanol directly from the electrolysis hydrogen and additional carbon dioxide coming from concentrated industrial sources.

To ensure competitive costs of the methanol and the operability of the synthesis plant the before-mentioned synthesis is combined with the classical fossil methanol synthesis using synthesis gas consisting of hydrogen and carbon monoxide. This synthesis gas can be produced from coal or natural gas by means of partial oxidation using the oxygen from the electrolysis.

The produced methanol can be classified as renewable fuel according to EU regulations requiring a greenhouse gas emission saving of (only) 35%. The methanol can be used as chemical feedstock or as excellent fuel for spark ignition combustion engines. A special advantage of the methanol is its usability as injection coolant for the warm compressed gas of supercharged combustion engines after the intercooler. The methanol injection results in considerable increases of power and efficiency of the engines.

The vision is the large-scale methanol production from water, wind, and solar power in remote regions where these energies are available to a great extent but without other exploitability. The long-distance transport of methanol and carbon dioxide is state of the art. This vision opens a new renewable system of worldwide supply of chemical feedstock and fuel.

Dr. S. Elango Elangovan
Ceramatec, USA

*Demonstration of Technology Options for Storage of
Renewable Energy*

Energy and environmental factors are the two dominant market forces that will determine technology and policy matters of 21st century. Competing forces of increasing demands for energy, a need for lowering environmental footprint, and reliance on fossil fuels must be balanced in order to sustain economic growth.

Renewable power generation is challenged in current electric grid markets. Transportation fuels are of higher value and expose most societies to greater economic and strategic vulnerability than grid power. The technologies required to efficiently reverse the fossil fuel combustion cycle, converting carbon dioxide to liquid hydrocarbon transportation fuels as a store of renewable energy, have been demonstrated and are on the verge of economic feasibility.



Mr. Wolfgang Verdegaal

SunFire GmbH, Germany

Business Model for Power to Gas/Liquids – Potentials, Challenges and Uncertainties

Converting renewable energy into hydrocarbon fuels, referred to as Power-to-Liquids (PtL) or Power-to-Gas (PtG), is considered as one of very few viable options for large-scale fossil fuel replacement and long-term energy storage.

The SunFire GmbH develops and commercializes PtG and PtL processes. The required hydrogen is generated using high-temperature steam electrolysis (SOEC). Thereby fuel and gas can be produced from electricity with an efficiency of up to 70% for PtL and 80% for PtG.

Due to its high efficiency the SunFire process can cope with higher average electricity input prices (0.05 €/kWh) than legacy technologies. This enables a base-load operation mode (ca. 7,000 h/a), reducing the amount of charges on the electricity procurement side to a minimum, with an additional bonus for offering positive control power when supply from renewable energy sources in the grid drops. This business model differs from negative control power models where only cheap electrical surpluses can be afforded. This model could already be self-sufficient. Additionally, a change in EU legislation (2009/28/EC) will increase returns for renewable liquid and gaseous fuels of non-biological origin significantly.



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Bio-Methanol from Forest Product Industry Byproducts

The forest product industry has a unique possibility for cost effective and rapid deployment of biorefinery processes. This industry already handles biomass in the million ton per year scale and has the necessary knowhow to make them the ideal site of new advanced chemical processes that utilize forest byproducts.

One particularly interesting option is to utilize the black liquor that is a byproduct of chemical pulping as a fuel for gasification. In the presentation the results from a complete demonstration of black liquor to DME and subsequent field tests in commercial trucks (the BioDME project) will be reported and assessed. The project outcome has confirmed that the large scale gasification of black liquor and upgrading into methanol and DME is an industrially mature route to second generation motor fuels with the potential to replace a significant fraction of current use of gasoline and diesel in countries with strong forest products industry, e.g. Sweden and Finland.

The potential for this process is also very large in the rest of EU, USA and other industrialized parts of the world if sustainable forest and agricultural byproduct-streams are used as gasifier feedstock, either directly in a solid biomass gasifier or after upgrading to liquid pyrolysis oil in a liquid fuel gasifier similar to that in the BioDME project. For EU-25 the potential for replacement of gasoline and diesel with methanol and DME is about 28% and in the USA it is about 33% compared to the current level. Many other parts of the world have a similar potential. While this estimate is encouraging it also shows that more fuel-efficient vehicles, a larger fraction of electrical vehicles and innovative logistic solutions are necessary in order to develop a sustainable transport system.

If the large potential for production of methanol and DME is going to be realized two major challenges must be overcome. The first is how to develop a market for the new fuels and the fuel distribution infrastructure at the same time. The second is how to create stable and predictable economical conditions during the lifetime of a new large-scale biorefinery process. Recent developments that might lead to the removal of both of these challenges will be described in the presentation.

4. Conclusion

The international workshop “Sustainable Fuels from Renewable Energies” organised at IASS on November 19th-20th 2013 provided an opportunity for leading scientists and industrialists to exchange ideas and discuss possible technological pathways to sustainable fuels production and utilisation. The theme followed on from the concept of synthetic methanol and the “Methanol Economy” defined in the 1990’s by Nobel Laureate George Olah. Methanol (and its dehydrated counterpart, dimethyl ether (DME)) can be directly integrated into existing fuel delivery/use infrastructure without excessive investment costs, as an excellent fuel for internal combustion engines. Using similar synthetic chemistry (e.g. syn-gas based routes), higher (octane or cetane) fuels can also be produced whilst methanol itself can also be transformed into a variety of commercially relevant compounds (e.g. olefins for polymer production). The advantages of sustainable fuels including methanol, dimethyl ether and potentially synthetic gasoline are now reaching a well-documented maturity (e.g. liquid energy carrier, combustion efficiencies, drop-in-fuels, and greenhouse gas emission mitigation, etc.). Moreover from a technical point of view, aside from carbon dioxide from the air, their introduction appears on a prima facie basis an accessible goal. The capability to store (intermittent) renewable electrical energy (e.g. wind, solar) in the production of such fuels is also a considered necessity with regard to a reduction in greenhouse gases and carbon footprint – a sustainable alternative to Carbon Capture and Sequestration.

During the course of the workshop, chemical technologies associated with the highly efficient generation of hydrogen (e.g. necessary for the hydrogenation of carbon dioxide) and syn-gas were discussed including those under substantial market consideration (i.e. solid oxide electrolyzers), nearing commercialisation (e.g. solar thermal cycles) and future blue sky

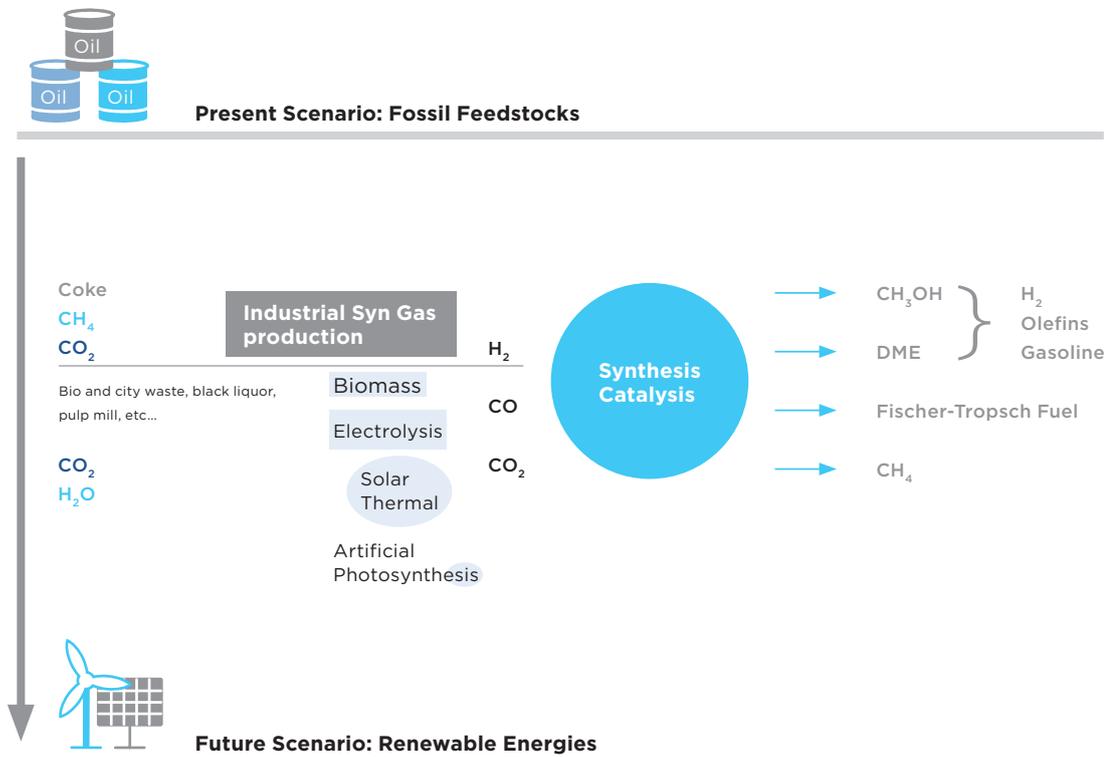
approaches (i.e. photochemical catalysis based on semiconductor/hydrogenase hybrids). The concept of “met-gas” was also introduced as a route to synthesis methanol from the combination of CH_4 , H_2O , and recycled CO_2 . Mechanistic discussion and (industrial) catalyst characterisation was also discussed in the context of CO_2 hydrogenation to CH_3OH (and formic acid) and the reverse process to evolve “on-demand” H_2 (for use in fuel cell applications); demonstrating the potential of CO_2 to act as a H_2 energy vector. The latest commercialisation efforts regarding the “power-to-liquid” and “power-to-gas” concepts in the energy mixes of Germany and Denmark were introduced, as was a Swedish approach to methanol production utilising paper mill waste as the syn-gas precursor. The interest of power train and marine vehicle companies in sustainable fuels (e.g. methanol and DME) to curb not only CO_2 but SO_2 to urban and boundary layers was also highlighted.

During discussions and in particular during a final round-table, workshop participants reached a common consensus on a number of highly significant points. There is no one solve-all solution to the question of energy/fuel demand. Specific geographic and socio-economic conditions may encourage the adoption of particular routes to synthetic fuel and chemical production (e.g. abundance of wind energy in Denmark, shale gas in the USA, limited fossil resources in Germany, etc.). However, there is a general theme underlying all these scenarios. If fuel and chemicals are to be produced synthetically, it must be done with as minimal (ideally neutral or negative) a carbon footprint as possible, with the incorporation of renewable electrical energy and recycled CO_2 highly desirable. With comparison to other fuels and chemical precursors, a number of developing “sustainable” (with a particular accent on the flexible base compound methanol) fuel enterprises were

highlighted in the course of the workshop, each with their individual merits. Whilst markets are currently in the progress of opening (e.g. as a marine fuel), the overall demand and penetration of sustainable fuels (excluding bioethanol in Brazil) and chemical precursors for transportation, industry and power generation is still relatively limited. With this in mind, the increased market uptake of sustainable fuels (e.g. renewable methanol, synthetic gasoline) will largely be determined by a number of critical socio-economic and political factors.

The production of sustainable fuels must be demonstrated at increasingly large volume, commercially viable production pathways, which have a beneficial economic attraction as compared to conventional or other renewable fuels. This can in part be achieved by well-designed, highly efficient, integrated processes (assisted by the introduction of new chemical technologies) but on the short term further statu-

tory instruments (e.g. directives, regulations, etc.) or financial incentives (e.g. tax breaks, subsidies, feed-in-tariff equivalents, etc.) must be introduced to support the utilisation of recycled CO₂ and sustainable fuels. Such measures will ultimately be enhanced in efficacy if associated markets (e.g. the chemical industry) are also in turn encouraged to adopt sustainable feedstock based processes. While optimistic on the future of synthetic fuels from renewable energies, the participants highlighted a perceived gap between the strength of scientific argument and technology development on one hand, and the lack of political awareness and action on the other hand. Therefore, increased advocacy efforts directed to enhance the awareness of policy makers and indeed the general public needs to be conducted if there is to be a true, long term adoption of a sustainable fuel concept in Germany, the European Union and beyond. ■





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